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Short communication

Does the novel fast-GC coupled with PTR-TOF-MS allow a significant advancement in detecting VOC emissions from plants?

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ABSTRACT

Most plants produce and emit a wide blend of biogenic volatile organic compounds (BVOCs). Among them, many isoprenoids exhibit a high atmospheric reactivity toward OH radicals and ozone. In the last few years, Proton Transfer Reaction–Mass Spectrometry (PTR–MS) has been widely used in both field and laboratory determination of BVOCs, complementing the traditional methods using gas chromatography–mass spectrometry (GC–MS) for their identification in air and emission sources. This technical note reports a number of experiments carried out with a PTR- (Time-of-Flight) TOF-MS equipped with a prototype fast-GC system, allowing a fast separation of those isobaric isoprenoid compounds that cannot be identified by a direct PTR-TOF-MS analysis. The potential of this fast-GC system to adequately complement the information provided by PTR-TOF-MS was investigated by using the BVOC emissions of *Quercus ilex* and *Eucalyptus camaldulensis* as reliable testing systems, due to the different blend of isoprenoid compounds emitted and the different dependence of their emission from environmental parameters. While the oak species is a strong monoterpene emitter, the eucalyptus used is one of the few plant species emitting both isoprene and monoterpenes. The performances provided by the type of fast-GC used in the new PTR-TOF-MS instrument were also compared with those afforded by conventional GC–MS methods. The results obtained in this investigation showed that this new instrument is indeed a quick and handy tool to determine the contribution of isoprene and eucalyptol to m/z 69.070 and monoterpenes and (*Z*)-3-hexenal to m/z 81.070, integrating well the on-line information provided by PTR-TOF-MS. However, some limitations emerged in the instrument as compared to traditional GC–MS, which can only be solved by implementing the injection and separation processes.

1. Introduction

Terrestrial plants produce and emit a wide variety of BVOCs, representing an important input of carbon into the atmosphere (Guenther et al., 1995). In unperturbed leaves, isoprenoids (isoprene, monoterpenes and sesquiterpenes) are the most abundant BVOCs emitted by terrestrial plants (Guenther et al., 1995). Their emission seems to have a specific ecological role. While isoprene can protect leaves from abiotic stresses (Loreto and Schnitzler, 2010; Sharkey and Loreto, 1993; Sharkey et al., 2008; Sharkey and Singsaas, 1995), and can stimulate flowering processes (Terry et al., 1995), mono- and sesquiterpenes can attract pollinators, and protect plants against insects and animals (Harborne, 1991; Brilli et al., 2009). Since many isoprenoids are much more reactive with ozone and OH radicals than the majority of VOCs released by man-made activities (AVOCs) (Fuentes et al., 2000), and their emission at a global scale largely exceeds that of AVOCs (Guenther et al., 1995, Fuentes et al., 2000), they can considerably affect the earth climate. They can produce ozone acting as a greenhouse gas, and secondary organic aerosols (SOA) altering the albedo of the earth by acting as cloud condensation nuclei (CCN) (Andreae and Crutzen, 1997). The BVOC emission from *Quercus ilex* has been extensively studied in the last three decades because it is the only abundant oak species present in the Mediterranean area (Pausas et al., 2008) emitting monoterpenes at a high rate with

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the same light and temperature dependent mechanism of isoprene emitting oaks (Staudt and Seufert, 1995; Loreto et al., 1996a,b). Some plant species of the *Eucalyptus* genus are also quite common in Mediterranean areas, and most of them display the unique feature of acting as isoprene and monoterpene emitters through two different emission mechanisms (Guenther et al., 1991; Winters et al., 2009). Due to the exponential dependence of isoprenoid emission from leaf temperature (Tingey et al., 1980; Guenther et al., 1995), it is important to assess how global warming can enhance the isoprenoid emission in the Mediterranean area (Peñuelas and Staudt, 2010), which is one of hottest spots of photochemical pollution on the Earth. Since the potential to generate ozone and secondary organic aerosols is strictly related to the amounts and type of isoprenoids released by terrestrial plants, they need to be identified and quantified on an individual basis (Fuentes et al., 2000).

In recent years, many attempts have been made to quantify the BVOC emission of terrestrial plants by PTR–MS because it allows their real-time determination at low atmospheric levels (ppbv–pttv) (Aprea et al., 2006; Lindinger et al., 1998; Kim et al., 2009; Lusini et al., 2014; Müller et al., 2006; Pallozzi et al., 2013). Due to the low resolving power afforded by quadrupole filters, PTR–MS instruments using this ion separation method (indicated here as PTR-QMS) were unable to distinguish the $(M+1)^+$ ions generated by the reaction of protons with compounds having the same nominal mass. In particular, the interferences on the isoprenoid signals generated by other compounds determined that the quantification of isoprene and total monoterpenes was affected by the content of interfering compounds present in the sample (Warneke et al., 2003; De Gouw et al., 2003). To reduce the uncertainty and extend the real-time detection to isoprenoid with a higher molecular mass (sesquiterpenes), PTR–MS instruments have been recently equipped with time-of-flight ion filters, able to separate $(M+1)^+$ ions (or their fragments) generated by compounds differing by 0.01 Da in their exact mass (Graus et al., 2010). These instruments have been used for the real-time determination of BVOCs in a number of environmental samples (Kaser et al., 2013; Brilli et al., 2014). Since many mono- and sesquiterpenes have the same exact molecular mass, there was no possibility to obtain information on their composition in plant emission by PTR-TOF-MS and conventional methods based on GC–MS were still needed to accomplish this specific task. GC–MS methods do not have, however, a real-time capability, and often require a substantial enrichment of the sample to identify and quantify all isobaric isoprenoids present in it (Ciccioli et al., 2002). Depending upon the emission rates, volumes from 0.5 to 5 L of air are often necessary to get an accurate quantification of the whole spectrum of BVOCs emitted from plant leaves. High volumes are needed because the branch enclosures containing the vegetation must be flushed with relatively high flow rates of external air to keep the leaves under the same physiological conditions experienced by those located in the ambient (Niinemets et al., 2011). The enrichment of BVOCs is usually performed on adsorption traps able to completely retain all BVOCs up to a maximum volume of ca. 5 L, and to quantitatively release them by thermal desorption (Ciccioli et al., 2002). With this sampling approach, an additional enrichment step is required to fully exploit the resolving power of capillary GC for the analysis of isoprenoids. In order to limit an excessive spreading of the sample during the injection step, compounds released from the adsorption trap need to be further concentrated in a smaller volume before the injection. This is usually done with a cryofocusing process performed on a very short capillary tube having a total volume of few μL (Ciccioli et al., 2002). If the tube is empty, the cryofocusing step is performed at temperatures equal or lower than −150 °C. The use of cryogenic liquids can be avoided if the capillary tube is filled with small amounts of solid sorbents, as the bulk of BVOCs can retained at a temperature (−30 °C) that can be easily reached by a Peltier cooler. A fast injection of BVOCs into the GC capillary column is obtained by a ballistic heating (>15 °C min^{-1}) of the cooled tube where compounds were concentrated, and by keeping the initial temperature of the column as lower as possible. To better separate low molecular weight compounds, the column can be operated at sub-ambient temperatures (Ciccioli et al., 2002). All these steps make the GC–MS determination of BVOCs rather expensive and time consuming. By considering that the maximum flow rate that can be passed through the adsorption trap is ca. 200 mL min^{-1}, the sampling time required for a complete analysis of BVOCs can span from 3 to 25 min, as a function of the emission rate of the plant investigated and the amount of biomass contained in the enclosure. The analysis time is even longer, as it can go from less than 30 min up to more than 1 h as a function of the complexity of the sample to analyze, and the amount and polarity of the liquid coating covering the internal walls of the capillary column (Ciccioli et al., 2002). Although the recent introduction of fast-GC has allowed to drastically reduce the analysis time, some limits still exist to the fastest temperature gradient that can be applied to a capillary column, because a sufficient resolution must be maintained to separate the numerous isobaric isoprenoids, such as mono- and sesquiterpenes, emitted by plants. Based on the data obtained by Jones et al. (2014), an analysis time of 13 min is still required to get enough resolution to identify and quantify most of the isobaric BVOCs by fast-GC. The complementary features of PTR–MS and GC–MS implies that both of them are needed to investigate the emission behavior of BVOCs from terrestrial plants, in the laboratory and in the field. While the former technique provides a real-time determination of the cumulative content of isobaric BVOCs in plant emission (Brilli et al., 2014; Grabmer et al., 2006), the latter allows to identify and quantify each one of them (Ciccioli et al., 2002)

In the attempt to combine these two complementary features in one instrument, a prototype system has been developed where a fast-GC system has been coupled to a PTR-TOF-MS. In principle, this system is very promising, because the same detection system is used for real-time and discontinuous GC determinations of BVOC, by sending the sample directly to the PTR-TOF-MS or by injecting a fraction of it into a fast-GC system. By using a rather short column coated with a low polar phase, and by applying a very fast temperature gradient, the analysis of VOC mixtures can be performed in less than a minute. However, the capabilities of this system to perform an accurate determination of isoprenoids emitted from terrestrial plants needs still to be tested. Since no sample enrichment is performed, the sensitivity can be lower than that of conventional GC–MS systems used for BVOC determination. It is not clear also if and how the drastic reduction in the sampling and analysis time compromises the column resolution.

To clarify these aspects, the performances of the prototype system combining on-line PTR-TOF-MS detection with a fast-GC were evaluated by using *Q. ilex* L. and *Eucalyptus camaldulensis* as testing systems. These species were selected because they show not only a marked difference in the amount and composition of emitted isoprenoids, especially the isobaric ones, but are also characterized by a different dependence of their emission from temperature.

2. Materials and methods

2.1. Plant material

Three-year-old *Q. ilex* saplings were potted into 10 dm^3 pots containing commercial soil. All saplings were grown outdoor in Monterotondo Scalo (RM), Italy (42°06′27.9″N 12°38′17.6″E) under natural sunlight conditions, regularly watered to pot water capacity and fertilized once a week. Two-year-old *E. camaldulensis* saplings