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Feasibility of membrane inlet mass spectrometry for on-site screening of volatile monoterpenes and monoterpene alcohols in forest soil atmosphere

Raimo A. Ketola[1)]*, Jari T. Kiuru[2)], Tapio Kotiaho[3)4)], Veikko Kitunen[5)] and Aino Smolander[5)]

[1)] *Centre for Drug Research, P.O. Box 56, FI-00014 University of Helsinki, Finland (*corresponding author's e-mail: raimo.ketola@helsinki.fi)*
[2)] *VTT Expert Services Ltd., P.O. Box 1001, FI-02044 VTT, Finland*
[3)] *Department of Chemistry, P.O. Box 55, FI-00014 University of Helsinki, Finland*
[4)] *Division of Pharmaceutical Chemistry, P.O. Box 56, FI-00014 University of Helsinki, Finland*
[5)] *Finnish Forest Research Institute, Vantaa Research Unit, P.O. Box 18, FI-01301 Vantaa, Finland*

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Volatile monoterpenes and monoterpene alcohols exist in the forest soil atmosphere and they may play an important role in controlling microbial processes related to C and N cycling in boreal forest soils. Therefore, information is needed about their actual concentrations in the soil atmosphere. Here, we developed and applied membrane inlet mass spectrometry (MIMS) with a simple sampling probe for an on-site determination of the most common monoterpenes and monoterpene alcohols in the forest soil atmosphere. The MIMS method was also compared with a chamber method for collection samples into sorbent tubes and an off-line static headspace GC-FID analysis. The sampling principles of the methods are different: the chamber method measures a bulk concentration of a 3-liter sample whereas with MIMS it was possible to measure smaller sample volumes at more localized sites. The chamber method gave higher concentrations than MIMS did, partly due to a fact that roots, cut during the installation of the chamber into the soil, could increase the concentrations of monoterpenes in the soil atmosphere and partly due to a possible interference of ambient air with MIMS measurements. The MIMS method can reliably give only the total concentrations of monoterpenes and monoterpene alcohols. On the other hand, the MIMS method is very rapid and easy to use and can provide analytical tools for direct on-site screening.

Introduction

Terpenes are a complicated group of secondary metabolites that occur in almost all plants. The composition of terpenes is species dependent (Obst 1998) as mono-, sesqui- and diterpenes are typical for conifers, whereas birch contains predominantly sterols and other higher terpenes, such as betulin. By definition, a monoterpene is a compound of two isoprene-derived units totalling at least 10 C atoms and can be either cyclic or acyclic. Plants produce monoterpenes and

other terpenes for defense against plant pathogens as well as insect and mammalian herbivores. Although little is known about the persistance of monoterpenes in soil, there is evidence that monoterpenes may play an important role in controlling microbial processes related to N cycling in boreal forest soils (Smolander *et al*. 2006). The impact of monoterpenes on soil microbes is complex since, while they may stimulate activity and growth of some microbial groups, they may inhibit others (Amaral and Knowles 1998).

Volatile organic compounds (VOCs) in the soil atmosphere can be collected with a variety of passive samplers or with common sorbent materials using external pumping which are then afterwards analyzed in the laboratory with common gas chromatographic (GC) techniques, such as GC-FID, headspace GC-FID, GC-MS, and purge-and-trap-GC-MS (Stahl and Parkin 1996, Steinbrecher *et al*. 1997, Demeester *et al*. 2007, Kloskowski *et al*. 2007, Partyka *et al*. 2007, Leff and Fierer 2008, Seethapathy *et al*. 2008). A thorough investigation of different sampling methods for sesquiterpenes in vegetation enclosure experiments has been presented by Helmig *et al*. (2004). The results show that terpenes can be efficiently analyzed with solid adsorbents and a subsequent off-line measurement with a GC-FID or GC-MS instrument. However, terpenes are easily adsorbed onto material surfaces, thus methods with a minimum exposure time to sampling material would be beneficial for sampling and analysis of terpenes from the soil atmosphere. Monoterpene emissions from soil under a Sitka spruce stand were characterized using either a dynamic soil enclosure or a dynamic branch enclosure technique combined with trapping with a solid adsorbent and GC-FID with a thermal desorber (Hayward *et al*. 2001). Performance of different types of steady-state, non-steady-state, through-flow or non-through-flow chamber techniques has been evaluated by measurement of soil CO_2 efflux (Pumpanen *et al*. 2004). It was noticed that non-steady-state non-through-flow chambers can underestimate the efflux, whereas through-flow chambers gave more reliable results. An automated dynamic chamber system has also been constructed for efficient flux measurement (Pape *et al*. 2009). VOCs, including terpenes, from soil were also sampled into Teflon bags and analyzed in the laboratory with proton-transfer reaction-mass spectrometry (PTR-MS) (Asensio *et al*. 2007) but PTR-MS or other direct measurement techniques have not yet been applied to a monoterpene analysis directly from the soil atmosphere. Recently, a chamber method was introduced for collection of monoterpenes from the forest soil atmosphere with a subsequent analysis with GC-FID (Smolander *et al*. 2006). Many of the methods mentioned are laborious and time-consuming because after sampling the samples must be brought to a laboratory for the off-line sample treatment and analysis.

In membrane inlet (introduction) mass spectrometry (MIMS), introduced for the first time in 1963 (Hoch and Kok 1963), organic compounds are separated from water or air by a thin membrane (typically polydimethylsiloxane, also known as silicone) installed between the sample and the ion source of a mass spectrometer (Kotiaho *et al*. 1991, Wong *et al*. 1995). Organic compounds diffuse through the membrane and evaporate directly into the ion source. Because the flow of the analyte matrix, usually water or air, through the membrane is proportionally smaller than the flow of the desired organic analytes, analyte enrichment is obtained. This facilitates very sensitive levels of detection, as low as ng l^{-1} in water and ng m^{-3} in air. This makes MIMS a very attractive analytical technique for environmental applications (Ketola *et al*. 2002). Various MIMS techniques and methods have been developed for the rapid and sensitive analysis of VOCs and semi-volatile organic compounds (SVOCs) in air samples (Cisper and Hemberger 1997, Ketola *et al*. 1998, Riter *et al*. 2001, Cotte-Rodriguez *et al*. 2005, Thompson *et al*. 2006) and for the direct analysis of ambient gases in soil, peat, and sediment (Benstead and Lloyd 1996, Lloyd *et al*. 1996, Kana *et al*. 1998, Cowie and Lloyd 1999). However, monoterpenes have not been measured directly from the forest soil atmosphere with MIMS.

The purpose of this research was to develop a rapid on-site MIMS method with a sampling probe for the analysis of monoterpenes from the forest soil atmosphere and to compare the analytical results obtained with MIMS with those obtained with a steady-state chamber method for

the collection of monoterpenes and a subsequent off-line GC-FID analysis. Furthermore, the effect of soil temperature and root cutting on the concentrations of monoterpenes was evaluated.

Material and methods

Reagents and chemicals

The following standard reagents were obtained from Fluka Chemie AG, Buchs, Switzerland: (–)-α-pinene 99%, (–)-β-pinene > 99%, myrcene 90%, Δ-3-carene 99%, r(+)-limonene 98%, (±)-linalool 97% and geraniol > 99.5%. The stock solutions of standard compounds were made by weighing half a gram of a standard compound and dissolving it in 50 ml of methanol (nanograde purity from Mallinckrodt Speciality Chemicals, Paris, KE, USA). Further dilutions of the stock solutions were also made with methanol.

Sampling sites

Two sampling sites were used in this study. The first was a tree species experiment of the Finnish Forest Research Institute in Kivalo, northern Finland. It had plots dominated by silver birch (*Betula pendula*), Norway spruce (*Picea abies*), and Scots pine (*Pinus sylvestris*), growing on *Pleurozium shreberi–Vaccinium myrtillus* site type [classification according to Cajander (1949)]. Site properties and tree stands are described in detail by Smolander and Kitunen (2002). For Norway spruce and Scots pine, MIMS-method measurements were carried out within three 25 × 25 m plots: 8 sampling locations were selected in each plot 2 m and 4 m from each corner of the plot towards its center, totalling 24 sampling locations. For silver birch, MIMS-method measurements were carried out within one 25 × 25-m plot (8 sampling locations selected as above). The sampling using the chamber method was performed in 6 sampling locations (selected as above but two locations were omitted) within only one 25 × 25-m Scots pine plot.

The second study site was a 110-year-old tree stand dominated by Norway spruce growing on *Vaccinium myrtillus* site type in Ruotsinkylä experimental forests of the Finnish Forest Research Institute in Vantaa, southern Finland; soil type there was podzol and humus-type mor. This site was used for preliminary studies of on-site MIMS, and three sampling locations close to each other (about 2 m apart) were chosen for the experiments.

The chamber method sampling and gas chromatographic analysis

The chamber method sampling was made using a stainless steel cylindrical chamber, modified from Haselmann *et al*. (2000) and described in detail by Smolander *et al*. (2006). The GC/FID method used for the analysis of sorbent samples collected is also described by Smolander *et al*. (2006). Briefly, a stainless steel cylindrical chamber (diameter 19 cm, depth 12 cm, volume 3.4 l) was hammered as deep as possible into the forest soil (Fig. 1a). The chamber was used as a steady-state sampling because compensation air was not added to the chamber during sampling. Ground vegetation was not removed in order to interfere with the soil atmosphere as little as possible. A sorbent sampling tube (activated carbon, Anasorb CSC, SKC, Eighty Four, PA, USA) was connected to the chamber, and a gaseous sample from the soil atmosphere was pumped out of the soil through the tube at a flow rate of 0.5 l min^{-1} for 6 minutes (about 3 litres of air). The sampling started right after installing the chamber into the soil to minimize the increase of concentrations of monoterpenes due to release from the cut roots. VOCs in the activated carbon tubes were desorbed with 2 ml of a carbon disulphide (CS_2):methanol (MeOH) (95:5 v/v) solution using a sonicator. To a 0.5-ml aliquot of the extract, 10 ml of deionized water was added in a 20-ml headspace vial, and this sample was analyzed by means of static headspace gas chromatography (HSGC) using a flame ionization detector (FID) (HP 7694 HS-sampler and HP 5890 Series II GC, Agilent, Germany) and an external standard method. The analytical column used was HP-5 (Agilent, Germany; length 30 m, inside diameter 0.25 mm, phase thickness 1.0 μm), the carrier gas was helium (99.999%),

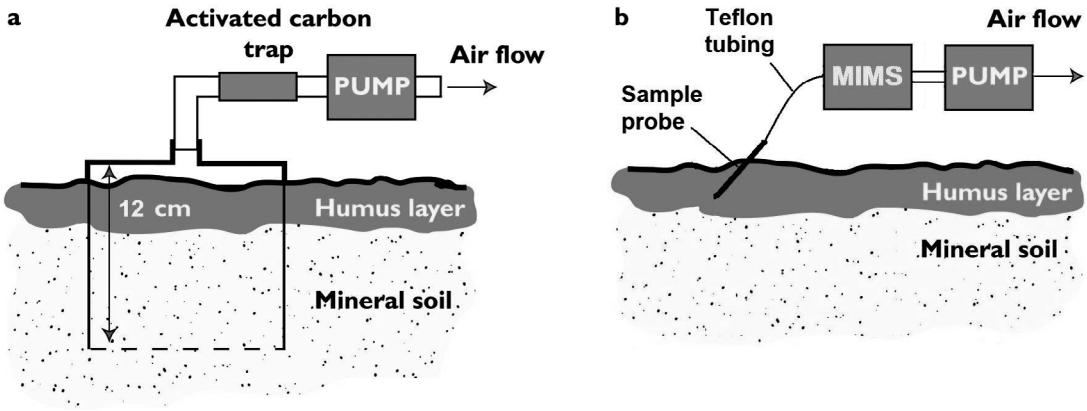

Fig. 1. (**a**) The setup of the chamber method for active sampling, and (**b**) the sampling probe and the setup for on-site measurement using MIMS. The inner volume of the chamber was 3.4 l and the flow rate of gaseous sample during the active sampling period (6 min) was 0.5 l min^{-1}. The flow rate of the sample gas in MIMS measurement was 250 ml min^{-1}.

and the GC temperature programme was from 40 to 230 °C (10 °C min^{-1}).

Root-cutting and temperature-evaluation experiments

The roots cutting experiments and the temperature evaluation experiments were performed at the Kivalo site. To test the effects of root cutting on the concentration of released monoterpenes, roots were cut in pine plots from the chamber area just before the chamber was inserted into the soil. Roots were cut using a sharp knife to about the depth of the chamber but at least from the humus layer. We made six straight 30-cm-long lines of cuttings in the soil. The lines were 3 cm away from each other, and other six similar lines were made perpendicular to the original first lines to form an even grid. The chamber was then inserted in the middle of the grid. Thus, the total length of cuttings was about 2.4 m which is four times the length without additional cutting (the circumference of the chamber was 59.7 cm). The monoterpene measurements were performed as above. In temperature evaluation experiments, temperature of the soil air was measured from the middle of the organic layer at two locations at a few centimetres distance from the chamber with a soil temperature probe. The root cutting experiments were performed in August 2001 and the temperature evaluation experiments were performed on five occasions: September 2000, June 2001, August 2001, October 2001, and September 2002.

On-site membrane inlet mass spectrometry

Measurements were made using a Balzers-Omnistar portable quadrupole mass spectrometer (Balzers, Lichtenstein) with an m/z range of 1–300 and equipped with a customized closed electron (70 eV) impact ion source. Customization of the ion source was performed by drilling holes into it in order to make the ionization chamber more open to increase the flow of organic compounds from the membrane surface into the ion source. The mass spectrometer was equipped with a membrane inlet made at the Technical Research Centre of Finland (VTT) (for details *see* Ketola *et al*. 1997). The membrane used was a silicone sheet (SSP-M100, Speciality Silicon Products Inc., Ballston Spa, NY, USA) with thickness of 25 μm and a contact area of 12 mm^2. The temperature of the inlet was 120 °C. Measurements were accomplished by using a full-scan mode (m/z 45–150) with one mass spectrum measured in one minute. The primary mass spectra of soil atmosphere samples were analyzed with the SPECTACS® program (Codator Oy, Espoo, Finland) (Ketola *et al*. 1999, Heikkonen *et al*. 2004, Ketola *et al*. 2008). Measurement results of standard air samples in a laboratory

were used as reference values in calculations. Gas standards were made by injecting standard solutions of pure reference compounds with a gas tight syringe to Gasmet Calibrator (Temet Instruments Oy, Helsinki, Finland). There was a 10-m-long Teflon tube (inside diam. 4.06 mm and outside diam. 6.35 mm) between the calibrator and the membrane inlet of the mass spectrometer, and the flow of dilution gas (air) was 250 ml min^{-1}. The concentrations of individual monoterpenes in standard air samples produced varied from 10 $\mu g\ m^{-3}$ to 50 mg m^{-3}. The signals of monoterpenes in mass spectra measured showed a linear correlation with the concentration ($r^2 > 0.995$), thus the mass spectra measured at a concentration level of approximately 1 mg m^{-3} were used as the reference mass spectra in calculations with the SPECTACS® program.

The setup for the on-site measurement using MIMS is shown in Fig. 1b. The sampling probe consisted of a steel tube (25 cm long, inside diam. 6 mm, and outside diam. 8 mm) with a closed, sharpened tip, and a 4-cm-long mesh (mesh size 250 μm) was mounted 1 cm away from the tip to prevent solid particles from flowing inside the tube. A thinner steel tube (12 cm long, inside diam. 3 mm, and outside diam. 4 mm) with a glass fiber sinter (mesh size 75 μm) at the end of the tube was inserted into the larger tube, and it was sealed with a rubber seal. The other end of the thin tube was connected to a 10-m-long Teflon tube (inside diam. 4.06 mm and outside diam. 6.35 mm) which, in turn, was connected to the membrane inlet. The sampling probe was pushed into the soil to the depth of approximately 3 cm in the organic (humus) layer. Air from the soil atmosphere was pumped through the membrane inlet with a diagraph pump (LABOPORT® N86 KT.18, KNF Neuberger, Freiburg, Germany) at a rate of 250 ml min^{-1}. All the connections were made with Swagelok® fittings. In the forest, the mass spectrometer was powered by a portable generator and carried by hand from one sampling point to another. The sampling tip was changed when it clogged up. The dirty tip was cleaned by knocking, warm water and ethanol (Primalco, Rajamäki, Finland) and dried in stream of air before reusing. The ambient air was measured as a background signal (at height of approximately 1.5 m) before soil atmosphere measurements. After inserting the sampling probe into the soil, the soil atmosphere was flushed through the probe and the membrane inlet for approximately 5 min before mass spectra were measured.

The preliminary studies using the on-site MIMS method were carried out in the tree stand in Ruotsinkylä on 3 October 2001. The experiments for the comparison of MIMS with the chamber method were performed at Kivalo site between 24 and 26 August 2004.

Results and discussion

Evaluation of the chamber method

The chamber method has previously been used for collection of air samples for the analysis of halogenated organic compounds and terpenes from the forest soil atmosphere (Haselmann *et al.* 2000, Smolander *et al.* 2006). It has been noticed that also roots can be important sources of terpenes in soil (Asensio *et al.* 2008). In this study, we wanted to test how the installation of the chamber into the soil can affect the concentrations of terpenes because during the installation the chamber could cut existing roots in the soil and this might release terpenes into the soil atmosphere. The root density can vary from place to place within the same study plot, thus increasing the variation of the concentrations of monoterpenes from sample to sample. Also, the relationship between prevailing soil temperature and terpene concentrations in the soil atmosphere was investigated because terpenes need to evaporate into the soil atmosphere and the temperature greatly affects the evaporation. The concentrations of the three major terpenes were measured from the soil atmosphere of three control samples without additional root cutting, and from three samples taken from locations where all roots were cut into smaller pieces just before the chamber was inserted (Fig. 2). The results show that additional root cutting can increase terpene concentrations by up to 100%. The average of relative standard deviations (RSDs) of the concentrations of α-pinene, β-pinene, and Δ-3-carene ($n = 3$ for both sample types) was also large — around ±30%. Despite that, the dif-

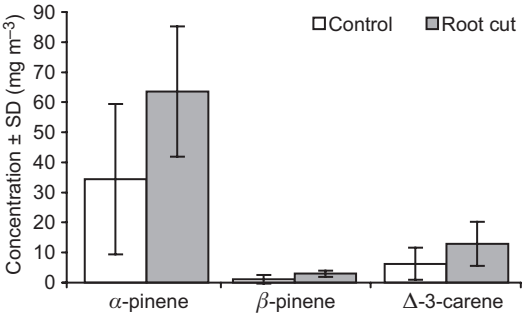

Fig. 2. The effect of root cutting on the concentrations of major monoterpenes in the pine soil atmosphere. The terpenes were collected into a sorbent tube using the chamber method and analyzed with GC-FID. The control sample and the root-cut sample were normal soil atmosphere samples without and with additional cut roots inside the chamber, respectively.

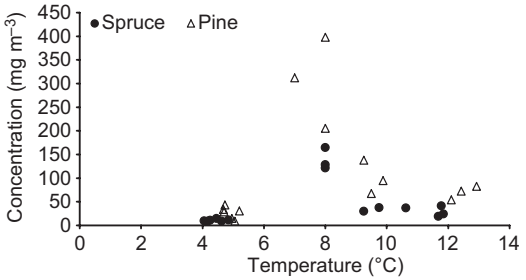

Fig. 3. The effect of the organic layer temperature on the total concentrations of monoterpenes in the soil atmosphere in pine and spruce plots. The samples were collected from Kivalo tree species experiment on five sampling occasions between September 2000 and September 2002 using the chamber method with adsorbent tubes and analyzed with GC-FID.

ference between the concentrations in the control and the root-cut samples was statistically significant ($p < 0.05$) only for β-pinene. These results mean that the concentrations of terpenes can be overestimated with the chamber method if the soil contains a lot of roots. In addition, the variation between samples over a small area can be large if the soil is heterogenous.

The relationship between the soil temperature and terpene concentrations in the soil atmosphere was investigated by measuring the soil temperature simultaneously with the gas collection from the middle of the organic layer adjacent to the chamber. The same chamber method for sample collection and the same analytical procedure were utilized in this research as in the case of root cutting experiments.

At temperature below 5 °C the total concentrations of monoterpenes remained almost constant, regardless of the sampling location, but already at temperatures of 7–8 °C the total concentrations increased (Fig. 3). As previously observed (Smolander *et al*. 2006), the concentrations measured at the same temperature and on the same day in the pine plots were a little higher than those in the spruce plots; the concentrations in birch plots were negligible. The overall variation in monoterpene concentrations was large, due to different sampling locations, different sampling times, varying humidity as well as different effect of root cutting at each sampling location. However, it can be concluded that at low temperatures, terpenes are not released in large quantities into the soil atmosphere. The increase of the cumulative amount of volatilized monoterpenes as a function of increase in soil temperature was already observed by van Roon *et al*. (2005). Since, the season can affect the emission rates of monoterpenes as indicated by Hellén *et al*. (2006), it is important to relate all measured concentrations to environmental conditions.

The performance of the MIMS method with a sampling probe tested in spruce forest

The applicability of MIMS using a home-made sampling probe to on-site measurement was tested at the Ruotsinkylä experimental site dominated by Norway spruce. Both the soil atmosphere and ambient air were sampled, and it was noticed that the intensities of ion peaks from monoterpenes, such as *m/z* 69, 77, 79, 93, 105, 107, 121, and 136 or from monoterpene alcohols, such as *m/z* 84, 111, 123, 136, and 154 in mass spectra measured from the ambient air were negligible, thus their concentrations were below the limit of detection of approximately 10 μg m^{-3}. The mass spectra of soil atmosphere samples, instead, contained mostly those ions and only a few ions of other VOCs (Fig. 4), thus it was evident that it was possible to identify monoterpenes and monoterpene alcohols from the samples. The concentrations were calculated

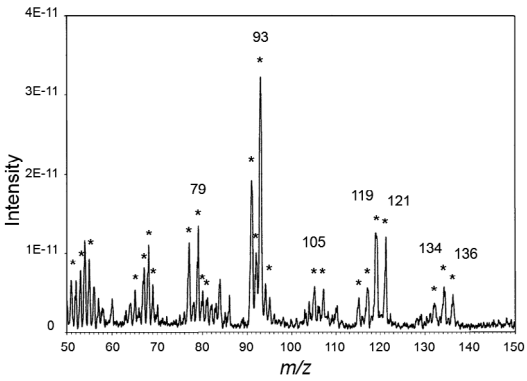

Fig. 4. A mass spectrum of a soil atmosphere sample measured with MIMS in a spruce plot at the Ruotsinkylä site. The main ions are shown, and the asterisks indicate other ions which can be derived from monoterpenes.

with the SPECTACS software, using calibration standards measured in the laboratory.

The concentrations calculated showed that in three replicate measurements from locations close to each other the total concentrations of monoterpenes and monoterpene alcohols varied (RSD) only slightly, 12% and 5%, respectively; the average concentrations being 0.48 and 0.17 mg m^{-3}, respectively. The concentrations of individual terpenes, however, varied much more, from 40% to 140% (RSD). This is not surprising because with direct MS one multicomponent mass spectrum is measured and all monoterpenes have quite similar mass spectra. This is especially true in the case of α-pinene and β-pinene which have the same ions with only a little difference in the intensities of the ion peaks. Thus, it was concluded that this direct sampling probe together with MIMS could not be used for accurate quantitative analysis of concentrations of individual monoterpenes but rather for accurate determination of the total concentrations of monoterpenes and monoterpene alcohols as noticed previously in the analysis of terpenes from water samples with MIMS (*see* Ojala *et al.* 1999). In our experiment, however, the accuracy of the method could not be tested because it was not possible to introduce known concentrations into the soil atmosphere. The identification and quantitation of individual monoterpenes can be used for screening only. The method was easy to use and fast as a single analysis could be performed in a few minutes, including installation of the sampling probe, measurement of the mass spectra of the sample, and calculation of the final concentrations with the SPECTACS software.

The applicability of the MIMS method for on-site measurement and comparison with the chamber method

The applicability of MIMS using a home-made sampling probe to a quantitative on-site measurement was further tested in the tree species experiment in Kivalo, and the comparison between the on-line MIMS and the off-line chamber method was performed.

There are two major differences in the concentrations of the main monoterpenes measured in the Kivalo pine stand with the MIMS method (Table 1) and the chamber method (Table 2): (1) the chamber method gives higher concentrations; and (2) with MIMS, monoterpene alcohols can be measured while they are not detected with the chamber + off-line GC-FID method. It is worth noting that in two locations (nos. 9 and 12) the total concentrations of monoterpenes measured with the chamber method were only 1.3 to 2.1-fold higher than those measured using the MIMS method. In other locations, the difference was 23 to 48-fold, but one must bear in mind that the measurements were not made in same locations but in adjacent ones. One reason for the higher concentrations can be the fact that in the chamber method the total volume of a sample is approximately 3 litres while with MIMS it is around 250 ml. A sample is collected with the chamber from the surface to the depth of about 12 cm, and the ambient air cannot enter the chamber during collection. Furthermore, as shown above, the chamber method could overestimate the concentrations due to the root cutting. Instead, the sampling probe in the MIMS method was located at depth of around 3 cm in the organic layer because most of decomposing litter and also roots are located in that layer. Also, the ambient air might interfere with sample collection with the sampling probe, thus decreasing actual concentrations. It is also possible that the flushing period of the sampling probe (5 min) before starting the MIMS measurement was too long, thus the highest concentrations of monoter-

penes were not necessarily observed. A general difference of the methods is that the chamber method measures the bulk concentrations in a larger volume and results can also be expressed on soil surface area basis. On the other hand, the on-line MIMS method measures local concentrations and has the advantage of not cutting the roots before or during the measurement. However, different parameters, such as composition and amount of vegatation, humus and organic litter, and the root density, can easily alter the monoterpene concentrations in field measurements. Therefore, extensive experimental studies are needed to obtain enough data on the effect of

Table 1. Concentrations (mg m^{-3}) of monoterpenes and monoterpene alcohols in a Scots pine plot determined with the on-line MIMS method.

Sampling location	α-pinene	β-pinene	myrcene	limonene	monoterpenes[a]	monoterpene alcohols[b]
1	nd	nd	nd	nd	nd	0.19
2	0.10	nd	nd	0.03	0.13	0.10
3	0.22	nd	nd	nd	0.22	0.32
4	8.8	13.9	nd	1.6	24.3	nd
5	nd	0.01	nd	0.03	0.04	0.19
6	0.26	0.29	nd	0.08	0.63	0.20
7	0.10	0.02	nd	0.04	0.16	0.03
8	0.04	nd	nd	0.01	0.05	0.18
9	0.24	0.22	nd	0.04	0.50	0.24
10	nd	0.01	nd	nd	0.01	0.14
11	0.05	nd	nd	nd	0.05	0.12
12	0.44	0.33	nd	0.07	0.85	nd
13	0.07	nd	nd	0.03	0.10	0.10
14	0.55	0.11	nd	0.07	0.73	nd
15	0.09	0.01	nd	0.03	0.12	0.06
16	0.11	0.06	nd	0.02	0.19	0.06
17	0.40	0.14	nd	0.01	0.55	nd
18	0.08	0.08	nd	0.03	0.18	0.19
19	0.97	0.14	nd	0.14	1.3	nd
20	nd	0.06	nd	nd	0.06	0.09
21	0.27	nd	nd	0.11	0.38	0.36
22	7.4	0.68	0.19	0.25	8.5	0.39
23	0.19	nd	nd	0.09	0.28	0.39
24	1.6	0.26	0.11	0.21	2.2	0.17

[a] total concentration of α-pinene, β-pinene, myrcene, and limonene. [b] total concentration of linalool and geraniol. nd = not detected.

Table 2. Concentrations (mg m^{-3}) of monoterpenes in Scots pine plot determined with the chamber method and GC-FID.

Sampling location[a]	α-pinene	β-pinene	myrcene	Δ-3-carene	monoterpenes[b]
8	7.6	nd	nd	0.8	8.4
9	1.3	nd	nd	0.31	1.6
10	5.3	0.26	nd	1.8	7.3
11	5.9	0.15	nd	1.8	7.9
12	1.1	nd	nd	nd	1.1
13	4.0	0.21	0.42	nd	4.6

[a] the sampling location numbers refer to those presented in Table 1, although they are not exactly the same spots but adjacent ones. [b] total concentration of α-pinene, β-pinene, myrcene, and Δ-3-carene. nd = not detected or the concentration was below 0.15 mg m^{-3}.

these parameters on monoterpene concentrations before one can draw proper conclusions regarding soil atmosphere composition.

In addition, as shown above, soil temperature can affect concentrations measured, even though the sorbent samples were collected at the same time — as in the case of the MIMS — in order to minimize the effect of temperature changes. Additional difference might be caused by poor adsorption of monoterpene alcohols to the sorbent or poor adsorption from the sorbent to the solvent used. The average of the total sum of monoterpenes and monoterpene alcohols was 2.0 and 5.1 mg m^{-3} for the on-line MIMS and the chamber method, respectively. The total content of monoterpenes showed substantial variation between sampling locations and plots, which was also found in previous studies (Wilt *et al*. 1988, White 1991). Again, it was not possible to find out which concentration values were the most accurate. As already stated above, the monoterpene concentrations measured in the spruce and birch plots (Tables 3 and 4, respectively) are both lower than those in the pine plots (Table 1; *see* also Smolander *et al*. 2006). The average concentrations in the spruce forest were 0.58 mg m^{-3} for monoterpenes and 0.33 mg m^{-3} for monoterpene alcohols (Table 3) which were very close to the values measured in preliminary studies in the spruce forest at the Ruotsinkylä site (0.48 and 0.17 mg m^{-3} for monoterpenes and monoterpene alcohols, respectively). This also gives a further confirmation that the sampling probe in the MIMS method works properly. However, as the MIMS method can give only the total concentration of terpenes, it is suitable for measuring of terpenes on-site, and a traditional air sampling and off-line analysis in the laboratory should be performed if the concentration of each individual terpene is needed.

Table 3. Concentrations (mg m^{-3}) of monoterpenes and monoterpene alcohols in a Norway spruce plot determined with the on-line MIMS method.

Sampling location	α-pinene	β-pinene	myrcene	limonene	monoterpenes[a]	monoterpene alcohols[b]
1	0.02	nd	nd	0.25	0.27	0.92
2	nd	nd	nd	nd	nd	0.27
3	0.04	nd	0.09	0.10	0.23	0.04
4	0.13	nd	0.26	0.29	0.68	0.04
5	1.1	0.70	nd	0.49	2.3	0.32
6	nd	nd	nd	nd	nd	0.13
7	nd	nd	nd	nd	nd	0.35
8	nd	nd	nd	0.10	0.10	0.22
9	1.2	0.41	0.33	0.21	2.2	0.24
10	0.22	0.03	nd	0.12	0.37	0.84
11	0.13	0.15	nd	0.14	0.42	0.45
12	nd	nd	nd	nd	nd	0.41
13	nd	nd	nd	0.03	0.03	0.34
14	nd	nd	nd	0.03	0.03	0.13
15	nd	nd	nd	nd	nd	0.16
16	0.34	0.49	nd	0.05	0.88	0.95
17	nd	nd	nd	nd	nd	0.25
18	nd	nd	nd	0.05	0.05	0.22
19	nd	nd	nd	0.04	0.04	0.14
20	nd	nd	nd	0.02	0.02	0.16
21	nd	nd	nd	0.03	0.03	0.22
22	nd	nd	nd	nd	nd	0.20
23	nd	nd	nd	0.05	0.05	0.12
24	1.5	0.05	0.47	0.09	2.1	0.72

[a] total concentration of α-pinene, β-pinene, myrcene, and limonene. [b] total concentration of linalool and geraniol. nd = not detected.

Table 4. Concentrations (mg m^{-3}) of monoterpenes and monoterpene-alcohols in a silver birch plot determined with the on-line MIMS method.

Sampling location	α-pinene	β-pinene	myrcene	limonene	monoterpenes[a]	monoterpene alcohols[b]
1	nd	nd	nd	nd	nd	0.28
2	nd	nd	nd	nd	nd	0.32
3	0.01	nd	0.06	0.05	0.12	nd
4	nd	nd	nd	nd	nd	0.20
5	nd	nd	nd	nd	nd	0.25
6	nd	nd	nd	nd	nd	0.26
7	nd	nd	nd	nd	nd	0.17
8	0.36	nd	nd	0.12	0.48	0.05

[a] total concentration of α-pinene, β-pinene, myrcene, and limonene. [b] total concentration of linalool and geraniol. nd = not detected.

Conclusions

An on-site MIMS method using a simple sampling probe was developed for a direct measurement of monoterpenes and monoterpene alcohols in the forest soil atmosphere. The method was easy to use, and it was fast as a single on-site analysis could be performed in a few minutes. The method was compared with a chamber method combined with a off-line static headspace GC-FID analysis, and the results show that the two methods give comparable results, although they do not measure exactly the same type of samples. Based on the results, it seems that the chamber method would be suitable for the measurement of bulk concentrations, whereas the on-site MIMS method is better suited for the investigation of local concentrations. Thus, the MIMS method could be applied for depth profiling or for the analysis of differences among sites where, for example, the amount of humus or litter, or the number of roots vary from site to site.

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