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Atmospheric Measurement Techniques Discussions

Volatilizable biogenic organic compounds (VBOCs) with two dimensional gas chromatography-time of flight mass spectrometry (GC × GC-TOFMS): sampling methods, VBOC complexity, and chromatographic retention data

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Abstract

Two dimensional gas chromatography (GC × GC) with detection by time-of-flight mass spectrometry (TOFMS) was applied in the rapid analysis of air samples containing highly complex mixtures of volatilizable biogenic organic compounds (VBOCs). VBOC analytical methodologies are briefly reviewed, and optimal conditions are discussed for sampling with both adsorption/thermal desorption (ATD) cartridges and solid-phase microextraction (SPME) fibers. Air samples containing VBOC emissions from leaves of two tree species (*Cedrus atlantica* and *Calycolpus moritzianus*) were obtained by both ATD and SPME. The optimized gas chromatographic conditions utilized a 45 m, 0.25 mm I.D. low-polarity primary column (DB-VRX, 1.4 µm film) and a 1.5 m, 0.25 mm I.D. polar secondary column (Stabilwax®, 0.25 µm film). Excellent separation was achieved in a 36 min temperature programmed GC × GC chromatogram. Thousands of VBOC peaks were present in the sample chromatograms; hundreds of tentative identifications by NIST mass spectral matching are provided. Very few of the tentatively identified compounds are currently available as authentic standards. Method detection limit values for a 5 l ATD sample were 3.5 pptv (10 ng m^{-3}) for isoprene, methyl vinyl ketone, and methacrolein, and ~1.5 pptv (~10 ng m^{-3}) for monoterpenes and sesquiterpenes. Kovats-type chromatographic retention index values on the primary column and relative retention time values on the secondary column are provided for 21 standard compounds and for 417 tentatively identified VBOCs. 19 of the 21 authentic standard compounds were found in one of the *Cedrus atlantica* SPME samples. In addition, easily quantifiable levels of at least 13 sesquiterpenes were found in an ATD sample obtained from a branch enclosure of *Calycolpus moritzianus*. Overall, the results obtained via GC × GC-TOFMS highlight an extreme, and largely uncharacterized diversity of VBOCs, consistent with the hypothesis that sesquiterpenes and other compounds beyond the current list of typically determined VBOC analytes may well be important contributors to global atmospheric levels of organic particulate matter.

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1 Introduction

Organic compounds volatilize to the atmosphere from both anthropogenic and biogenic sources. Anthropogenic emissions of non-methane volatile organic compounds (VOCs) have been estimated at 110 to 150 $Tg\,y^{-1}$ (Muller, 1992; Piccot et al., 1992). In contrast, the global input to the atmosphere of non-methane biogenic volatile organic compounds (BVOCs) has been estimated at ~1100 $TgC\,y^{-1}$ (Guenther et al., 1995), much of that amount being plant related. The non-methane BVOCs are: (1) important in the geochemical cycling of carbon (Guenther, 2002); (2) have significant effects on tropospheric ozone levels (Williams et al., 1997; Starn et al., 1998); (3) affect hydroxyl radical concentrations (Tan et al., 2001; Lelieveld et al., 2008) and thus the lifetimes of ozone-depleting and greenhouse gases (Kaplan et al., 2006); and (4) are oxidized in the atmosphere to products that can condense (Haagen-Smit, 1952) and thereby form atmospheric organic particulate matter (OPM) that can affect the radiative and cloud nucleation properties of atmospheric particles (Goldstein et al., 2009; Pöschl et al., 2010).

European Union Directive 1999/13/EC defines a VOC as any organic compound having a vapor pressure of $\geq 10^{-2}$ kPa (10^{-4} atm) at 293.15 K. Isoprene as a pure liquid at this temperature has a vapor pressure of $p_L^o = 70$ kPa (0.7 atm). A semivolatile organic compound (SVOC) has been defined as a compound with a p_L^o value in the range from 10^{-2} kPa (10^{-4} atm) down to 10^{-9} kPa (10^{-11} atm) (Bidleman, 1988). By definition, an SVOC has significant affinity for condensed phases, yet is sufficiently volatile that it can partition significantly to the atmosphere, particularly when other mechanisms (e.g., oxidation) continually remove the compound from the gas phase and thus maintain the driving force for volatilization. De Gouw et al. (2011) have reported observations that suggest that SVOCs can evaporate from spilled crude oil, be oxidized in the atmosphere to lower vapor pressure compounds, and thereby lead to formation of atmospheric OPM. At $p_L^o \approx 10^{-3}$ kPa (10^{-5} atm) at 293 K, sesquiterpenes (e.g., farnesene) are relatively volatile SVOCs, and are of significant interest here for their

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contribution to both gas- and particle-phase processes. Therefore, in place of the term BVOCs, we use the term "volatilizable biogenic organic compounds" (VBOCs) to refer to the full span of biogenic compounds of interest here. (The VBOC group does not include methane.)

Plants release VBOCs simply because in plant tissues these compounds tend to be lost to the surrounding environment by diffusive transport mechanisms; accelerated loss can occur because of mechanical/herbivore wounding. Of particular interest is the fact that certain VBOCs are released when plants experience environmental stress (Heiden et al., 2003). Stress indicator compounds include ocimene, farnesene, methyl salicylate, salicylic acid, jasmonic acid, and a group of C_6 aldehydes, alcohols, and esters referred to as "green-leaf volatiles" (Heil and Ton, 2008; Kännaste et al., 2008; Staudt and Bertin; 1998).

Overall, VBOCs are highly diverse and include: (1) numerous terpenes including isoprene (C_5H_8) which is a hemiterpene, monoterpenes ($C_{10}H_{16}$), sesquiterpenes ($C_{15}H_{24}$), and diterpenes ($C_{20}H_{32}$); (2) terpenes that have been functionalized (e.g, oxidized) in numerous ways and at a variety of positions; (3) alkanes and alkenes; (4) alkyl aldehydes and ketones; (5) alkyl alcohols, ethers, acids, and esters; and (6) chiral variants such as (±)-α-pinene, (±)-β-pinene, and (±)-limonene (Williams et al., 2007; Yassaa et al., 2010). The complexity of the VBOC group is therefore due both to the variety of chemical sub-classes represented, and to the substantial numbers of compounds in many of the sub-classes. Another complicating factor is that the reactivities of individual VBOCs vary widely. With regard to functionalized compounds, the term VBOC, as used here, explicitly includes early oxidation products of plant-produced compounds (caryophyllene oxide is an example of such an oxidation product).

The chemical variety, numbers, and reactivities of VBOCs have posed considerable challenges in efforts designed to develop quantitative understandings of important processes governing the VBOCs. First, large uncertainties remain regarding simply the overall magnitude of the total annual mass emissions of VBOCs and whether unidentified or undetected compounds contribute significantly to those emissions (e.g.,

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Goldstein and Galbally, 2007). Even when the list of VBOCs considered is relatively "comprehensive" (e.g., isoprene, α-/β-pinene, α-phellandrene, camphene, Δ^3-carene, limonene, myrcene, α-/γ-terpinene, terpinolene, linalool, nopinone, methyl-chavicol, α-bergamotene, β-caryophyllene, α-/β-farnesene, longifolene), the measured fluxes and atmospheric concentrations do not appear to account for total VBOC mass emissions. For example, measured fluxes have not always been consistent with observed levels of OH reactivity (Di Carlo et al., 2004), observed O_3 fluxes (Goldstein et al., 2004), or emissions data from co-located enclosure samples (Goldstein et al., 2004; Bouvier-Brown et al., 2009a). Moreover, observations of higher than expected secondary organic aerosol levels have been cited as evidence of "missing" VBOCs (e.g., Goldstein and Gallbally, 2007). There are numerous difficulties that complicate the acquisition of accurate VBOC emission estimates. First, mass emission estimates are difficult for reactive terpenoids, even in locations where the emission rates are relatively high (Bouvier-Brown et al., 2009a, b; Ortega et al., 2007). Second, large uncertainties remain regarding the variabilities in VBOC emissions by plant species, geographic location, and season (e.g., Helmig et al., 2007). For example, annual emissions in the US of isoprene and a number of monoterpenes may be changing by amounts and for reasons that are not adequately understood (Purves et al., 2004), and the responses of VBOC emissions to changing climate parameters remain highly uncertain (Rosenstiel et al., 2003; Guenther et al., 2006; Chen et al., 2009, Penuelas and Staudt, 2010). Third, almost nothing is known concerning either the relative importance of chiral variants (e.g. (+) vs. (−)α-pinene, (+) vs. (−)β-pinene, etc.), or how much important biogeochemical information is held within chiral patterns of VBOC emissions (Williams et al., 2007; Yassaa et al., 2010). Overall, despite the fact that many BVOC emission studies currently appear each year in the scientific literature, most have targeted only a few compounds as analytes. In contrast, investigators making the effort to look for other compounds (e.g., Jardine et al., 2010) have found a wide range of VBOCs.

Given the significant impact of VBOC emissions on biosphere-atmosphere interactions and air chemistry, there is a great need for development and application of new

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analytical methodologies capable of characterizing the complex nature of VBOC emissions. Development of new methodologies can be obtained by: (1) application of suitable sample collection methods; (2) application of high-separation gas chromatography (GC) methods that can adequately address VBOC complexity; and (3) accumulation of GC retention index information based on as many authentic standard compounds as possible (many VBOCs of interest are not easily obtained in pure form). Here we describe the collection, tentative identification and determination, and chromatographic characterization of VBOCs in highly complex samples using two-dimensional gas chromatography/time-of-flight mass spectrometry (GC × GC/TOFMS), the latter being the most powerful separation+detection methodology currently available for VBOCs. We preface the description of the laboratory measurements with a brief review of available methods for sampling and analysis.

2 Available sampling and analysis methods

2.1 Determination with field-deployed instrumentation

Analytical instruments have often been deployed to the field in studies of plant-derived VBOCs in ambient air and as emanating from plants within experimental enclosures. Though often costly and logistically difficult, field deployment of instruments is advantageous when plant emissions and ambient concentrations are subject to short time variations: VBOCs that are moderately-to-highly reactive are of particular interest in this regard. Field-deployed analytical approaches are discussed in a recent review (Ortega and Helmig, 2008) and include: (1) chemiluminescence for detection of isoprene (Guenther et al., 1996; Singsaas and Sharkey, 2000); (2) proton transfer reaction mass spectrometry (PTR-MS) for the direct simultaneous detection of multiple compounds (Karl et al., 2001; Bamberger et al., 2010; Mielke et al., 2010); (3) solid phase microextraction (SPME) fiber collection of analytes followed by thermal desorption to a field GC instrument; and (4) adsorption/thermal desorption (ATD) cartridge sampling of a known air volume (e.g., 1–10 l) followed by thermal desorption of the

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analytes to a field GC instrument. PTR-MS has been employed when VBOC concentrations are subject to high temporal variability (e.g., minutes) as in studies of forest air (e.g., Mielke et al., 2010), fluxes by eddy co-variance measurements (e.g., Karl et al., 2001; Bamberger et al., 2010), and emission processes in dynamic enclosure studies (e.g., Grabmer et al., 2006; Bouvier-Brown et al., 2007). Good agreement has been obtained for total sesquiterpenes in field-deployed PTR-MS vs. SPME (Bouvier-Brown et al., 2007). (PTR-MS cannot distinguish different structural isomers because it only measures molecular masses, e.g., cannot distinguish individual monterpenes, individual sesquiterpenes, etc.)

2.2 Determination in the laboratory

ATD cartridges are easily transported to and from the field, and provide a simple, sensitive, and quantitative approach for determining a wide range of VOCs at ambient atmospheric levels (Pankow et al., 1998, 2003). Laboratory-based ATD determinations of VBOCs in field samples have utilized GC/FID, GC/MS, and GC × GC-TOFMS (Saxton et al., 2007). (FID = flame ionization detector.) Several considerations are important in the implementation of ATD with VBOCs. First, losses of reactive VBOCs may need to be prevented by removal of oxidants, particularly ozone, prior to passage of the sample air through the cartridge (Cao and Hewitt, 1994; Calogirou et al., 1996). Numerous different ozone removal methods have been used (Helmig, 1997; Fick et al., 2001; Pollmann et al., 2005). These have involved sodium thiosulfate on filters (Helmig et al., 1998), potassium iodide on glass wool or filters (Helmig and Greenberg, 1994), manganese dioxide on porous nets or copper screens (Hoffmann, 1995; Calogirou et al., 1996), and titration of ozone with nitrogen monoxide (Komenda et al., 2003). Second, because atmospheric concentrations decrease strongly with decreasing VBOC volatility (viz., vapor pressure), if the goal is the simultaneous quantitation of a wide range of compounds, it may be necessary to use a large sample volume. That choice usually leads to the need for multiple sorbents in the bed: weaker sorbent first, then

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the stronger sorbent. The low p_L^o compounds are retained on the weaker sorbent, and the higher p_L^o compounds pass onto and are retained by the stronger sorbent. After sampling, the thermal desorption flow occurs in a backflush direction so that the lower p_L^o compounds are not exposed to the stronger sorbent. Given the large dynamic range in concentration usually accompanying such samples, currently it can be helpful to employ a unit such as the TurboMatrix 650 ATD (PerkinElmer, Waltham, MA) for the thermal desorption. With the latter, the desorption flow can be divided so that part (e.g., 30 %) goes to the GC and the remainder goes to a pre-cleaned cartridge to be held for a possible second GC run. For the first GC run, the injector split ratio might be 1 in 10. If the injector split ratio in the second GC run is lower (e.g., 1 in 5), then the method sensitivity in the second run can be higher than in the first run (e.g. (70/30)(0.2/0.1) $\approx 4\times$). This can allow less abundant compounds to become quantifiable, though some of the early-eluting compounds may then be overloaded.

Common ATD adsorbents for VBOCs include the porous organic polymer Tenax® TA and several more strongly sorbing carbon-based materials (Table 1). Attractive characteristics of these adsorbents are their good abilities to reversibly sorb analytes, low water affinities (i.e., low breakthrough volume (BV) values for water), and complementary sorption strengths (Dettmer and Engewald, 2002; Arnts et al., 2010). BV values for monoterpenes on Tenax® TA are high (Table 1) so that for sample volumes of a few liters and ~100 mg of Tenax® TA monoterpenes are quantitatively retained. That is not the case for isoprene and other volatile compounds, retention of which requires the additional presence of a carbon-based sorbent. Many current ATD applications utilize 0.25 inch O.D. × 3.5 inch cartridges packed with ~100 mg of Tenax® TA followed by ~100 mg of either Carbotrap™ B or Carbograph™ 1TD (Komenda et al., 2001; Sartin et al., 2001; Hakola et al., 2006; Helmog et al., 2006; Ortega and Helmig, 2008; Haapanala et al., 2009; Geron and Arnts, 2010). The Tenax® TA prevents compounds like the monoterpenes from substantively reaching the carbon-based sorbent whereon they would not only be strongly retained but also possibly chemically altered. Significant interconversion of several monoterpenes has been reported on Carbotrap® 200

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and Carbotrap® 300 (Greenberg et al., 1999a). Similar results have been reported by Cao and Hewitt (1993).

SPME fibers provide an alternative to ATD cartridges (Bouvier-Brown et al., 2009b). SPME, however, can be considerably less sensitive than ATD (as with highly volatile analytes that are weakly sorbed and/or with low volatility compounds at low concentrations), does not provide as much overall sample stability (Bouvier-Brown et al., 2007; Baker and Sinnott, 2009), and is labor intensive to calibrate in quantitative applications. Nevertheless, SPME becomes exceedingly attractive for its convenience when the analyte concentrations are high, the work is proceeding in/near a laboratory, and/or the desired determinations are only qualitative or semi-quantitative in nature. SPME has been used in laboratory-based measurements with GC-FID to determine isoprene emission rates from enclosed tree seedling branches (Tsui et al., 2009), and with GC/FID, GC/MS and 100 l Tedlar bags to measure sesquiterpene emissions from whole trees (*Pinus sabiniana* and *Pinus ponderosa*) (Baker and Sinnott, 2009).

"Whole-air" sampling with canisters or bags provides an alternative to ATD cartridges and SPME fibers as a means to collect and transport sample analytes to a conventional laboratory for analysis. Whole air in a canister or bag can be aliquotted with a sample loop, cryofocused (e.g., at −150 °C on a trap containing 60/80 mesh glass beads as in method TO-14 , US EPA, 1999a), sampled using ATD (Pressley et al., 2004) or SPME (Bouvier-Brown et al., 2007), or cryofocussed directly on the GC column (Pankow, 1986). For canisters, inert internal surfaces are important, and both Summa-polished® stainless steel and Silcosteel® canisters are used (US EPA, 1999a,b). However, canisters are still subject to losses at high humidity (Batterman et al., 1998), and are costly and complicated to clean. Teflon bags suffer from blank problems, frequently leak, and are difficult to clean after use (Greenberg et al., 1999a); Tedlar bags are subject to similar problems. Available data indicate that many analytes are more stable when stored on ATD cartridges than in bags, especially when oxidant species are present in the sample air. Evidence of losses in Teflon bags for methacrolein, methyl vinyl ketone, and α-pinene have been reported (Greenberg et al., 1999a). A summary of

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minimum detection limit (MDL) values for VBOCs by various methodologies is provided in Table 2.

2.3 GC × GC-TOFMS

Applications of GC × GC usually utilize a primary column with either a non-polar or low-polarity stationary phase. Co-elution of some peaks from the primary column is inevitable with highly complex samples. With GC × GC (aka 2D GC), periodic slices of effluent from the primary column are individually: (1) cryofocused at the end of the column; then (2) thermally desorbed to a secondary column with a more polar stationary phase. Separation of compounds that co-exist in a given slice can be accomplished on the secondary column if the compounds differ in polarities and/or polarizabilities. GC × GC-TOFMS has been applied with success in the analysis of diesel fuel (Arey et al., 2005), weathered petroleum (Frysinger et al., 2003), urban aerosol particulate matter (Hamilton et al., 2004), tobacco smoke particulate matter (Cochran, 2008), and tissue extracts (Welthagen et al., 2005). GC × GC chromatographic retention index data have been tabulated for diesel fuel hydrocarbons (Arey et al., 2005), but not for VBOCs.

The varying polarizabilty/polarity characteristics of the VBOCs are imparted by varying numbers of rings, double bonds, and polar functionalizations. GC × GC with a less-polar primary column and a more-polar secondary column is well suited for separating VBOC mixtures. GC × GC-TOFMS has been used to determine VBOCs in ATD samples of forest canopy air and air from branch and leaf enclosures (Saxton et al., 2007). Quantitative measurements were reported for isoprene, α-pinene, β-pinene, camphene and limonene, as were relative peak intensities for 11 tentatively identified compounds (Saxton et al., 2007).

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3 Experimental

3.1 Chemicals and standard mixtures

21 VBOC chemicals (≥95 % pure) were obtained from Sigma-Aldrich (St. Louis, MO) (isoprene, α-pinene, camphene, myrcene, β-pinene, α-phellandrene, Δ^3-carene, limonene, terpinolene, *p*-cymene, nopinone, linalool, 4-terpinenol, terpineol, eucalyptol, camphor, estragole (methyl chavicol), α-cedrene, caryophyllene, aromadendrene, and α-humulene). Optimally, the list of standard compounds would have included many tens of C_{10}-and-higher VBOCs. Unfortunately, authentic standard materials are not readily available for the vast majority of such compounds, and even just having doubled the number of standard compounds would have required use of multi-component "essential oils", with concomitant prior quantitation of the VBOC components of interest. Such efforts are underway in our laboratories, but were not applied in this study. Standard mixes of the 21 VBOCs in methanol were prepared at per-component concentrations from 0.5 ng μl^{-1} to 20 ng μl^{-1}. A gas standard containing four internal standard (IS) compounds (fluorobenzene, toluene-d_8, 4-bromofluorobenzene, and 1,2-dichlorobenzene-d_4) at 80 ng ml^{-1} per component was prepared in a stainless steel canister as described elsewhere (Pankow et al., 1998).

3.2 ATD cartridges – NCAR preparation and procedures for field sampling

Field samples discussed here were collected by the Biosphere-Atmosphere Interactions Group of the National Center for Atmospheric Research (NCAR). Details regarding sample collection are available (Greenberg et al., 1999a, b, 2004). Briefly, samples were obtained using stainless steel, 0.25 inch O.D. × 3.5 inch, dual sorbent cartridges (Tenax^{TM} TA plus Carbotrap^{TM} B, or Tenax^{TM} GR plus Carbograph^{TM}). Prior to sampling, cartridges were cleaned by heating for 8 h at 275 °C with a 50 ml s^{-1} flow of ultra-high purity N_2 gas. Clean cartridges were capped and stored at 10 °C until used. The apparatus consisted of an O_3 trap, the sample cartridge, and a flow-controlled

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pump. Samples were collected at a flow rate of 200 cm^3 min^{-1} for 30 min. After sampling, cartridges were sealed, shipped at ambient temperatures back to the laboratory (maximum 1 week shipping time), then maintained at 10 °C until analyzed. After four weeks at ambient temperatures, losses were <10 % for C_3 to C_6 compounds of interest (Greenberg et al., 1999a).

3.3 ATD cartridges and SPME fibers – PSU preparation and procedures for samples obtained in the laboratory

In laboratory ATD sampling of air from vials holding plant materials, each glass cartridge contained 100 mg of Tenax™ TA plus 120 mg of Carbotrap™ B. (Prior to packing, 5 g of Tenax™ TA was placed in a glass column and cleaned with a 250 ml flow of 50/50 *(v/v)* acetone/hexane.) After packing, each cartridge was conditioned for 1 h at 300 °C with 100 ml min^{-1} of He gas (precleaned using a U-shaped hydrocarbon trap in liquid N_2). Each conditioned cartridge was sealed with brass Swagelok endcaps that had been precleaned by rinsing in 50:50 acetone/hexane followed by baking (90 min, 150 °C). The endcaps were fitted with Teflon ferrules precleaned with methanol and water. Each sealed cartridge was stored in a clean glass culture tube. Other cartridge handling procedures were as described elsewhere (Pankow et al., 1998). The SPME assembly was obtained from Sigma-Aldrich (St. Louis, MO) and utilized with fibers coated with polydimethylsiloxane/divinylbenzene (coating thickness 65 µm). Prior to sampling, the fibers were cleaned for 30 min at 250 °C in a GC injector through which pre-cleaned He was flowing at 50 ml min^{-1}.

Plant material samples (needles) were collected from a mature (>20 m) *Cedrus atlantica* tree located on the Portland State University (PSU) campus. Three samples of 0.5 to 1.0 g each were collected in October–December (2010) at ~2 m above ground level from tips of branches with full-sun exposure. Each sample was placed in an individual precleaned 40 ml clear glass vial fitted with a Teflon-lined septum. After 60 min of exposure at ~20 °C to a cool light source (air-ported halogen lamp, 300 watt,

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1000 µmol photons m^{-2} s^{-1}), sampling by SPME or ATD occurred as air was passing through the vials (Fig. 1). The air was either cleaned laboratory air (CLA) or uncleaned laboratory air (ULA). Cleaning of the air was accomplished using a Perkin-Elmer hydrocarbon trap. Use of the uncleaned laboratory air greatly increased the complexity of the samples and thereby facilitated a more rigorous test of the ability of GC × GC-TOFMS to adequately separate and detect VBOCs in the presence of myriad other VOCs. ATD air sampling occurred at 60 ml min^{-1} for 60 min (3.6 l). ATD cartridges were either analyzed immediately or within three weeks after storage at −15 °C; standard cartridges analyzed after three weeks at −15 °C showed no evidence of analyte loss. Each SPME sampling event was carried out for a specific time period (10 to 60 min) under "dynamic" conditions (=continuous air flow (50 ml min^{-1}) through the vial during fiber exposure). SPME samples were analyzed immediately.

3.4 GC × GC-TOFMS Measurements

All ATD and SPME samples were analyzed using a Leco Pegasus 4D GC × GC-TOFMS (Leco, St. Joseph, Michigan). Unlike the efforts using ATD, with SPME no calibration standard runs were made: the primary purpose of the SPME runs was to provide samples that could easily indicate the level of sample complexity that is to be encountered in analyses of VBOCs, and easily provide needed retention time data. For all ATD cartridges (standard or sample or blank, NCAR or PSU), prior to analysis each cartridge was loaded with the IS compounds by injecting 0.2 ml of the IS gas standard into a 50 ml min^{-1}, 5 min flow of precleaned N_2 leading to the sample inlet end of the cartridge. For a standard cartridge, the 21 target analyte compounds were then added by injecting 4 µl of one of the methanolic standard mix solutions into the inlet of the cartridge; most of the methanol was then removed and the analytes were moved further onto the cartridge by a 50 ml min^{-1}, 5 min flow of precleaned N_2.

The ATD 400 (Perkin-Elmer, Waltham, MA) thermal desorption apparatus was connected to the GC injector by a fused silica transfer line (220 °C). Each ATD cartridge

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was thermally desorbed (270 °C, 10 min) at 40 ml min^{-1} with zero split to a focusing trap (45 mg of Tenax® TA, 10 °C) in the ATD 400. The focusing trap was desorbed (290 °C, 3 min) with zero split to the fused silica transfer line and thus the GC injector. Flow from the GC injector to the primary GC column occurred with a 1-in-15 split. (Increased method sensitivity could have been achieved by reducing the split to as low as 1-in-5 without reduction of chromatographic performance.) SPME fibers were desorbed splitless for 3 min in the GC injector (225 °C) which contained an SPME liner (Restek, Bellefonte, PA). Thereafter, an injector purge flow of 100 ml min^{-1} was kept open for 4 min. Each GC × GC run was initiated immediately upon beginning of the heating of the focusing trap (ATD), or after the SPME fiber was inserted into the injector (SPME). In every case, TOFMS data collection was delayed 180 s. An initial set and an improved set of GC columns/conditions were used (Table 3).

4 Results and discussion

4.1 Detection limits

The particular MDL values for the 21 target compounds investigated here are provided in Table 4. For isoprene, the MDL was 3.5 pptv (10 ng m^{-3}). For the monoterpenes, the MDL values were in the range 0.7–2.1 pptv (4 to 12 ng m^{-3}). For the sesquiterpenes, the MDL values were ~1 pptv (~10 ng m^{-3}).

4.2 Chromatograms

Figure 2a and b are GC × GC-TOFMS chromatograms obtained by ATD for the 21-compound standard mix using the "improved" set of chromatographic conditions (Table 3). Good separation was achieved for all of the compounds except for α-cedrene and caryophyllene. The latter two compounds possess sufficiently different EI mass spectra that they are differentiable even when not fully resolved chromatographically.

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In sample runs, the peak selection criteria (PSC) used to decide upon which chromatographic peaks would receive further consideration were applied on the Leco data system as follows: signal to noise ratio >200, peak area >100 000, and match similarity of >780 with an entry in the NIST mass spectral library. For each sample, some of those peaks corresponded to target compounds, and eluted at the proper retention times, and so were positively identified. Other peaks passing the PSC but not corresponding to the target compounds are considered only tentatively identified. Table S1 (Supplement) summarizes the information acquired for 438 chromatographic peaks (including 21 standard compounds) that met the PSC in the various chromatograms presented here.

Figure 3 is a chromatogram for an ATD sample obtained during an NCAR enclosure experiment using the lower branch of a tree (*Calycolpus moritzianus*) growing in a tropical forest in South America (Columbia, 11.0704° N, 74.0411° W). The "initial" set of chromatographic conditions was used (Table 3). The peaks for 15 of the 21 standard compounds met the PSC and were positively identified based on their chromatographic retention times and mass spectra (Table S2, Supplement); four of these (α-pinene, limonene, α-terpineol, and caryophyllene) are known constituents of *C. moritzianus* essential oils (Valdés et al., 2006; Diaz et al., 2008). Peaks for another two standard compounds were positively identified based on their mass spectral and retention time data, though were too small to meet the PSC. The number of tentatively identified peaks meeting the PSC in Fig. 3 totaled 127 (Table S2) and included four monoterpenes and 10 sesquiterpenes. In addition, at levels moderately larger than blank levels, three of the 127 peaks were identified as salicylates (methyl salicylate, 2-ethylhexyl salicylate, and homomenthyl salicylate). Two of the 127 peaks matched well as isomers of cumene and two matched well as isomers of aromadendrene. Overall, at least 13 sesquiterpene compounds were present at easily detectable concentrations. For these and the tentative identifications discussed below for Figs. 4–6, confirmed identifications will await acquisition of suitable authentic standards.

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Figure 4 is a chromatogram for VBOCs emitted from *Cedrus atlantica* needles sampled in Portland (December, 2010). The "improved" set of chromatographic conditions was used (Table 3). Sampling took place with SPME using the cleaned laboratory air (CLA) using dynamic sampling conditions as described above. The peaks for 10 of the 21 standard compounds met the PSC and were positively identified based on their chromatographic retention times and mass spectra (Table S3, Supplement); peaks for another five standard compounds were positively identified based on their mass spectral and retention time data, though were too small to meet the PSC. The number of tentatively identified peaks meeting the PSC totaled 92; these included tentative identifications for methacrolein, methyl vinyl ketone, hexenal, two monoterpenes, four oxygenated monoterpenes, four sesquiterpenes, and one oxygenated sesquiterpene (Table S3).

Figure 5 is a chromatogram with *Cedrus atlantica* needles sampled in Portland (October, 2010). The "improved" set of chromatographic conditions was used (Table 3). Sampling took place with SPME using ULA and dynamic sampling conditions. The considerably greater complexity in Fig. 5 compared to Fig. 4 is the consequence of: (a) the many VOCs present in the ambient laboratory air (i.e., in the ULA); and (b) the presumed higher level of biological activity for the Fig. 5 sample (collected in October) as compared to that for the Fig. 4 sample (collected in December). The peaks for 18 of the 21 standard compounds met the PSC and were positively identified based on their chromatographic retention times and mass spectra (Table S4, Supplement); the peak for one additional standard compound was positively identified based on its mass spectral and retention time data, though was too small to meet the PSC. The 18 compounds included all 10 of the PSC-satisfying standard compounds found in the Fig. 4 chromatogram. In Fig. 5, the number of tentatively identified peaks meeting the PSC totaled 312 (Table S4). Compared to the Fig. 4 chromatogram, the Fig. 5 chromatogram evidenced the presence of the following numbers of additional compounds: six monoterpenes; 30 oxygenated monoterpenes; 26 sesquiterpenes; 10 oxygenated sesquiterpenes. As compelling evidence of the complexity of the VBOC group, among

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the 312 tentative identifications, there are nine examples of multiple peaks matching well as the same compound: (1) four peaks as E,E-2,6-dimethyl-1,3,5,7-octatetraene; (2) two peaks as 3-methyl-undecane; (3) two peaks as γ-terpinene; (4) three peaks as d-verbenol; (5) two peaks as trans-1-methyl-4-(1-methylethly)-2-cyclohexen-1-ol; (6) two peaks as β-cubebene; (7) two peaks as germacrene D; (8) two peaks as longipinocarvone; and (9) four peaks as caryophyllene oxide.

Figure 6 is a chromatogram for the VBOCs emitted from needles of *Cedrus atlantica* obtained using ATD and the CLA. The "improved" set of chromatographic conditions was used (Table 3). Compared to Fig. 4 (SPME with CLA), Fig. 6 is considerably more complex for low primary retention times ($t_1 < 950$ s). This is due to the greater ability of ATD to collect highly volatile compounds: the gas-to-fiber partition coefficients for SPME for such compounds are low. The peaks for 15 of the 21 standard compounds met the PSC and were positively identified based on their chromatographic retention times and mass spectra (Table S5, Supplement); peaks for another three standard compounds were positively identified based on their mass spectral and retention time data, though were too small to meet the PSC. In Fig. 6, the number of tentatively identified peaks meeting the PSC totaled 127 (Table S5).

4.3 Chromatographic retention information

4.3.1 First dimension retention index

For the primary column, the t_1 retention time data were transformed into Kovats retention index values I_1 so as to obtain generally useful measures of retention that are much more system-independent than simple t_1 values. On the primary column, for compound i eluting at retention time $t_{1,i}$ and between straight-chain alkanes with carbon numbers j and $j+1$, the non-isothermal retention index values were calculated as (Guiochon, 1964)

$$I_{1,i} = 100\left[j + \frac{t_{1,i} - t_{1,j}}{t_{1,j+1} - t_{1,j}}\right] = 100 n_{C,i} \quad (1)$$

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The $t_{1,j}$ and $t_{1,j+1}$ values were available because of the natural presence in the samples of 15 straight-chain alkanes (C_5 to C_{19}). $n_{C,i}$ is the carbon number for the hypothetical equivalent straight-chain alkane that elutes in the first dimension at $t_{1,i}$. For most i, $n_{C,i}$ will not be an integer. Table S1 provides I_1 values for the 21 target analyte BVOCs in the standard mix utilized here and for 417 tentatively identified compounds found in the four different sample chromatograms discussed above.

4.3.2 Second dimension retention ratio

Because of the shortness of the secondary column, the maximum retention time in the second dimension is only a few seconds and thus too short to allow elution of bracketing compounds before and after every compound appearing in any given secondary chromatogram. Thus, a retention index analogous to that defined by Eq. (1) is difficult to achieve for the second dimension, and a simple retention time ratio $R_{2,i}$ is more practical. The secondary retention time t_2 of the hypothetical straight-chain alkane with carbon number $n_{C,i}$ is a logical choice for use as the normalizing t_2 value according to

$$R_{2,i} = \frac{t_{2,i}}{t_{2,n_{C,i}}} \quad (2)$$

The needed values of $t_{2,n_{C,i}}$ were obtained as follows. The value of the secondary retention time t_2 was determined for each actual straight-chain alkane with integer value of n_C. Data pairs (t_{2,n_C}, n_C) were thus available from the 15 straight-chain alkanes (C_5 to C_{19}) naturally present in the samples. Those data were fit to obtain t_{2,n_C}, expressed as a 6th order polynomial in n_C. The polynomial was used to calculate the needed $t_{2,n_{C,i}}$ values. Table S1 provides R_2 values for the 21 target analyte VBOCs in the standard mix utilized here and for the 417 tentatively identified compounds found in the four different sample chromatograms. The I_1 and R_2 values in Table S1 will be generally useful in subsequent studies that seek to identify and quantify individual compounds in complex VBOCs samples.

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5 Conclusions

The results from this and other studies illustrate the enormous complexity of the VBOC group. Any serious effort to comprehensively examine this complexity will need to involve GC × GC. As shown here even a small number of different types of samples can be expected to reveal the presence of many hundreds (if not thousands) of compounds of interest for atmospheric chemistry. For example, even though the annual global mass emissions of individual sesquiterpenes may be very low, the aggregate emission of all sesquiterpenes may well be a significant source for the carbon present in global atmospheric OPM. For VBOC sample collection, while SPME is a valuable method, for quantitative measurements ATD is significantly more robust and more easily applied in quantitative measurements.

Although the analytical methodologies required for comprehensive characterization of VBOCs in all sample types of interest are in place (i.e., either ATD or SPME interfaced with GC × GC-TOFMS), progress in this field will be much accelerated when substantially more VBOCs can be obtained as authentic, high purity standard materials. In the meantime, advances can be made by resorting to impure mixtures, as with essential oils known to contain particular VBOCs of interest. Much additional GC × GC retention time data for authentic standard compounds of the type collected here are needed.

Supplementary material related to this article is available online at: http://www.atmos-meas-tech-discuss.net/4/3647/2011/amtd-4-3647-2011-supplement.pdf.

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Table 1. Properties of adsorbent materials used in collection and analysis of volatilizable biogenic organic compounds (VBOCs) using adsorption/thermal desorption (ATD).

sorbent	surface area ($m^2\,g^{-1}$)	max. temp. (°C)	type	class	range	water capacity ($mg\,g^{-1}$)[a]	breakthrough volume (BV) at 20 °C ($l\,g^{-1}$)			
							water	pentane	benzene	limonene
Tenax™ TA	35	350	porous polymer	weak	C_6-C_{30}	< 3.3[b]	0.039[c] 0.065[d]	5[d]	70[d]	12 000[d]
Tenax™ GR	24	350	porous polymer + graphitized carbon	weak	C_6-C_{30}	< 2.0[b]	0.092[c]	1.7[e]	9[e]	
Carbotrap™ B	100	> 400	graphitized carbon	medium/weak	C_5-C_{12}	< 1.2[b]		5.9[f]	11.7[f]	
Carbopack™ B	100	> 400	graphitized carbon	medium/weak	C_5-C_{12}					
Carbograph 1TD™	100	> 400	graphitized carbon	medium/weak	C_5-C_{12}					
Carbotrap™ X	240	> 400	graphitized carbon	medium/strong	C_3-C_9					
Carbopack™ X	240	> 400	graphitized carbon	medium/strong	C_3-C_9					
Carbograph 5TD™	100	> 400	graphitized carbon	medium/strong	C_3-C_7	24[g]				
Carboxen™ 569	485	> 400	carbon mol. sieve	strong	C_2-C_5	403[b]	0.257[c]	200[h]	85[h]	16000 [h]
Carboxen™ 1000	1200	> 400	carbon mol. sieve	very strong	C_2-C_5	445[g]	0.418[c]			
Carbosieve™ SIII	975	> 400	carbon mol. sieve	very strong	C_2-C_5	395[b]	0.378[c]	600[i]		

[a] Water sorption capacities at 20 °C and relative humidity = 95–100 %.
[b] Helmig (1995).
[c] Dettmer and Engewald (2002).
[d] http://www.sisweb.com/index/referenc/tenaxta.htm, last access: March 2011.
[e] http://www.sisweb.com/index/referenc/tenaxgr.htm, last access: March 2011.
[f] http://www.sigmaaldrich.com/etc/medialib/docs/Supelco/Bulletin/4501.Par.0001.File.tmp/4501.pdf, last access: March 2011.
[g] Fastyn et al. (2005)
[h] http://www.sisweb.com/index/referenc/carbo569.htm, last access: March 2011.
[i] http://www.sisweb.com/index/referenc/carbs111.htm, last access: March 2011.

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Table 2. Minimum detection limit (MDL) values reported in this work and in other studies.

	This Work		Mielke et al. (2010)		Langford et al. (2010)		Karl et al. (2008)		Misztal et al. (2010)		Saxton et al. (2007)		Hahula et al. (2006)		Greenberg et al. (2004)		Greenberg et al. (1999a)	
collection	ATD, 5 l		direct inlet		direct inlet		direct inlet		ATD, 1 l		ATD, 3 l		ATD, 3 l		ATD, 6 l		ATD, 6 l	
detection	GC × GC-TOFMS		PTR-MS		PTR-MS		PTR-MS		GC/MS		GC/MS		GC/MS		GC/MS SIM[a]		GC-FID	
MDL definition	signal/noise (S/N) = 10		3σ of the blank noise		signal/noise (S/N) = 2		not stated		1.5 σ of the blank noise		not stated		not stated		not stated		not stated	
compound	pptv[b]	ng m^{-3}	pptv	ng m^{-3}	pptv	ng m^{-3}	pptv	ng m^{-3}	pptv	ng m^{-3}	pptv	ng m^{-3}	pptv	ng m^{-3}	pptv	ng m^{-3}	pptv	ng m^{-3}
methyl vinyl ketone	3.5	10	120	350	70	204											1	3
methacrolein	3.5	10	67	200	70	204											1	3
isoprene	3.5	10	93	260	200	566			100	280	5	14	11	32	1	3	1	3
monoterpenes	0.7–2.1	4–12	110	620	40	226	5	28	50	280			2–11	11-60	1	6	1	6
sesquiterpenes	0.9–1.4	8–12							400	3400			9	79				
methyl salicylate							2	13										

[a] SIM = selected ion monitoring mode for the mass spectrometer (i.e., not full scanning mode).

[b] pptv = parts per trillion by volume; conversion between ng m^{-3} and pptv assumes T = 293 K and total pressure = 1 atm.

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Table 3. Summary of GC × GC-TOFMS conditions used in VBOC determinations.

	initial	improved
GC injector	250 °C; split 20:1 for ATD	225 °C; split 15:1 for ATD, splitless for SPME
column flow	1.2 ml min^{-1} (mass flow controller)	1.0 ml min^{-1} (mass flow controller)
primary column	non-polar: Rxi-5ms, 30 m, 0.25 mm I.D., 0.25 µm film (Restek, Bellefonte, PA)	low polarity: DB-VRX, 45 m, 0.25 mm I.D., 1.4 µm film (Agilent, Santa Clara, CA)
GC × GC modulation	4 s period, 0.8 s hot pulse	4 s period, 0.9 s hot pulse
GC × GC modulator	trap with cold gas from LN2, then hot pulse at 20° above primary oven for release to secondary column	
secondary column	polar: BPX-50, 1.25 m, 0.10 mm I.D., 0.10 µm film (SGE, Austin, TX)	polar: Stabilwax®, 1.5 m, 0.25 mm I.D., 0.25 µm film (Restek, Bellefonte, PA).
GC program (primary oven)	40 °C for 5 min, 15 °C min^{-1} to 300 °C, then hold at 300 °C for 5 min	45 °C for 5 min, 10 °C min^{-1} to 175 °C, hold at 175 °C for 2 min, 4 °C min^{-1} to 240 °C, then hold at 240 °C for 10 min
MS source	200 °C, electron impact (70 eV)	
MS detector	1550 V	
MS data acquisition	150 spectra s^{-1}; 35 to 500 amu	

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Table 4. Minimum detection limit values (MDL)[a] at 10 to 1 signal to noise for determination by adsorption/thermal desorption ATD with a sample volume of 5 l followed by GC × GC-TOFMS.

compound	molecular formula	CAS number[a]	MDL[b] ng m^{-3}	MDL[b] pptv[c]
hemiterpenes				
isoprene	C_5H_8	78-79-5	10	3.5
monoterpenes and related compounds				
α-pinene	$C_{10}H_{16}$	80-56-8	8	1.4
camphene	$C_{10}H_{16}$	79-92-5	8	1.4
α-myrcene	$C_{10}H_{16}$	123-35-3	8	1.4
β-pinene	$C_{10}H_{16}$	127-91-3	8	1.4
α-phellandrene	$C_{10}H_{16}$	99-83-2	12	2.1
Δ^3-carene	$C_{10}H_{16}$	13466-78-9	8	1.4
limonene	$C_{10}H_{16}$	138-86-3	12	2.1
p-cymene	$C_{10}H_{14}$	527-84-4	4	0.7
eucalyptol	$C_{10}H_{18}O$	470-82-6	8	1.2
terpinolene	$C_{10}H_{16}$	586-62-9	6	1.1
linalool	$C_{10}H_{18}O$	78-70-6	12	1.9
nopinone	$C_9H_{14}O$	38651-65-9	12	2.1
camphor	$C_{10}H_{16}O$	76-22-2	8	1.3
4-terpinenol	$C_{10}H_{18}O$	562-74-3	10	1.6
erpineol	$C_{10}H_{18}O$	98-55-5	12	1.9
estragole	$C_{10}H_{12}O$	140-67-0	10	1.6
sesquiterpenes				
α-cedrene	$C_{15}H_{24}$	469-61-4	12	1.4
caryophyllene	$C_{15}H_{24}$	87-44-5	12	1.4
aromadendrene	$C_{15}H_{24}$	489-39-4	8	0.9
humulene	$C_{15}H_{24}$	6753-98-6	8	0.9

[a] CAS numbers are for the forms of the compounds as purchased (Sigma-Aldrich, St. Louis, MO) for use as standard materials.
[b] No blank contamination problems were encountered for any of the compounds; zero split during desorption from sample cartridge to secondary focusing trap within ATD unit; 1 in 15 split between secondary focusing trap and the primary column; total fraction of sample mass transferred to column = 6.7 %. Other GC × GC and TOFMS conditions as given in text.
[c] pptv = parts per trillion by volume. Conversion between ng m^{-3} and pptv by the ideal gas law and assuming temperature T = 293 K and total pressure P = 1 atm.

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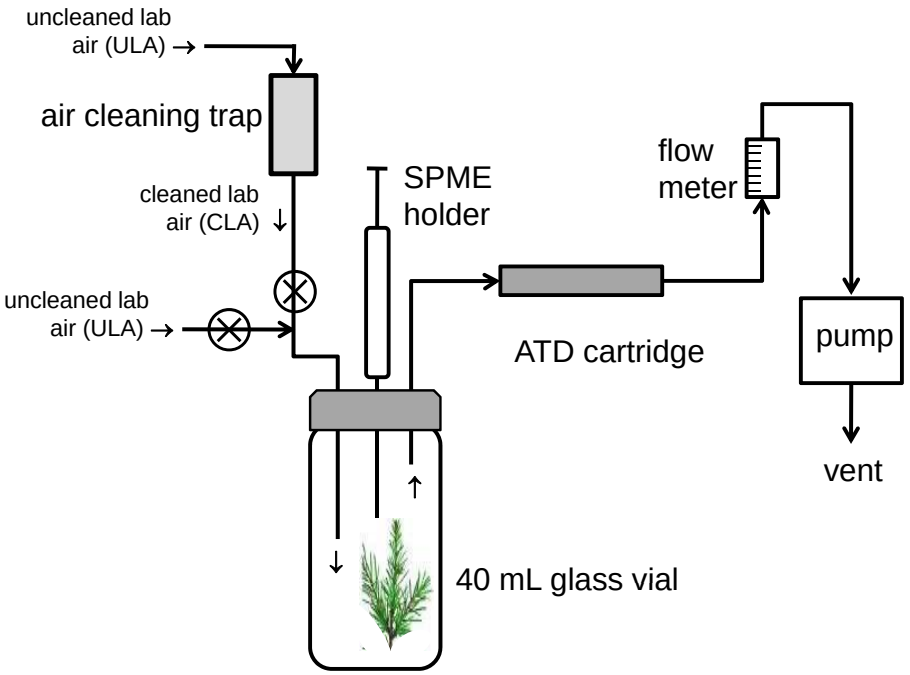

Fig. 1. Diagram of system used to obtain SPME and ATD samples of VBOCs in the laboratory with samples of *Cedrus atlantica*.

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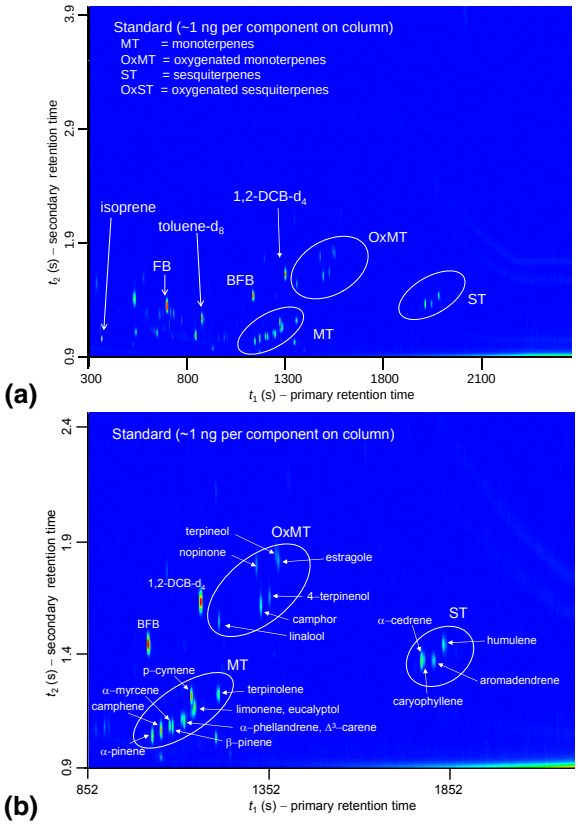

Fig. 2. **(a)** GC × GC-TOFMS chromatogram of a standard containing 21 VBOCs at ~1 ng per component on-column; internal standard compounds are fluorobenzene (FB), toluene-d8, bromofluorobenzene (BFB), and 1,2-DCB-d4 (1,2-dichlorobenzene-d4); obtained using the improved chromatographic conditions (Table 3). **(b)** Enlarged region of GC × GC-TOFMS chromatogram showing 20 VBOCs at ~1 ng per component on-column.

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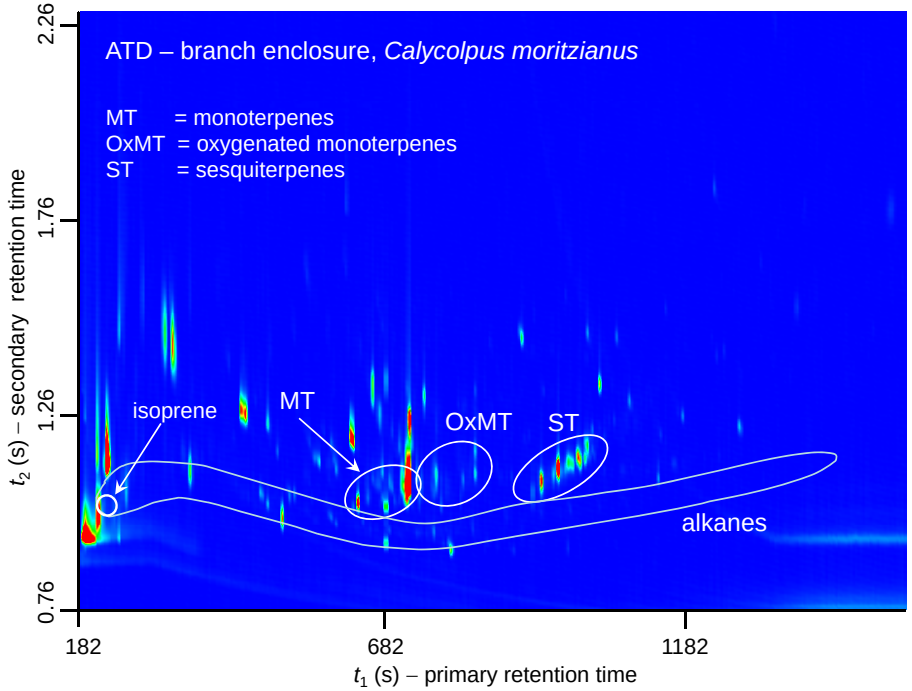

Fig. 3. GC × GC-TOFMS chromatogram of VBOCs from *Calycolpus moritzianus* by ATD using a branch enclosure in the field; obtained using the "initial" chromatographic conditions (Table 3).

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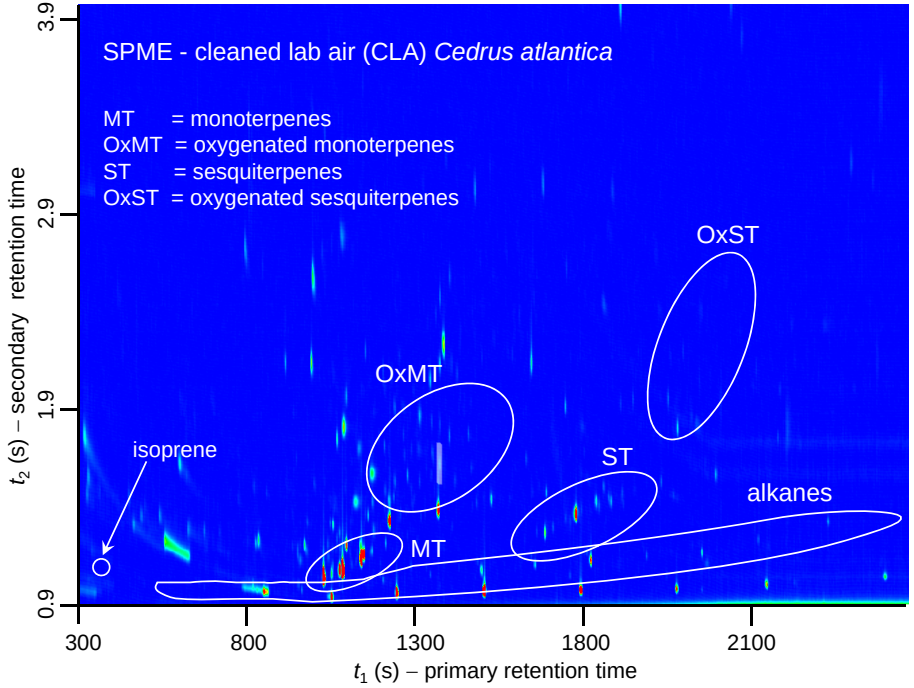

Fig. 4. GC × GC-TOFMS chromatogram of VBOCs from *Cedrus atlantica* by SPME and using cleaned laboratory air (CLA); obtained using the "improved" chromatographic conditions (Table 3).

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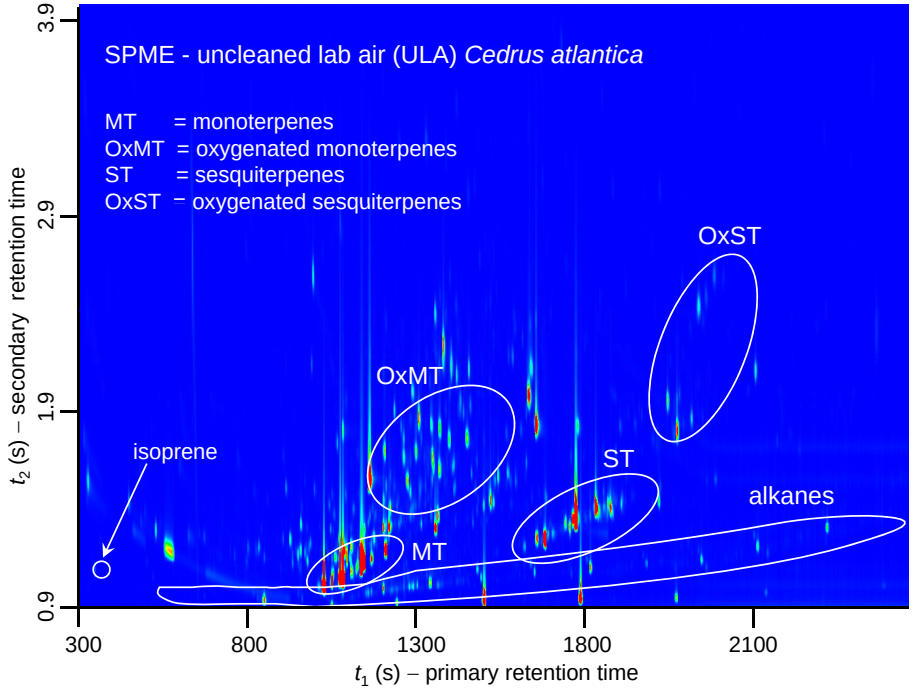

Fig. 5. GC × GC-TOFMS chromatogram of VBOCs from *Cedrus atlantica* by SPME using uncleaned laboratory air (ULA); obtained using the "improved" chromatographic conditions (Table 3).

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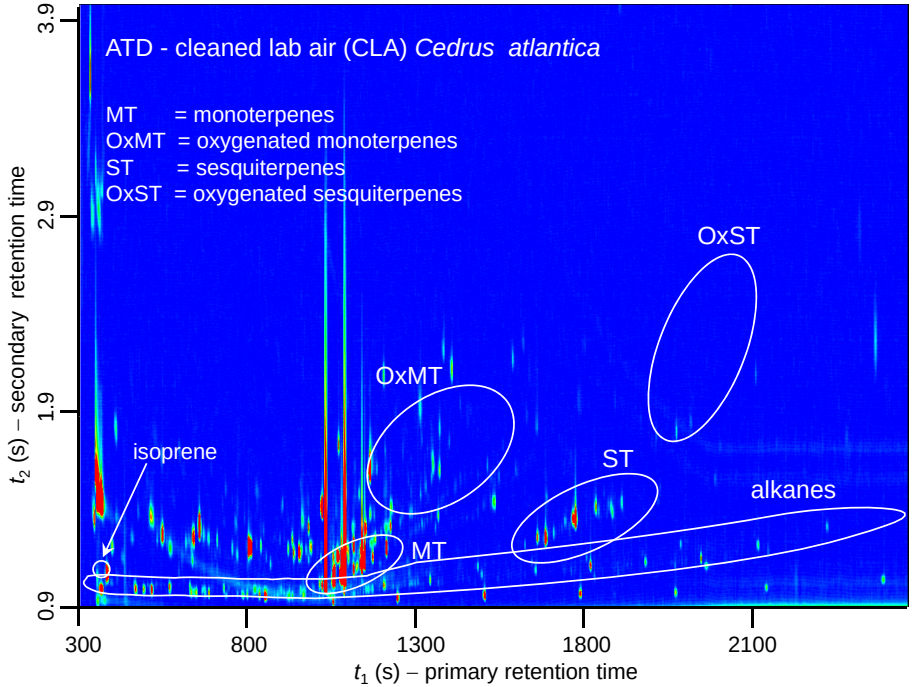

Fig. 6. GC × GC-TOFMS chromatogram of VBOCs from *Cedrus atlantica* by ATD using cleaned laboratory air (CLA); obtained using the "improved" chromatographic conditions (Table 3).

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