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Atmospheric Measurement Techniques Discussions

A novel Fast Gas Chromatography based technique for higher time resolution measurements of speciated monoterpenes in air

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Abstract

Biogenic emissions supply the largest fraction of non-methane volatile organic compounds (VOC) from the biosphere to the atmospheric boundary layer, and typically comprise a complex mixture of reactive terpenes. Due to this chemical complexity, achieving comprehensive measurements of biogenic VOC (BVOC) in air within a satisfactory time resolution is analytically challenging. To address this, we have developed a novel, fully automated Fast Gas Chromatography (Fast-GC) based technique to provide higher time resolution monitoring of monoterpenes (and selected other C_9–C_{15} terpenes) during plant emission studies and in ambient air. To our knowledge, this is the first study to apply a Fast-GC based separation technique to achieve quantification of terpenes in air. Three chromatography methods have been developed for atmospheric terpene analysis under different sampling scenarios. Each method facilitates chromatographic separation of selected BVOC within a significantly reduced analysis time compared to conventional GC methods, whilst maintaining the ability to quantify individual monoterpene structural isomers. Using this approach, the C_{10}–C_{15} BVOC composition of single plant emissions may be characterised within a ∼ 14 min analysis time. Moreover, in situ quantification of 12 monoterpenes in unpolluted ambient air may be achieved within an ∼ 11 min chromatographic separation time (increasing to ∼ 19 min when simultaneous quantification of multiple oxygenated C_9–C_{10} terpenoids is required, and/or when concentrations of anthropogenic VOC are significant). This corresponds to a two- to fivefold increase in measurement frequency compared to conventional GC methods. Here we outline the technical details and analytical capability of this chromatographic approach, and present the first in situ Fast-GC observations of 6 monoterpenes and the oxygenated BVOC linalool in ambient air. During this field deployment within a suburban forest ∼ 30 km west of central Tokyo, Japan, the Fast-GC limit of detection with respect to monoterpenes was 4–5 ppt, and the agreement between Fast-GC and PTR-MS derived total monoterpene mixing ratios was consistent with previous GC/PTR-MS comparisons. The measurement uncertainties associated

with the Fast-GC quantification of monoterpenes are ≤ 10 %, while larger uncertainties (up to ∼ 25 %) are associated with the OBVOC and sesquiterpene measurements.

1 Introduction

Volatile organic compounds (VOC) play a key role in tropospheric processes that influence air quality and climate forcing, such as ozone production and secondary organic aerosol (SOA) formation (Andreae and Crutzen, 1997; Sillman, 1999; Fuentes et al., 2000 and references therein). Biogenic VOC (BVOC) constitute the largest fraction of the total global non-methane VOC supplied to the planetary boundary layer (> 90 %, Greenberg et al., 1999), with the global BVOC flux estimated to be of the order of 1100 Tg C yr^{-1} (Guenther et al., 1995), compared to just 50–100 Tg C yr^{-1} anthropogenic VOC (Holzke et al., 2006). Furthermore, BVOC are typically highly reactive with respect to the atmospheric oxidants OH and O_3 (atmospheric lifetimes range from minutes to days for monoterpenes, Atkinson and Arey, 2003), and hence in the presence of NO_x even relatively low concentrations of these trace gases can initiate efficient tropospheric ozone production cycles (Chameides et al., 1988).

Despite the potential impact of biogenic emissions with respect to both the global carbon cycle and local scale oxidant budgets, there are substantial uncertainties associated with the current understanding of BVOC-mediated tropospheric photochemistry. These uncertainties are highlighted by efforts to constrain measurements of the total OH reactivity of ambient air using concurrent trace gas observations. In forested regions, the directly measured total OH reactivity of boundary layer air (defined as the sum of the concentrations of each individual OH sink multiplied by their respective reaction rate coefficients) is frequently greater than the equivalent estimated OH reactivity, derived from simultaneous VOC observations (Di Carlo et al., 2004; Sinha et al., 2010; Nölscher et al., 2012; Edwards et al., 2013). This discrepancy between measured and calculated OH reactivity reveals the presence of an unidentified OH sink (or sinks) within the forest boundary layer, which may potentially be attributed to

unmeasured primary BVOC emissions (Di Carlo et al., 2004; Sinha et al., 2010), unmeasured oxidation products of primary BVOC following atmospheric processing (Lou et al., 2010; Taraborrelli et al., 2012; Edwards et al., 2013), or a combination of these sources (Nölscher et al., 2012). As such, it is apparent that a more detailed characterisation of the ambient air BVOC composition is necessary in order to effectively constrain the forest boundary layer oxidant budget. However, the chemical complexity of air influenced by biogenic emissions makes achieving comprehensive measurements of BVOC analytically challenging.

Emissions from vegetation typically comprise a vast number of terpenes with a wide range of volatilities, including isoprene (C_5H_8), monoterepenes ($C_{10}H_{16}$), sesquiterpenes ($C_{15}H_{24}$) and numerous oxygenated terpenoids. Each class of terpene consists of multiple structural isomers, which are indistinguishable by some analytical techniques, yet have greatly varying reactivities with respect to atmospheric oxidants (see Table 1). As such, quantification of each individual isomer is fundamental to achieving a comprehensive characterisation of the impact of BVOC upon the oxidation capacity of the troposphere. Furthermore, BVOC emission rates are generally dependent upon environmental conditions such as sunlight, temperature, humidity and CO_2 concentration, which often results in emission profiles with substantial diurnal variability (as well as a potential sensitivity to long-term changes in climate). As a consequence of these variable emission rates, and the relatively short lifetimes of many terpenes with respect to atmospheric oxidants, ambient air concentrations of BVOC such as monoterpenes typically demonstrate significant short-term variability, which necessitates a high time-resolution measurement technique. Established measurement techniques for in situ BVOC monitoring typically offer a trade-off between sample frequency and speciation. Detailed information regarding chemical composition may be obtained via conventional gas chromatography methods (GC-FID and GC-MS) which can quantify individual terpene isomers, but with a limited sample frequency (typically one 10–30 min averaged sample, every ∼ 50–60 min, e.g. Bouvier-Brown et al., 2009; Jones et al., 2011; Hopkins et al., 2011). In contrast, near real-time terpene observations may be

obtained by proton transfer reaction (PTR) mass spectrometry techniques (e.g. Rinne et al., 2005; Langford et al., 2010), however this approach does not provide quantification of individual structural isomers. As a consequence of the complex chemical composition of air influenced by biogenic emissions, and the associated instrument limitations, observations of BVOC in ambient air are limited in comparison with those of anthropogenic VOC.

To address the current instrumental limitations, we have developed a fully automated fast gas chromatography-flame ionisation detection (Fast-GC-FID) method for quantification of a range of C_9–C_{15} BVOC, including multiple structural isomers. This Fast-GC based technique retains the separation capability of conventional gas chromatography, yet offers significantly improved measurement frequency. Here we outline the instrument specifications and present the first applications of Fast-GC for BVOC analysis in plant emission chamber studies and in situ ambient air monitoring.

2 Methods

The BVOC targeted for Fast-GC analysis in this study include monoterpenes, C_9–C_{10} oxygenated terpenoids, and sesquiterpenes (individual structural isomers are listed in Table 1). A Fast-GC system has been developed for BVOC quantification under two scenarios; (1) to quantify these BVOC in emissions from a single plant during chamber experiments; (2) to monitor mixing ratios of BVOC in ambient air. The experimental details regarding sample pre-concentration, chromatography and calibrations for the quantitative analysis of these trace gases using a Fast-GC instrument are outlined in the following sub-sections.

2.1 BVOC pre-concentration

Due to the relatively low concentrations (ppt–ppb) of BVOC in both plant chamber emissions and ambient air, it is necessary to pre-concentrate these trace gases prior to GC

analysis. To achieve this, a Unity2 Thermal Desorber with 3 channel Airserver (Markes, UK) containing a Peltier-cooled Tenax cold trap is used in-conjunction with the Fast-GC instrument. Tenax sorbent was selected for this application due to its hydrophobicity and ability to trap VOC $> C_6$ at ambient temperatures, which is particularly advantageous when sampling air in humid environments, where high moisture levels may give rise to instrument difficulties. In addition, previous studies have reported quantitative pre-concentration of volatile and semi-volatile terpenes using this sorbent material (e.g. Bouvier-Brown et al., 2009). The cold trap is Peltier-cooled to 20 °C during sampling in order to effectively trap C_6–C_{15} VOC, whilst minimising the amount of water vapour retained on the trap. Following a fixed sampling time, the trap is back-flushed with dry helium gas at 30 mL min^{-1} for 1–2 min in order to remove moisture, before rapidly heating ($\sim 100\,^{\circ}C\,s^{-1}$) to 300 °C while helium carrier gas is diverted through the trap, such that the pre-concentrated VOC are desorbed and delivered to the GC column via a heated transfer line (deactivated silica capillary, 130 °C). The Fast-GC instrument used for this study (300 Series GC, Ellutia – for details see Sect. 2.2) contains a unique automatic column insertion (ACI) mechanism, whereby the GC column is not manually connected to the heated transfer line and detector using conventional fittings, but is mechanically inserted via an automatic mechanism. This means that pre-concentrated VOC cannot be delivered from the Unity2 Thermal Desorber cold trap via a conventional silica transfer line inserted through the GC injector port and connected directly via a union fitting to the GC column. Instead, a modified transfer line/GC column interface is utilised; a "needle-terminated" transfer line (Agilent) houses a conventional 0.25 mm fused silica capillary within an insulated cover which is fitted with a needle connection at the GC terminal. This needle is simply inserted through the septum of the GC injector port, which is heated to 210 °C under normal operating conditions. This set-up (outlined in Fig. 1) allows for continuous automated sampling of VOC in air.

Sampling conditions for C_9–C_{15} BVOC pre-concentration were optimised using an in-house prepared gaseous mixture containing $\sim$ 0.5–1.5 ppb of each BVOC diluted in nitrogen. All trapping efficiency tests were performed within a 6 h period, and

quantitative trapping was achieved for sample volumes of up to 1.5 L, with a flow rate of 75 mL min^{-1}. Sampling parameters for the analysis of BVOC in single plant emissions and in ambient air were selected in light of these tests, based upon the required instrument sensitivity and sampling frequency for each application; the comparatively higher concentrations of BVOC in plant chamber air typically allow a shorter sampling time (5–7 min × 50 mL min^{-1} = 250–350 mL sample volume), while the generally lower BVOC concentrations in ambient air necessitate a larger sample volume (10 min × 75 mL min^{-1} = 750 mL sample volume). As a general rule, the sampling period is minimised as much as possible in order to fully utilise the high time resolution facilitated by the Fast-GC technique, as well as to limit the amount of water retained on the trap.

2.2 Chromatography methods

In principle, fast gas chromatography may be achieved through the use of a relatively short GC column (~ 5–20 m), fast temperature ramp rates (~ 20–200 °C min^{-1}) and high carrier gas linear velocities (~ 60–120 cm s^{-1}). Purpose-built Fast-GC instruments typically employ direct resistive heating of the capillary column, which negates the need for a large GC oven and enables rapid heating during chromatographic separation, as well as faster post-separation cooling. The rapid heating and cooling of these columns contributes to an overall cycle time (defined as the time interval between the start of two consecutive measurements) that is substantially reduced in comparison with conventional GC methods. While these chromatography conditions may potentially lead to some reduction in separation efficiency, this can be offset to some extent by using narrow i.d. columns and a thin film stationary phase coating. Moreover, the combination of fast temperature ramps and high carrier gas flow velocities generates exceptionally sharp chromatographic peaks; consequently, while the absolute peak to peak separation between two analytes may be reduced, baseline resolution is often maintained due to a reduction in peak widths. While previous studies have utilised Fast-GC techniques to perform qualitative analyses of the BVOC composition of essential oils (e.g. White

et al., 2009) and plant emissions (e.g. Yassaa et al., 2010), to our knowledge this is the first study to apply Fast-GC separation to the quantitative analysis of terpenes in air.

Single plant chamber studies represent a simplified scenario for measuring BVOC in air, since the BVOC composition is limited to primary emissions from one plant species, while mixing ratios of non-biogenic VOC are below the instrument detection limit, and the formation of BVOC oxidation products is minimised due to the absence of significant levels of atmospheric oxidants within the chamber. As such, single plant emissions are typically relatively high concentration (~ ppb), low component BVOC mixtures, and thus are potentially well suited to fast gas chromatographic separation. That said, the presence of multiple terpene structural isomers with similar physical properties (boiling point, polarity) does limit the separation capacity to some extent, and extensive method development was carried out in order to utilise the capability of Fast-GC to minimise analysis time, whilst maintaining effective chromatographic separation of these complex BVOC mixtures.

In contrast to single plant emissions, the VOC composition of ambient air is generally much more complex, and may potentially comprise a large number of primary BVOC emitted from a variety of tree species, multiple oxidation products resulting from atmospheric processing of primary BVOC, and anthropogenic VOC, all at significant concentrations. Analysis of BVOC in ambient air therefore necessitates a more sophisticated chromatographic approach.

In order to quantify BVOC in air under these various composition scenarios, three distinct chromatography methods have been developed. The GC_CHAMBER method was designed for analysis of C_{10}–C_{15} BVOC in plant chamber air, the GC_AMBIENT I method has been optimised for quantification of individual monoterpene structural isomers in unpolluted ambient air, and the GC_AMBIENT II method facilitates analysis of C_9 and C_{10} BVOC in ambient air influenced by both biogenic and anthropogenic emissions. In all cases, chromatographic separation of the monoterpene structural isomers was prioritised, with analysis of other terpenes considered a secondary objective. A 300 Series Gas Chromatograph (Ellutia) was utilised for all analyses, in

conjunction with a resistively heated stainless steel capillary column (Restek) and helium carrier gas. The GC_CHAMBER chromatography method was developed using a 20 m × 0.18 mm i.d. non-polar MXT-1 column, while a 15 m × 0.25 mm i.d. non-polar MXT-5 column is employed for analysis of BVOC in ambient air. Direct resistive heating of the inert coated steel capillary columns facilitates rapid heating during analysis, as well as rapid post-analysis cooling. Chromatograms recorded using each of these methods are presented in Figs. 2–4. The relevant temperature programmes and carrier gas flow velocities are also illustrated in Figs. 2–4, and are summarised in Table 2.

The GC_CHAMBER chromatography method utilises a Fast-GC based approach to achieve separation of a number of monoterpenes and sesquiterpenes within a ∼ 14 min period. Moderately fast chromatography conditions are employed throughout the C_{10} and C_{15} elution periods (temperature ramps of 11 and 9 °C min^{-1} respectively, see Table 2) to ensure resolution of the multiple structural isomers, while faster chromatography (temperature ramp of 42 °C min^{-1}) is utilised during other periods, in order to minimise the total analysis time. The GC_CHAMBER method facilitates quantification of the monoterpenes α-pinene, camphene, β-pinene, myrcene, α-phellandrene, Δ-3-carene, α-terpinene, limonene, ocimene and γ-terpinene (note ocimene and γ-terpinene are not shown in Fig. 2), the C_{10} oxygenated terpenoids linalool, limonene oxide and methyl chavicol (methyl chavicol not shown in Fig. 2) and sesquiterpenes α-copaene, α-cedrene, β-caryophyllene and α-humulene, within a total measurement cycle time of ∼ 16.5 min. Limitations of this method include the partial separation of the chromatographic peak pairs Δ-3-carene and α-terpinene, and α-cedrene and β-caryophyllene. Resolution of the Δ-3-carene and α-terpinene peaks is generally sufficient to provide quantification, albeit with increased uncertainty (see Sect. 2.3), whereas generally only the combined α-cedrene and β-caryophyllene mixing ratio can be reported. It should be noted that throughout the initial method development and testing period, peak identification and/or BVOC quantification was supported by independent offline GC-MS analysis when necessary.

In clean air with very little to no anthropogenic influence (such as remote forest sites), the GC_AMBIENT I chromatography method may be used to determine the ambient air monoterpene composition. This method provides efficient separation of the chromatographic peaks corresponding to the monoterpenes α-pinene, camphene, β-pinene, myrcene, α-phellandrene, Δ-3-carene, α-terpinene, limonene, ocimene, γ-terpinene and terpinolene, and the C_{10} alkyl benzene p-cymene (sometimes classed as a monoterpene), within an ∼ 11 min analysis time (13.5 min cycle time). Using this method, the majority of chromatographic peaks are fully baseline resolved (exceptions being a very small amount of overlap between the α-phellandrene and Δ-3-carene peaks, as well as a slightly greater degree of overlap between the p-cymene and limonene peaks), allowing individual quantification of these 12 C_{10} terpenes.

Recent studies suggest that BVOC potentially contribute a significant fraction of the boundary layer ozone formation within urban centres (particularly during summertime pollution episodes, e.g. Lee et al., 2006; Curci et al., 2009), providing motivation for in situ observations of these trace gases in polluted atmospheres with biogenic influence (such as a city surrounded by forest land), as well as within the pristine forest boundary layer. Since GC analysis of BVOC in polluted air requires resolution of a vast number of closely eluting chromatographic peaks (numerous anthropogenic VOC, as well as multiple terpene isomers), we have found that typical fast chromatography is not a viable technique for quantification of terpenes in air influenced by both biogenic and anthropogenic emissions. However, we demonstrate that by combining periods of moderately fast chromatography, more conventional chromatography conditions, and isothermal separation, satisfactory separation of a range of monoterpenes and oxygenated C_9–C_{10} terpenoids can be achieved. For these more complex VOC compositions, the GC_AMBIENT II method facilitates chromatographic separation of the monoterpenes listed above, as well as the oxygenated terpenes linalool, α-terpineol, limonene oxide, terpinen-4-ol, methyl chavicol, and the β-pinene oxidation product nopinone, within a ∼ 19 min period. Furthermore, these 18 BVOC are sufficiently separated from potentially co-eluting anthropogenic VOC commonly found in urban air, such

as the propylbenzene and trimethylbenzene isomers (see Fig. 4). Analytical limitations of this method include partial co-elution of the chromatographic peak pairs corresponding to linalool and α-terpineol, β-pinene and 1,3,5-trimethylbenzene, and nopinone and limonene oxide. When present at low to moderate concentrations, each of these partially co-eluting VOC peaks may be individually quantified, albeit with a slightly higher analytical uncertainty compared to other terpenes (see Sect. 2.3). As such, although GC separation of C_9–C_{10} BVOC in polluted air requires a longer analysis time compared to single plant emissions and clean ambient air, this Fast-GC system can still offer a moderate improvement in sampling frequency compared to conventional GC methods, as a result of periods of moderately fast chromatography, the reduced post-separation cooling time, and a fast temperature ramp rate at the end of each analysis (see Table 2).

It should be noted that quantification of sesquiterpenes in ambient air was not attempted during this study. This was primarily in order to optimise the chromatographic separation of monoterpenes whilst minimising analysis time, but was also due to the presence of co-eluting contaminant peaks introduced via the ozone filters used during ambient air sampling (see Sect. 3.2). Furthermore, developing a robust procedure for the accurate quantification of reactive, semi-volatile sesquiterpenes in ambient air is analytically challenging (e.g. the β-caryophyllene lifetime with respect to ozone is $\sim$ 2 min, Atkinson and Arey, 2003), and was considered beyond the scope of this work.

Overall, the Fast-GC methods outlined here facilitate quantification of multiple terpenes in air within a cycle time of 13–22 min per measurement, which corresponds to a measurement frequency that is 2–5 times faster than typical conventional GC methods (e.g. Bouvier-Brown et al., 2009; Jones et al., 2011; Hopkins et al., 2011).

2.3 Calibration

One of the major analytical challenges associated with accurate quantification of atmospheric terpenes is the implementation of a robust calibration technique. Due to the apparent instability of many terpenes when stored for prolonged periods in pressurised

gas canisters (Apel et al., 1999), certified gas standards containing multiple terpenes are not readily available, and hence calibration of these gases is generally less straightforward compared to that of other non-methane hydrocarbons (NMHC).

During the initial instrument development phase, the Fast-GC was calibrated with respect to BVOC by direct injection of liquid standards via the GC injector port, to derive the FID response factor for each terpene. However, simultaneous measurements of a dynamically diluted α-pinene permeation gas by the Fast-GC system and an independently calibrated Agilent GC-FID system (Kato et al., 2004), demonstrated an offset in the derived α-pinene mixing ratio, with the Fast-GC measurement consistently $\sim$ 20 % lower than the GC-FID value. This offset was attributed to a systematic over-estimation of the Fast-GC sample volume (presumably due to unsatisfactory parametersiation of the gas phase sampling conditions). Thus it was apparent that a gas phase calibration procedure was essential in order to achieve accurate terpene quantification (a conclusion that is consistent with other studies, e.g. Apel et al., 1999). Consequently, the calibration procedure for the Fast-GC instrument was modified, and is now based on analysis of a certified primary gas standard containing the monoterpenes α-pinene and β-pinene, in conjunction with the relative FID response factors for the other terpenes (determined by direct injection of BVOC liquid standards).

Gas phase calibration of the Fast-GC with respect to α-pinene and β-pinene is achieved using a 1 ppm 58 component primary VOC gas standard (PAMS-J58, Sumitomo-Seika Chemicals). VOC tend to exhibit better stability in gaseous mixtures at higher concentrations, however mixing ratios of 1 ppm are too high for use in routine day-to-day calibrations. Dilution of the primary standard to produce $\sim$ 5 ppb VOC mixtures generates effective secondary gas standards suitable for short-term use, however these diluted standards demonstrate significant degradation of the monoterpene components after $\sim$ 1 week. As such, independent terpene gas standards are prepared in-house, by injecting $\sim$ 1 µL volumes of a $\sim$ 5 mmol dm^{-3} liquid terpene standard into a nitrogen gas stream which is used to pressurise a 3 L silcosteel canister to $\sim$ 35 psi. 100 mL samples of these "working" terpene gas standards are directly calibrated for

α-pinene and β-pinene against small volumes (10–20 mL) of the 1 ppm PAMS-J58 primary standard, as well as 100 mL volumes of freshly diluted secondary standards. The mixing ratios of the other components in the terpene gas standard are subsequently derived based upon the ratio of their respective FID responses to the α-pinene response factor. Each terpene gas standard typically contains ~ 1–6 ppb of each terpene component, and is used for the day-to-day calibration of the Fast-GC instrument.

The relative response of the FID to each monoterpene, oxygenated terpenoid and sesquiterpene was determined by direct injection of 5 liquid standards containing target BVOC in the concentration range 3 µmol dm^{-3}–3 mmol dm^{-3}. The solutions were prepared volumetrically, by sequential dilution of pure BVOC liquids (Aldrich and Wako, all > 97–99 % purity) in dichloromethane solvent. Direct injection of 0.2 µL volumes of each liquid standard was used to derive the FID response to each species. The response factors for the individual monoterpenes were comparable (all within ~ 15 % of the α-pinene response), with the exception of myrcene, which produced an FID response ~ 25 % lower than that of α-pinene. It is notable that a similar myrcene/α-pinene relative FID response ratio was observed by Faiola et al. (2012). It should also be noted that since the monoterpene camphene is solid at room temperature, in this case the FID response was assumed to be equivalent to that of β-pinene.

In general, a new working terpene gas standard is prepared immediately prior to a field measurement campaign or series of plant chamber experiments, and is subsequently used for day-to-day calibration of the Fast-GC for the duration of that study (typically 2–6 weeks). Stability tests indicate that the monoterpenes are comparatively stable within these low pressure terpene gas mixtures for a period of ~ 10 weeks. Periodic analysis of a single terpene gas standard (twice a week over a 10 week period) revealed a 1σ variation in peak area of ±5–10 % for monoterpenes, with no statistically significant overall reduction in concentration outside of this uncertainty. The oxygenated terpenes exhibited a larger degree of variability, with peak areas varying by ±12–25 %. Although some OBVOC, such as methyl chavicol, did not undergo significant degradation over this period, other species (notably linalool and nopinone) demonstrated

an overall loss of ~ 20 % after 6 weeks, and as much as ~ 40 % degradation after 10 weeks. As such, the OBVOC in the working terpene standard were used for peak identification purposes only, and quantification was based on the relative FID response to α-pinene. A study by Faiola et al. (2012) demonstrates that the widely used effective carbon number (ECN) approximation of relative FID response is a valid approach for quantification of naturally occurring terpenes. Their results suggest that FID calibration for monoterpenes using the theoretical ECN and relative molar response approximation can achieve effective quantification within a 10 % measurement uncertainty.

For simplicity, β-caryophyllene was the only sesquiterpene included in the terpene standard, and showed a variation of ±14 % over a 10 week period, but no statistically significant degradation. It should be noted that other factors may contribute to the observed variations in terpene mixing ratios within the gas standard, such as small changes in instrument sensitivity.

The overall uncertainties in Fast-GC quantification using the methods outlined here are ±8–12 % for monoterpenes, ±14–26 % for OBVOC and ±15–20 % for sesquiterpenes. Where chromatographic peaks are not fully baseline resolved, the corresponding BVOC are subject to the higher uncertainties (e.g. ± ~11–12 % for Δ-3-carene and α-terpinene in plant chamber studies, and ±12 % for β-pinene in ambient air). The greater uncertainty associated with quantification of OBVOC and sesquiterpenes in comparison with monoterpenes is primarily due to reduced precision (presumably as a result of wall losses and/or memory effects, which are characteristic of the less volatile and/or more polar terpenes). It should be noted that this dual gas phase and liquid injection calibration method results in slightly higher measurement uncertainties for terpenes calibrated based upon their relative FID response (in order to account for errors in the liquid calibration procedure), however, in the absence of a reliable commercially available primary gas standard containing all terpenes of interest, this method offers an effective, practical alternative calibration procedure.

3 Applications for Fast-GC quantification of terpenes in air

This section provides a brief outline of two practical applications of Fast-GC based quantification of terpenes in air using the methods detailed in Sect. 2 – namely plant chamber experiments and ambient air monitoring. It should be noted that more in-depth discussions of each of these studies will be presented elsewhere.

3.1 Plant chamber studies

The Fast-GC instrument has been utilised to monitor the terpene composition of white spruce (*Picea glauca*) emissions during single plant chamber studies. During these experiments, an individual white spruce plant was enclosed in a ∼ 5 L teflon chamber and supplied with ∼ 3 L min^{-1} continuous zero air flow (including ambient CO_2 levels). The outflow from the chamber was diverted from a common sample line for simultaneous sub-sampling by Fast-GC (using the dedicated GC_CHAMBER chromatography method outlined in Sect. 2.2), a Proton Transfer Reaction Mass Spectrometer (PTR-MS) and a Laser Induced Fluorescence (LIF) instrument for OH reactivity measurements (Nakashima et al., 2013). The temperature and irradiance of the chamber were controlled such that emissions could be analysed under a range of different simulated environmental conditions. Prior to each experiment, plants were maintained within a dedicated greenhouse facility operated by the National Institute for Environmental Studies (NIES).

Figure 5 shows the mixing ratios of the monoterpenes α-pinene, β-pinene, limonene, camphene, myrcene and Δ-3-carene in white spruce emissions quantified by Fast-GC. During this experiment, the monoterpene mixing ratios were monitored continuously for a ∼ 6 h period with an average sampling frequency of one 6 min averaged measurement every ∼ 17 min, while the chamber was exposed to constant light conditions (∼ 900 µmol m^{-2} s^{-1}) and a variable temperature (23–31 °C). The monoterpene mixing ratios ranged from < 9 ppt to ∼ 1.9 ppb, with the higher concentrations coinciding with the higher chamber temperatures. Figure 5 also demonstrates the good agreement

between the sum of the individual monoterpenes quantified by Fast-GC and the PTR-MS total monoterpene signal.

3.2 Ambient air monitoring

The Fast-GC analytical system used throughout this study is smaller, lighter (and hence more portable) and operates with reduced power consumption (< 1 kW) compared to most conventional GC instruments, primarily since it does not contain a large GC oven. As such, this instrument is ideally suited to short-term in situ ambient air monitoring of VOC in the field. Our Fast-GC system was deployed to provide continuous automated measurements of monoterpenes and C_{10} OBVOC in boundary layer air at a suburban forest site within the Tokyo metropolis, for 10 days during September and October 2012. Ambient air monitoring was performed at the Field Museum Tama (FM Tama) measurement station (35°38′ N, 139°22′ E), which is operated by Tokyo University of Agriculture and Technology, as part of the AQUAS TAMA (Air Quality Study at FM Tama) 2012 field campaign. The site is located in a small forest ∼ 30 km west of central Tokyo, where the dominant tree species are *Cryptomeria japonica* (Japanese cedar), *Chamaecyparis obtusa* (Japanese cypress) and *Quercus serrata* (an indigenous Japanese oak). Throughout the 10 day continuous monitoring period, the site experienced daytime temperatures in the range ∼ 17–29 °C, and wind speeds of ∼ 1–5 m s^{-1} (increasing to ∼ 20 m s^{-1} during a typhoon from 30 September–1 October). To our knowledge, this study represents the first in situ Fast-GC observations of terpenes in ambient air.

Terpenes pre-concentrated from ambient air are susceptible to significant oxidant-mediated destruction within the sample lines and sorbent trap, as a result of their short atmospheric lifetimes with respect to ozone (Helmig, 1997, and references therein). Therefore, when monitoring terpenes in moderate to high ozone environments, it is desirable to incorporate an integrated ozone scrubber within the sampling system. Ozone-mediated destruction of monoterpenes within the Fast-GC sampling system was assessed using ∼ 2 ppb α-pinene in dry air, supplied via a permeation oven. In the presence of ∼ 50 ppb ozone, the α-pinene peak area was reduced by ∼ 6 ± 2 %

compared to samples without ozone. Furthermore, a chromatographic peak, which has been tentatively identified as the α-pinene oxidation product pinonaldehyde, was observed when sampling α-pinene in the presence of ozone. Consequently, during the AQUAS TAMA field study, a 25 mm sodium thiosulfate ($Na_2S_2O_3$) impregnated Acrodisc glass fibre filter (1 µm pore size) was installed between the main sampling manifold and Fast-GC sample line, in order to minimise oxidant interferences (for details regarding filter preparation and suitability for treating gaseous terpene samples, see Pollmann et al., 2005). The ozone removal efficiency of these filters was tested in situ, using a commercial ozone analyser (model 49C, Thermo Scientific). With the $Na_2S_2O_3$ filter inline, ambient ozone mixing ratios of ~ 60–80 ppb were effectively reduced to around 0.5–1.5 ppb. The filter was routinely changed after 5 days continuous sampling, however the used filters showed no reduction in ozone removal efficiency relative to the un-used filters. Helmig (1997) report that the capacity of these filters may be $> 1\,m^3$ air for ambient ozone levels, which, based on our sample volume and frequency, should theoretically allow continuous use for more than 2 weeks.

Tests to assess terpene losses to the $Na_2S_2O_3$ filter surface were performed prior to the AQUAS TAMA field study, using an in-house prepared gaseous mixture containing ~ 0.5–1.5 ppb monoterpenes and selected oxygenated C_{10} terpenes in nitrogen (for details see Sect. 2.3). The terpene gas standard was sampled with and without a $Na_2S_2O_3$ filter inline, and average losses of ~ 3±2 % for monoterpenes and ~ 5±2 % for oxygenated terpenoids were observed when sampling via the filter. Ambient air observations are corrected to account for these relatively small losses, which are within the measurement uncertainty.

Figure 6 shows the time series resulting from continuous Fast-GC observations of 6 monoterpenes and linalool in ambient air at FM Tama, from 24 September to 4 October 2012. As the site was subjected to some local pollution, the GC_AMBIENT II method was utilised for these observations, which resulted in a Fast-GC sampling frequency of 1 sample every ~ 22 min. Biogenic emissions at this site were dominated by isoprene, whilst monoterpenes were detected at comparatively lower concentrations.

The monoterpene composition was dominated by α-pinene, β-pinene and Δ-3-carene, whilst mixing ratios of limonene, myrcene and camphene were generally lower, and often close to the instrument detection limit. The highest monoterpene mixing ratios were typically observed at night, presumably since temperatures remained high enough to drive emissions, whilst oxidant levels decreased relative to daytime, and contraction of the boundary layer reduced vertical dilution of local emissions. Similar monoterpene diurnal profiles have also been reported at other sites (Bouvier-Brown et al., 2009; Nakashima et al., 2013). In contrast, the maximum linalool mixing ratio at FM Tama was observed during early afternoon, while night time concentrations were often close to the instrument detection limit, giving rise to a diurnal profile characteristic of primary BVOC with light and/or temperature dependent emission rates.

The sum of the individual monoterpenes quantified by Fast-GC was in reasonable agreement with the total monoterpene mixing ratio measured by a co-located PTR-MS (see Fig. 6), although the Fast-GC derived value was consistently lower (by an average of ~ 30 %). A similar offset was reported in the monoterpene fluxes derived by conventional GC-MS and PTR-MS instruments above a Californian ponderosa pine plantation (Lee et al., 2005), and indicates the presence of additional monoterpenes below the GC detection limit, and/or some interference from other compounds to the PTR-MS signal (m/z 81 and 137). It should be noted that during the AQUAS TAMA measurements, the offset between the PTR-MS and Fast-GC derived monoterpene mixing ratios was larger when the site was subjected to the typhoon weather system, from 30 September to 1 October (on average the Fast-GC value was ~ 70 % lower), however the reason for the increased discrepancy during this period is unclear.

4 Summary

We have developed a novel Fast-GC based approach for targeted analysis of a range of C_9–C_{15} BVOC in air, with flame ionisation detection. The three methods outlined in this study retain the chromatographic separation capability of conventional GC (to

provide quantification of individual terpene isomers), whilst offering improved sampling frequency to facilitate effective monitoring of short-term variations in the terpene composition of single plant emissions and ambient air.

We demonstrate that the terpene composition of pristine forest air (with minimal anthropogenic influence) and single plant emissions may be effectively analysed by moderately fast GC methods, with a measurement frequency of one sample every ∼ 13–16 min. However, in light of recent studies reporting significant BVOC mediated ozone formation within the urban boundary layer (Lee et al., 2006; Curci et al., 2009), there is increasing motivation for in situ observations of these biogenic gases in polluted atmospheres, as well as within clean forest air. As such, we have also developed a Fast-GC based method suitable for the quantification of monoterpenes and selected OBVOC in polluted environments, where significant concentrations of anthropogenic VOC and BVOC are present. Initial tests demonstrated that analysis of these more complex VOC compositions is not a viable application for very fast GC, and in order to avoid substantial peak co-elution it is necessary to use a combination of moderately fast gas chromatography in conjunction with periods of more conventional (and in some cases isothermal) separation. Under these conditions, the measurement cycle time is increased to ∼ 22 min.

Overall, the chromatography methods outlined in this study offer a procedure for comprehensive analysis of speciated monoterpenes, selected oxygenated terpenoids including the β-pinene oxidation product nopinone, and (in plant chamber studies) sesquiterpenes, with a measurement frequency 2–5 times higher than conventional GC methods. We have successfully applied these Fast-GC based methods to provide terpene composition analysis of single plant emissions and ambient air. Throughout the plant chamber studies, the sum of the Fast-GC derived monoterpene mixing ratios was generally in good agreement with the total monoterpene mixing ratio derived from simultaneous PTR-MS measurements. In contrast, during in situ ambient air observations, the Fast-GC and PTR-MS derived monoterpene mixing ratios demonstrated an average offset of ∼ 30 %. Such an offset has also been reported in previous studies

comparing GC and PTR-MS ambient monoterpene measurements (e.g. Lee et al., 2005), suggesting that this is a commonly observed instrumental inconsistency which requires further investigation by the atmospheric monoterpene measurement community.

Recent developments in analytical methodologies have advanced the ambient air terpene monitoring capabilities of both GC (e.g. this study; Purvis et al., 2013) and PTR-MS (e.g. Misztal et al., 2012) based techniques, as well as offline sampling methods (e.g. Yassaa et al., 2010). However, even these state-of-the-art techniques still focus primarily on isoprene and/or monoterpenes, while the number of ambient sesquiterpene and oxygenated terpene observations remain comparatively limited. Moreover, OH reactivity measurements suggest that the fraction of unidentified reactive BVOC in ambient air remains significant. As such, further instrumental developments to increase the chemical diversity and spatiotemporal resolution of terpene observations are fundamental to obtaining a more in-depth understanding of the role of these gases in atmospheric processes that influence air quality and climate.

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Table 1. BVOC targeted for quantification by Fast-GC, their rate constants with respect to reaction with the atmospheric oxidants OH and O_3, and limits of detection (LOD) for Fast-GC analysis of BVOC in plant chamber studies and in ambient air.

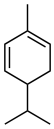
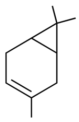
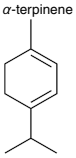
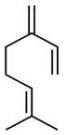
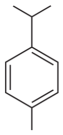
	$k_{OH} \times 10^{12}$ ($cm^3 molec^{-1} s^{-1}$)	$k_{O_3} \times 10^{18}$ ($cm^3 molec^{-1} s^{-1}$)	LOD (ppt) (a) AMBIENT (b) CHAMBER		$k_{OH} \times 10^{12}$ ($cm^3 molec^{-1} s^{-1}$)	$k_{O_3} \times 10^{18}$ ($cm^3 molec^{-1} s^{-1}$)	LOD (ppt) (a) AMBIENT (b) CHAMBER
Monoterpenes							
α-pinene	53.7	86.6	(a) 4; (b) 10	α-phellandrene	313.0	2980.0	(a) 5; (b) 11
							
Camphene	53.0	0.90	(a) 4; (b) 10	Δ-3-carene	88.0	37.0	(a) 5; (b) 11
							
β-pinene	78.9	15.0	(a) 4–5; (b) 9	α-terpinene	363.0	21 100.0	(a) 5; (b) 10
							
Myrcene	215.0	86.6	(a) 4–5; (b) 9	p-cymene	15.1[a]	< 0.05[b]	(a) 5; (b) –
							

Table 1. Continued.

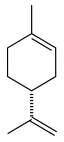
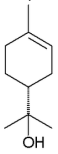
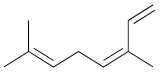
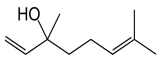
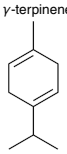
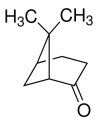
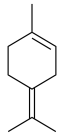
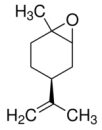
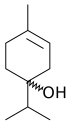
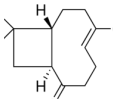
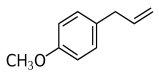
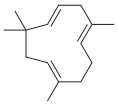
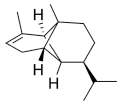
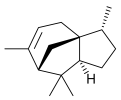
	$k_{OH} \times 10^{12}$ ($cm^3 molec^{-1} s^{-1}$)	$k_{O_3} \times 10^{18}$ ($cm^3 molec^{-1} s^{-1}$)	LOD (ppt) (a) AMBIENT (b) CHAMBER		$k_{OH} \times 10^{12}$ ($cm^3 molec^{-1} s^{-1}$)	$k_{O_3} \times 10^{18}$ ($cm^3 molec^{-1} s^{-1}$)	LOD (ppt) (a) AMBIENT (b) CHAMBER
				Oxygenated terpenes			
Limonene	171.0	200.0	(a) 4; (b) 9	α-terpineol	190.0[c]	300.0[c]	(a) 4; (b) –
							
Ocimene	252.0	540.0	(a) 4; (b) 9	Linalool	160.0[d]	430.0[d]	(a) 4; (b) 8
							
γ-terpinene	177.0	140.0	(a) 4; (b) 9	Nopinone	17.0[e]	< 0.005[e]	(a) 5; (b) –
							
terpinolene	225.0	1880.0	(a) 4; (b) –	Limonene oxide	11.1[a]	< 0.15[b]	(a) 5; (b) 8
							

Table 1. Continued.

	$k_{OH} \times 10^{12}$ ($cm^3 molec^{-1} s^{-1}$)	$k_{O_3} \times 10^{18}$ ($cm^3 molec^{-1} s^{-1}$)	LOD (ppt) (a) AMBIENT (b) CHAMBER		$k_{OH} \times 10^{12}$ ($cm^3 molec^{-1} s^{-1}$)	$k_{O_3} \times 10^{18}$ ($cm^3 molec^{-1} s^{-1}$)	LOD (ppt) (a) AMBIENT (b) CHAMBER
Terpinen-4-ol	170.0	250.0	(a) 4; (b) 8	*β*-caryophyllene	197.0	11 600.0	(a) –; (b) 12
							
Methyl chavicol	54.0[f]	12.0[f]	(a) 4; (b) 8	*α*-humulene	293.0	11 700.0	(a) –; (b) 11
							
Sesquiterpenes							
α-copaene	90.0	160.0	(a) –; (b) 11				
							
α-cedrene	67.0	28.0	(a) –; (b) 12				
							

Note that a range of ambient air LOD's are reported where the value is different for the two chromatography methods. LOD's for plant chamber analyses correspond to a sample volume of 350 mL. Rate constants are from Atkinson (1997) unless otherwise stated. [a] From Corchnoy and Atkinson (1990); [b] from Atkinson et al. (1990); [c] from Wells (2005); [d] from Atkinson et al. (1995); [e] from Calogirou et al. (1999); [f] from Bouvier-Brown et al. (2009).

Table 2. Carrier gas flow velocities and temperature programmes utilised during Fast-GC analysis of BVOC in ambient air and single plant emissions.

	Upper flow velocity ($cm\,s^{-1}$)	Upper temperature (°C)	Temperature ramp rate ($°C\,min^{-1}$)	Hold time (min)
GC_CHAMBER				
Initial	60	40	–	2.0
Ramp 1	80	110	11	0
Ramp 2	70	160	42	0
Ramp 3	65	200	9	0.5
Total analysis time				14.5 min
GC_AMBIENT I				
Initial	52	39	–	2.0
Ramp 1	56	46	6	0.4
Ramp 2	70	72	6	0.2
Ramp 3	90	85	18	0
Ramp 4	85	125	40	0
Ramp 5	75	215	55	0.2
Total analysis time				11.7 min
GC_AMBIENT II				
Initial	51	38	–	2.0
Ramp 1	55	44	1	0.2
Ramp 2	75	64	5	2.8
Ramp 3	88	94	15	0
Ramp 4	85	125	35	0
Ramp 5	75	215	75	0.4
Total analysis time				19.7 min

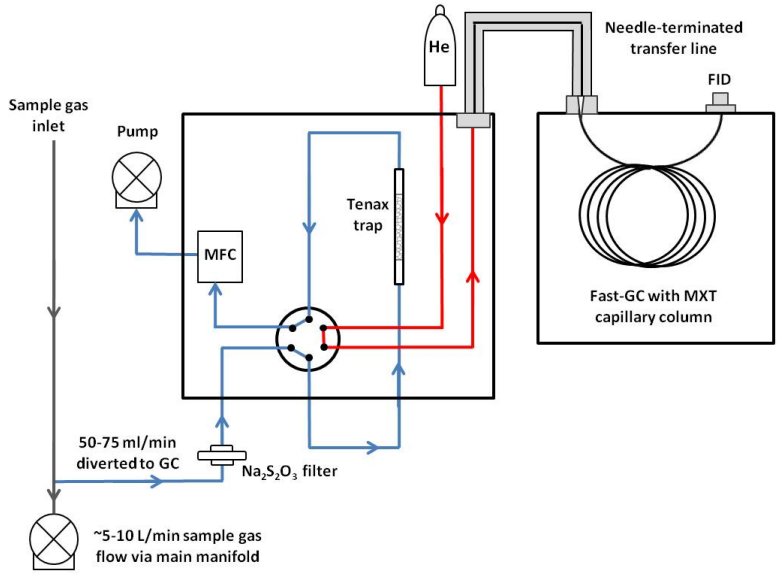


Fig. 1. Schematic of Fast-GC instrument, thermal desorber and needle-terminated transfer line, in the air sampling configuration. The sample gas flow path is illustrated in blue; helium carrier gas flow within the thermal desorber is shown in red.

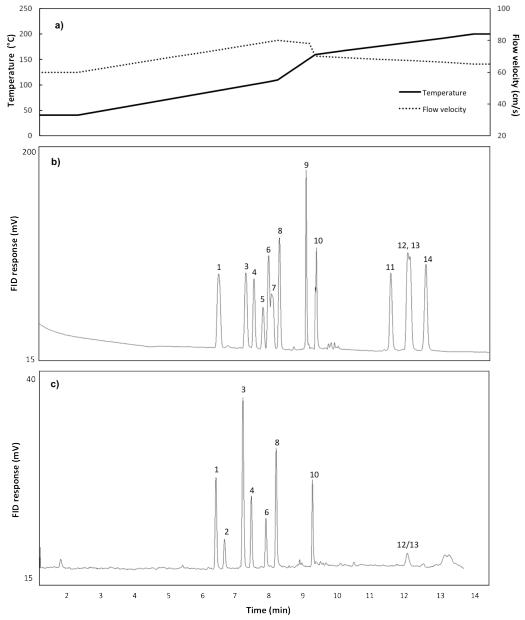


Fig. 2. Panel **(a)** shows the temperature and carrier gas flow velocity programmes used for the GC_CHAMBER method. Panel **(b)** shows a chromatographic trace recorded using the GC_CHAMBER method for analysis of BVOC in liquid standard (~ 2.0–8.0 mg L^{-1} terpenes in isop-propyl alcohol). Panel **(c)** is a chromatogram resulting from analysis of BVOC in air during a white spruce (*Picea glauca*) plant emission study. Chromatographic peaks correspond to the following BVOC; α-pinene(1), camphene(2), β-pinene(3), myrcene(4), α-phellandrene(5), Δ-3-carene(6), α-terpinene(7), limonene(8), linalool(9), limonene oxide(10), α-copaene(11), α-cedrene(12), β-caryophyllene(13), α-humulene(14).

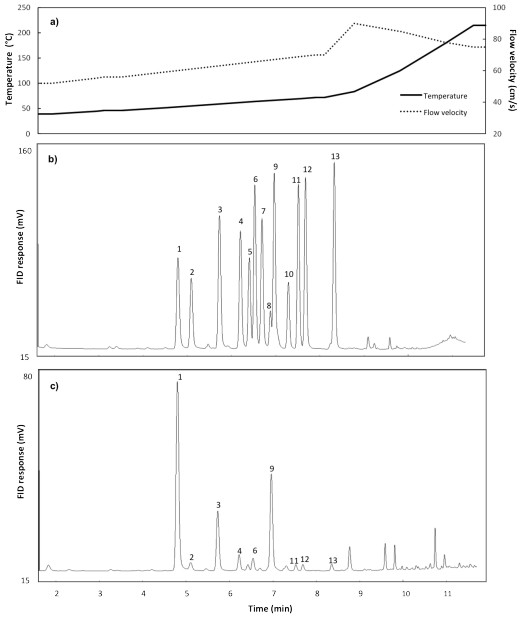


Fig. 3. Panel **(a)** shows the GC_AMBIENT I method temperature and carrier gas flow velocity programmes. Panel **(b)** shows a chromatographic trace recorded using the GC_AMBIENT I method for analysis of a monoterpene liquid standard (~ 1.0–5.0 mg L^{-1} monoterpenes in isop-propyl alcohol). Panel **(c)** demonstrates chromatographic analysis of monoterpenes in unpolluted ambient air using this method. Chromatographic peaks correspond to the following monoterpenes; α-pinene(1), camphene(2), β-pinene(3), myrcene(4), α-phellandrene(5), Δ-3-carene(6), α-terpinene(7), p-cymene(8), limonene(9), ocimene(10), unidentified terpene(11), γ-terpinene(12), terpinolene(13).

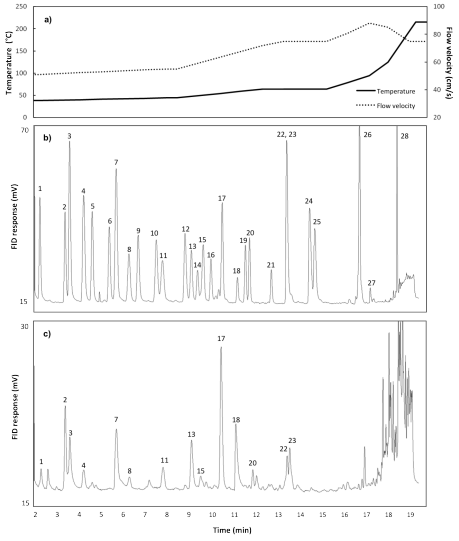


Fig. 4. Panel **(a)** shows the temperature and carrier gas flow velocity programmes used for the GC_AMBIENT II method. Panel **(b)** shows a chromatographic trace recorded using the GC_AMBIENT II method for analysis of VOC within an in-house prepared gas standard (containing ~ppb concentrations of BVOC and common anthropogenic VOC). Panel **(c)** shows a chromatogram resulting from analysis of VOC in ambient air. Chromatographic peaks are labelled as follows; ethylbenzene(1), p-xylene + m-xylene(2), styrene(3), o-xylene(4), nonane(5), iso-propylbenzene(6), α-pinene(7), camphene(8), n-propylbenzene(9), 1,3,5-trimethylbenzene(10), β-pinene(11), 1,2,4-trimethylbenzene(12), myrcene(13), α-phellandrene(14), Δ-3-carene(15), α-terpinene(16), limonene(17), ocimene(18), unidentified terpene(19), γ-terpinene(20), terpinolene(21), linalool(22), α-terpineol(23), nopinone(24) limonene oxide(25), terpinen-4-ol(26), methyl chavicol(27), β-caryophyllene(28).

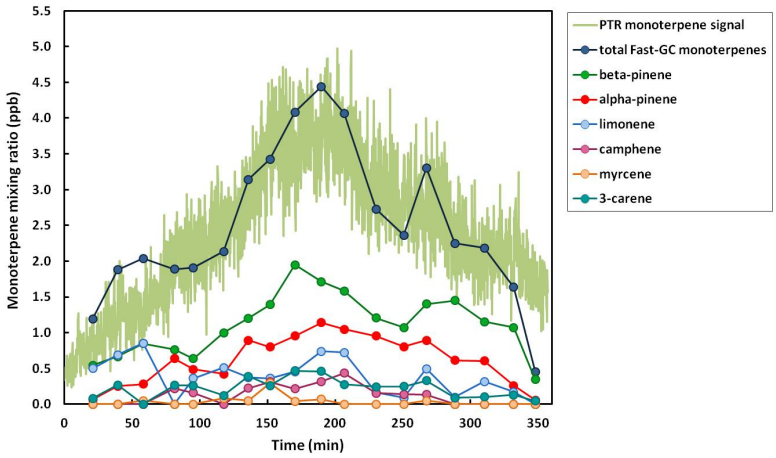


Fig. 5. Monoterpene composition of white spruce emissions, as determined by Fast-GC during a plant chamber study. The sum of the individual monoterpenes measured by Fast-GC is overlaid with the simultaneously measured PTR-MS total monoterpene signal (15 s averaged).

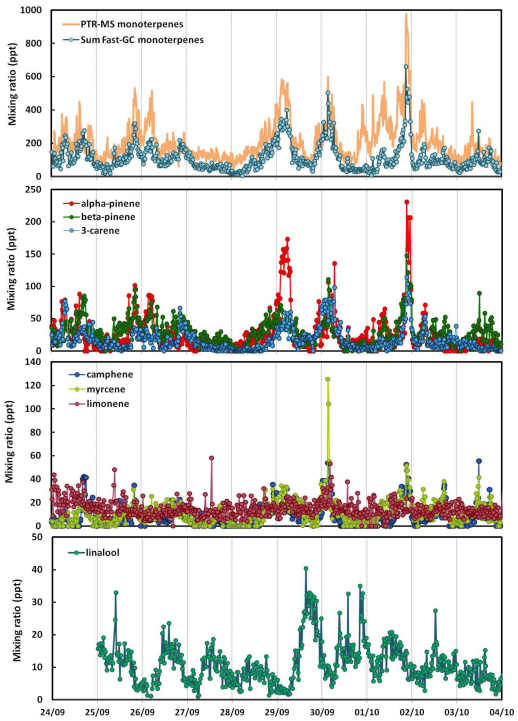


Fig. 6. Time series showing the sum of Fast-GC quantified monoterpenes and 10 min averaged PTR-MS monoterpene signal, as well as mixing ratios of selected individual terpenes monitored by Fast-GC at the FM Tama field station in the Tokyo metropolis, during September-October 2012. Fast-GC analyses were performed using GC_AMBIENT II method, resulting in a sample frequency of 1 measurement every ~ 22 min.