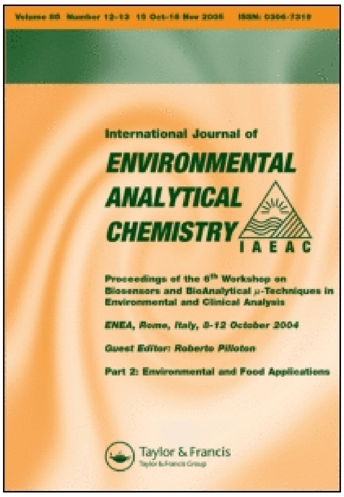

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Monoterpenes in Air Samples: European Intercomparison Experiments

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To cite this Article Steinbrecher, R. , Eichstädter, G. , Schürmann, W. , Torres, L. , Clement, B. , Simon, V. , Kotzias, D. , Daiber, R. and Van Eijk, J.(1994) 'Monoterpenes in Air Samples: European Intercomparison Experiments', International Journal of Environmental Analytical Chemistry, 54: 4, 283 — 297

To link to this Article: DOI: 10.1080/03067319408034095

URL: http://dx.doi.org/10.1080/03067319408034095

Intern. J. Environ. Anal. Chem., Vol. 54, pp. 283-297
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MONOTERPENES IN AIR SAMPLES: EUROPEAN INTERCOMPARISON EXPERIMENTS

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(Received, 23 November 1992; in final form, 25 June 1993)

An intercomparison experiment on preconcentration of monoterpenes from air samples was carried out by three European laboratories (Technische Universität München [TUM], Institut National Polytechnique de Toulouse [INP], Joint Research Center Ispra [JRC]) using Tenax porous polymer as an adsorbent. Sampling procedures, gas chromatographic analysis and standardisation methods differed in each laboratory and were compared in this study. Tenax adsorption tubes loaded with up to 10 monoterpenes (tricyclene, α-pinene, β-pinene, camphene, sabinene, myrcene, Δ^3-carene, p-cymene, 1,8-cineole and limonene) were created independently and exchanged for analysis between the working groups. For most monoterpenes the recoveries found by the different laboratories were 100%. The precision of analyses was better than 20%. Independent determinations of α-pinene mixing ratios in the air of the crown region in a natural spruce stand corresponded satisfactorily. Monoterpene emission rates of attached twigs in the sun crown of field grown spruce trees were also determined with good agreement.

KEY WORDS: Monoterpene hydrocarbons, gas chromatography, spruce forest atmosphere.

INTRODUCTION

Sampling of volatile organic compounds in air on solid adsorbents is a widely applied technique[1,2,3,4]. For analysing monoterpenes (MTs) in air the adsorbent Tenax TA, a porous polymer of 2,6-diphenyl-*p*-phenylenoxid, is preferred due to its high thermal stability, low retention volume for water and a negligible influence of water vapor on the retention of hydrocarbons, good adsorption and good thermal desorption behavior for hydrocarbons of medium to high volatility [5,6,7,8,9] However, some degradation products formed during air sampling and the thermal desorption processes may interfere with the MTs in the chromatogram and make their identification and quantification difficult[10,11]. The exact determination of monoterpene ambient air mixing ratios may also be influenced through oxidizing atmospheric species[12,13]. To test the comparability of MT data from different laboratories, intercomparison experiments were performed in the laboratory and in the field. The experiments of the Technische Universität München (TUM), Institut National Polytechnique de Toulouse (INP) and Joint Research Center Ispra (JRC), described in this paper, reveal the good quality of the MT analysis in the different laboratories which is responsible for the agreement of the monoterpene data. The experiments were performed in the framework of BIATEX (Biosphere, Atmosphere Exchange of pollutants, a subproject of the EUREKA environmental program EUROTRAC).

MATERIALS AND METHODS

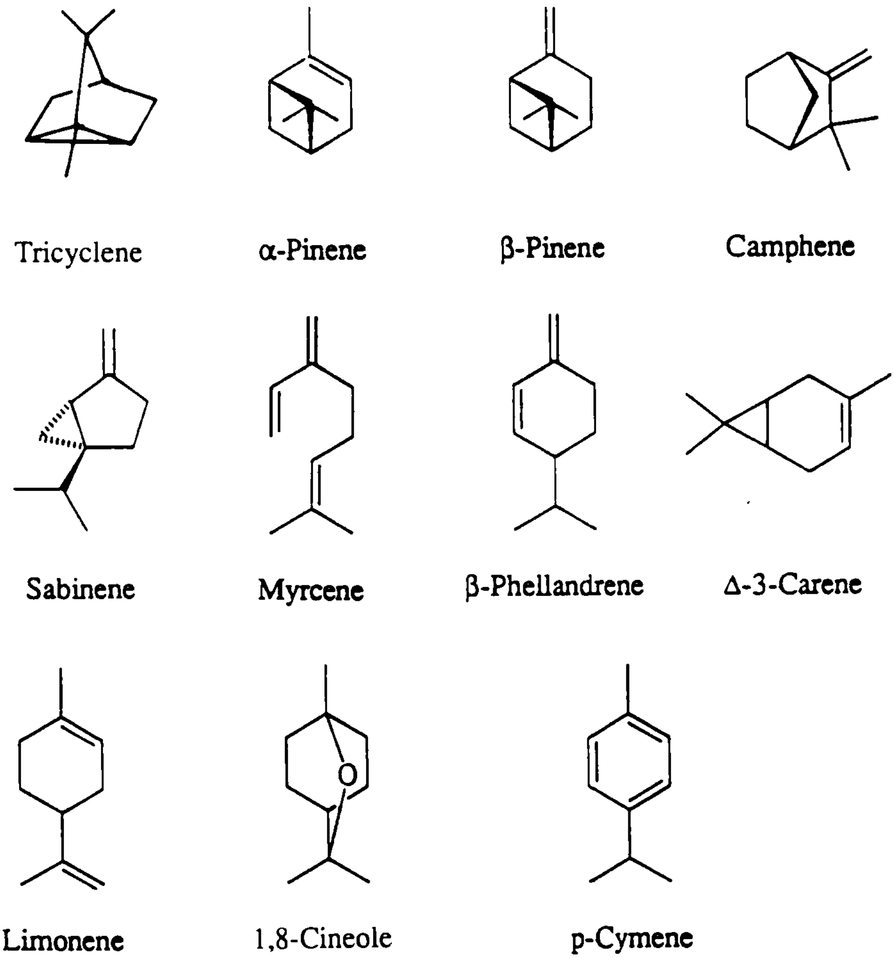
Preparation of standard

TUM For standard preparation, a permeation device was used[14]. Small dark glass vessels were filled with ca. 200 mg of the monoterpenes (Roth; Fluka) shown in Figure 1. The vessels were sealed with a teflon membrane (thickness 0.5 mm) and placed in a glass cuvette, flushed with 1 Sl (normalized to 0°C and 1013 hPa) min^{-1} of purified air. The cuvette was kept in a waterbath at 20°C. The permeation rate of the different monoterpenes was calculated from the time dependent weight loss of the vessels over four weeks.

Adsorption tubes loaded with known amounts of 10 MTs (tricyclene, α-pinene, β-pinene, camphene, sabinene, myrcene, Δ^3-carene, *p*-cymene, 1,8 cineole and limonene; for structures see Figure 1) by TUM were distributed to INP and JRC.

INP Standard gas samples were generated via the permeation technique. Small teflon cells (outside diameter 12 mm inside diameter 4 mm, useful length for permeation 13 mm) were filled with the compounds of interest and sealed. For preparation of a standard gas sample, the cells were placed in a generator with a known flow of a dilution gas. The whole generation device was temperature controlled. After stabilization in the generator, the permeation rates of the terpenes were determined by weighting the cells at regular time intervals. Adsorption tubes loaded with 6 MT standards (α-pinene, camphene, β-pinene, Δ^3-carene, myrcene and limonene) were distributed for analysis to TUM.

JRC Preparation of standard mixtures in liquid solvents is a common technique in GC. In this work liquid standards in methanol (5, 10, 20 ng μl^{-1} of the individual compounds) were used in conjunction with Tenax TA sorbent traps. A few microliters of the methanol standard solution were injected onto the Tenax tube and the methanol was then flushed out of the tube (from the opposite end). It is necessary to carefully adjust the back-flushing conditions for a complete retention of the monoterpene hydrocarbons on the standard tubes. Cartridges loaded with 8 MTs (tricyclene, α-pinene, β-pinene, camphene, myrcene, Δ^3-carene, 1,8-cineole and limonene) were sent for analysis to TUM.


Tricyclene α-Pinene β-Pinene Camphene

Sabinene Myrcene β-Phellandrene Δ-3-Carene

Limonene 1,8-Cineole p-Cymene

Figure 1 Structures of monoterpene hydrocarbons used in the European intercomparison experiments and present in ambient air samples from a natural spruce forest.

Sampling and GC techniques

TUM For preconcentration of MTs in air samples, adsorption tubes (HCl-deactivated Duran glass tubing: 200 mm × 6 mm; i. d. 4 mm) were used, which were filled with 125 mg Tenax TA 60–80 mesh (Alltech) and held in place with 10 mm of silanized (DMCS) glass wool plugs. The tubes were mounted in an automated sampling device developed by TUM. Subsequent loading of 12 adsorption tubes using defined sampling times and mass controlled sampling flow was possible. Standard preparation was performed with a sampling flow of 100 Sml min^{-1} and a sampling time of 10 min. Environmental air samples were pre-concentrated with a sampling flow of 150 Sml min^{-1} and a sampling time of 30 min. The adsorption tubes were inserted in a thermodesorption device developed by Nitz *et al.*[15]. A modified 1/4″ stainless steel Swagelok connection was used to connect the cartridges with the Dani programmed temperature vaporizer (PTV). The compounds adsorbed on Tenax TA were thermally desorbed (225 °C, heated air stream) and flushed with oxygen free helium 6.0 (40 ml min^{-1} for 13 min; split open) into a liquid nitrogen cooled pre-column (–100 °C; HCl-deactivated glass line: 55 mm × 1,8 mm) filled with DMCS treated glass wool, situated in the Dani-PTV injector (inlet pressure 1,000 hPa).

Cryofocused compounds were separated on a J & W fused silica capillary column DB 1701 (Alltech; 30 m × 0.32 mm; film thickness 1 µm; carrier gas: oxygen free helium 6.0; flow rate 2 ml min^{-1}) mounted in a Dani 6500 gas chromatograph (GC) equipped with a flame ionisation detector (FID) and using splittless injection by heating the PTV to 250 °C. A chromatogram of an air sample containing MTs as standards is shown in Figure 2A.

MTs were identified by GC-MS (Quadrupole Finnigan 1020 instrument directly coupled to a Perkin Elmer Sigma 3 GC equipped with a RSL 200, 25 m × 0.25 mm, film thickness 0.2 µm; Alltech). The interface temperature was 250°C. Retention times of co-eluted reference substances were measured on columns of different polarity. Column 1: RSL 200, stationary phase polyphenylmethylsiloxane; 25 m × 0.25 mm; film thickness 0.2 µm; (Alltech). Column 2: DB 1701, stationary phase polycyanopropylphenylmethylsiloxane; 30 m × 0.32 mm; film thickness 1 µm (Alltech).

INP The sampling trap used for preconcentration of atmospheric terpenes consisted of pretreated nickel or pyrex tubes[16] (220 mm × 6 mm; i. d. 3 mm) that were filled with 300 mg of Tenax TA 60–80 mesh, held in place with two silylated glass wool stoppers. The internal surfaces of these tubes are inactive with regard to reactive or labile compounds trapped by the adsorbent and desorbed at high temperatures. The trapping tube was part of the automated preconcentration thermodesorption module designed and developed in our group[17,18]. This module was connected to the injector of a Hewlett-Packard 58-I GC equipped with a mega-bore column (DB-5, 30 m × 0.5 mm, film thickness 1.5 µm; Interchim) and a FID.

Such a device was controlled by a computer (Omron C28K, France) which allowed fully automatic sampling and analysis of atmospheric terpenic compounds. Each analytical cycle involved the following steps:

(1) Terpene sampling. Atmospheric terpenes were adsorbed in the Tenax trap for about 20 min under an air flow of 200 Sml min^{-1}, controlled by a mass-flowmeter (split open).

(2) Thermodesorption and analysis. This step started with the thermodesorption at 270°C with a flow of 10 ml min^{-1} (split closed) for 15 min and starting the temperature program of the GC oven from – 20°C to 85°C at 5°C min^{-1}. The final temperature was held for 10 min.

(3) Cooling the trap. The trap was cooled down to room temperature before the next sampling.

The volatile organic compounds were identified by GC-MS (HP 5890-I/HP 5971 A).

JRC MTs in air were collected in glass tubes (150 mm × 6 mm; i. d. 4 mm) containing 160 mg Tenax TA. The flow rate of the air passing through the tubes was adjusted by needle valves between 150–250 ml min^{-1}. The total sample volume ranged from 3–5 Sl. At the maximum flow rate of 250 ml min^{-1} no adsorption efficiency problems were observed.

The GC used for the analyses was a HP 8590 instrument equipped with a FID and a commercially available device for thermal desorption and preconcentration of the compounds to be analysed (TCT, Chrompack, NL). The sampled monoterpenes were analysed after desorption of the compounds adsorbed on Tenax at 180°C with a flow of 20 ml min^{-1} (split open) and preconcentration in a liquid-nitrogen cooled capillary at –80°C and then transferred as a plug on top of the analytical column (carrier gas: helium, inlet pressure: 700 hPa) by heating the capillary trap to 250 °C. Chromatographic separation was achieved using a 25 m × 0.32 mm CP-Sil 8 fused silica capillary column (Chrompack, NL). A standard run is shown in Figure 2B.

Field intercomparison

At the BIATEX Schachtenau joint experimental site in the Bayerischer Wald national park (SE Germany), ambient air concentrations and emission rates of MTs and other trace gases have been determined in a natural Norway spruce (*Picea abies* [L.] Karst.) forest, in a series of experiments since 1987[14,19,20,21]. Ambient air concentrations of α-pinene and β-pinene were determined at 31 m above ground (canopy height) night and day on June 11–12, 1991, by TUM and INP. During that time period ozone ambient air mixing ratios varied between 20 and 60 ppbv at the 41 m level[22]. Both groups performed ambient air sampling without removing oxidizing species since a removal by scrubbers had no significant influence on the amount of trapped MTs[22]. In laboratory experiments no statistically significant loss of adsorbed monoterpenes on Tenax TA due to ozone application of 100 ppbv was observed (see Table 1).

MT emission rates from spruce twigs were compared by TUM and JRC by collecting air samples downstream of a climate controlled cuvette system[14] flushed with purified air containing a twig of the sun crown of a spruce tree. The cuvette system was installed on a platform of a tower at a height of 28 m above ground level.

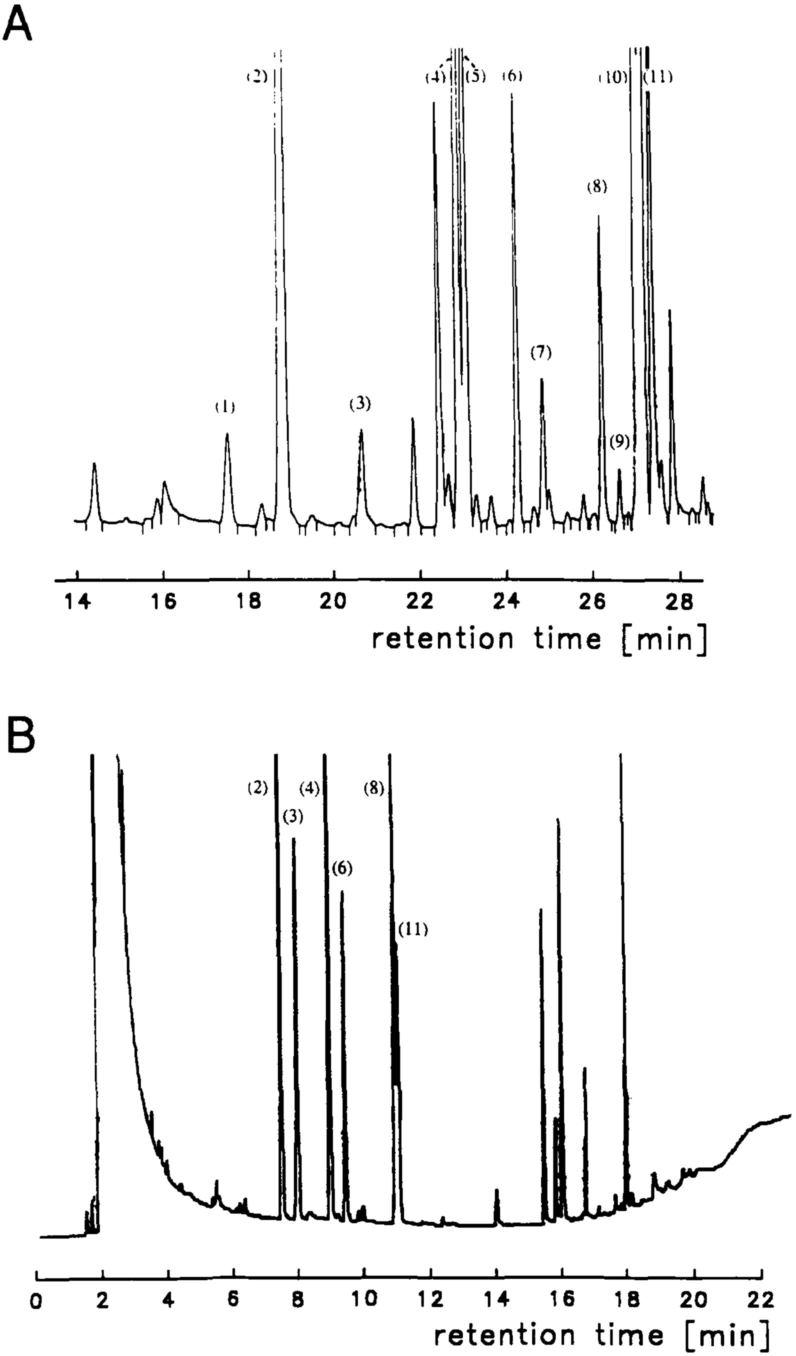


Figure 2 Chromatograms of the standard tubes prepared by TUM (A; gaseous standard preparation) and JRC (B; liquid phase standard preparation). TUM oven temperature program: 30 °C held for 2 min, 9 °C min^{-1} to 65 °C, 65 °C held for 12 min, 5 °C min^{-1} to 270 °C, which was held for 15 min. JRC oven temperature program: 60 °C held for 2 min, 3 °C min^{-1} to 100 °C, 20 °C min^{-1} to 240 °C. (1) tricyclene, (2) α-pinene, (3) camphene, (4) β-pinene, (5) sabinene, (6) myrcene, (7)Δ^3-carene, (8) limonene, (9) β-phellandrene, (10) *p*-cymene, (11) 1,8-cineole.

Table 1 Influence of ozone on terpenes preconcentrated on Tenax TA. After loading the tubes, one set was flushed for 10 min with a pure air flow of 150 ml containing 100 ppbv ozone. The control and the ozone treated cartridges were stored for 5 days before analysis. The experiments were carried out at the TUM laboratory in cooperation with Dr. Nolting, Fraunhofer-Gesellschaft für Aerosolforschung und Toxikologie, Hannover, FRG.

terpene	*without ozone*		*with ozone*		
	amount		*amount*		
	ng	*cv [%]*	*ng*	*cv[%]*	
tricyclene	1.81	4.7	1.78	1.8	n.s.
α-pinene	1.19	12.4	1.11	13.3	n.s.
camphene	0.80	12.2	0.60	4.4	n.s.
sabinene	0.33	5.9	0.30	12.9	n.s.
myrcene	0.56	10.1	0.51	11.1	n.s.

cv coefficient of variation
n.s. not significant ($n = 5$; Student t-test; $P > 0.05$)

RESULTS AND DISCUSSION

Laboratory experiments

For comparing the MT analysis in the three different laboratories, adsorption cartridges loaded with a known amount of standards were prepared by each laboratory and exchanged.

Standards from TUM Table 2 presents the results of an experiment where standards prepared by TUM were analysed by JRC and INP. For each laboratory a different set of standard tubes was prepeared. The amount of the different MTs on the cartridges varied from 2.8 to 43.3 ng tube^{-1}. The variation of the amount of MTs on the tubes distributed was small and the coefficient of variation (CV) was usually less than 10%.

The recovery of most MTs by JRC was good and the differences between the laboratories usually varied between 4 and 35 %, except limonene and tricyclene (Table 2a). The JRC analysis showed a reproducibility which was better than 10%.

The overestimation of the amount of limonene by the JRC laboratory point to the possiblity of a coelution of compounds diffused through the seals of the tubes or generated by decomposition of the Tenax polymer during the shipping procedure. The underestimation of the amount of tricyclene on the adsorption tubes may be due to decomposition during analysis or irreversible adsorption on Tenax.

A comparison of a set of TUM standards prepared for analysis in the INP laboratory indicated good agreement in the MTs α-pinene, camphene and limonene (Table 2b). The recovery was 100% within the range of variation and the reproducibility by the INP laboratory was better than 20%. The absolute amounts of MTs differed not more than 16%, except myrcene which was overestimated by a factor of 1.93.

In Table 2b, the 4 terpenes which allowed an exact quantification by the INP laboratory were considered. Broken seals led to a contamination of the cartridges during the shipping

Table 2a Intercomparison of laboratory quantification of monoterpenes by JRC and TUM. Standards on Tenax adsorption cartridges were prepared by TUM (gaseous standard preparation) and analysed by JRC (sd standard deviation; n number of cartridges analysed; Δ absolute difference in % between the two laboratories on the base of TUM values).

terpene	*JRC*			*TUM*			
	amount analysed			*amount prepared*			
	ng	*sd*	*n*	*ng*	*sd*	*n*	*Δ [%]*
tricyclene	7.1	0.54	4	14.4	0.99	9	51
α-pinene	13.2	0.46	4	11.6	0.99	9	14
β-pinene	7.4	0.75	4	7.1	0.41	11	4
camphene	4.6	0.22	4	3.4	0.08	9	35
sabinene	6.8	0.13	4	7.3	0.55	9	7
myrcene	4.0	0.47	4	5.9	0.86	10	32
Δ3-carene	3.8	0.29	4	2.8	0.14	10	35
limonene	128.8	0.41	3	33.6	0.82	9	283
1,8-cineole	22.6	0.66	4	19.3	0.31	9	17
p-cymene	26.4	0.06	4	20.1	0.74	10	31

Table 2b Intercomparison of laboratory quantification of monoterpenes by INP and TUM. Standards on Tenax cartridges were prepared by TUM (gaseous standard preparation) and analysed by INP (sd standard deviation; n number of cartridges analysed; Δ absolute difference in % between the two laboratories on the base of TUM values).

terpene	*INP*			*TUM*			
	amount analysed			*amount prepared*			
	ng	*sd*	*n*	*ng*	*sd*	*n*	*Δ [%]*
α-pinene	12.0	2.60	8	12.0	0.28	10	0
camphene	3.6	0.41	3	3.2	0.24	5	13
myrcene	11.6	1.27	4	6.0	0.59	5	93
limonene	36.3	7.3	6	43.3	1.13	10	16

procedure to INP and a separation of the MTs from other compounds was often not possible. Due to that coelution the number of cartridges and the number of MTs analysed was reduced. The observed overestimation of the myrcene amount in the TUM standards by INP may be a result of an unrecognized coelution.

Standards from INP The INP laboratory prepared tubes loaded with 6 MTS. The amount of the different MTs on Tenax varied from 8.3 to 37.3 ng tube^{-1}. The recovery by the TUM laboratory was 100% within the range of variation (Table 3). The differences in the amount of MTs detected by two laboratories were lower than 14%. During that intercomparison experiment the amount of MTs on the different tubes showed a high variation (CV up to 36%). The JRC laboratory did not take part in that intercomparison experiment.

For MTs analysis in the TUM laboratory a CV between 1 and 13% is usually observed (see Tables 1 and 5). The high variation in the amount of MTs on the different tubes from INP but comparable absolute values detected by TUM may be explained by difficulties during gaseous standard preparation by the permeation technique. Since TUM detected the absolute amounts of MTs given by INP an error regarding the determination of the permeation rates can be excluded. For preparing appropriate MT concentrations in air (lower

Table 3 Intercomparison of laboratory quantification of monoterpenes by INP and TUM. Standards on Tenax cartridges were prepared by INP (gaseous standard preparation) and analysed by TUM (sd standard deviation; n number of cartridges analysed; Δ absolute difference in % between the two laboratories on the base of INP values).

terpene	*INP*	*TUM*			
	amount prepared	*amount analysed*			
	ng	*ng*	*sd*	*n*	*Δ [%]*
α-pinene	37.3	42.7	9.76	3	14
β-pinene	23.6	22.3	6.69	3	6
camphene	9.4	10.2	3.01	3	9
myrcene	12.5	12.2	-	1	2
Δ3-carene	8.3	7.8	2.81	3	6
limonen	13.9	14.9	-	1	7

ppb levels) used for standard preparation the permeating MTs were diluted. Variations in the dilution gas flow possibly changed the air concentrations of MTs and the amount concentrated on Tenax causing the observed high variation between the different standard tubes. Variations in the sampled volume possibly caused by unexpected fluctuations of the standard gas passing through the tube during the concentration step also enhance the variation between the tubes.

Standards from JRC The standard tubes prepared by JRC contained 8 MTs ranging from 5.2 to 18.4 ng tube^{-1} (Table 4). The adsorption cartridges were sent to TUM for analysis. Myrcene and 1,8 cineole were recovered in comparable amounts by TUM (Table 4). Tricyclene was overestimated by 40%. Other MTs were underestimated, e.g. β-pinene by 17% and α-pinene by 31%, respectively. The variation within the standard tubes perpared by JRC was low with a CV lower than 18% and comparable to the variation usually observed in the TUM laboratory (see Tables 1 and 5). The INP laboratory did not take part in that intercomparison experiment.

Table 4 Intercomparison of laboratory quantification of monoterpenes by JRC and TUM. Standards on Tenax cartridges were prepared by JRC (liquid phase standard preparation) and analysed by TUM (sd standard deviation; n number of cartridges analysed; Δ absolute difference in % between the two laboratories on the base of JRC values).

terpene	*JRC*	*TUM*			
	amount prepared	*amount analysed*			
	ng	*ng*	*sd*	*n*	*Δ [%]*
tricyclene	13.4	18.7	3.30	3	39
α-pinene	5.4	3.7	0.38	3	31
β-pinene	5.2	4.3	0.35	3	17
camphene	18.4	13.6	0.97	3	26
myrcene	8.8	8.6	0.50	3	3
Δ3-carene	5.2	2.9	0.27	3	44
limonene	6.0	2.2	0.26	3	63
1,8-cineole	5.4	5.3	0.18	3	2

Table 5 Influence of storage time on the recovery of selected monoterpene standards on Tenax TA. The influence of the storage time on the amount of monoterpenes (m) was tested by Student t-test between freshly prepared and one month old standards (0,1) freshly prepared and 4 month old standards (0,4) and one month and 4 month old standards (1,4). The corresponding significance levels α are indicated as: n.s. not significant $P > 0,05$; * $0.05 \geq P > 0.01$; ** $0.01 \geq P > 0.001$; *** $P \leq 0.001$ (CV coefficient of variation; number of cartridges analysed: freshley prepared n = 7; one month old n = 6; 4 months old n = 4).

storage time	*0*			*1*			*4*		
	m[ng]	*CV[%]*	α	*M[ng]*	*CV[%]*	α	*m[ng]*	*CV[%]*	α
group tested			*0,1*			*1,4*			*0,4*
α-pinene	10.41	3.3	**	9.1	2.2	n.s.	9.19	1.0	*
β-pinene	4.93	0.6	***	4.18	2.9	n.s.	4.29	1.5	***
sabinene	4.28	3.2	n.s.	3.69	6.2	n.s.	3.78	1.7	*
myrcene	1.69	3.1	n.s.	1.51	5.1	n.s.	1.42	1.1	**
limonene	17.79	0.6	*	16.54	2.1	n.s.	17.38	0.6	*
1,8-cineole	21.69	1.2	n.s.	21.38	2.9	n.s.	20.15	2.0	*

The overestimation of tricyclene by TUM on standards from JRC may be explained by an unrecognized coelution of compounds (notice the high sd in Table 4). Usually the amounts of MTs on standard tubes from JRC were underestimated by TUM. On the other hand amounts of MTs on standards prepared by TUM were overestimated between 4 to 35% by the JRC laboratory (see Table 2a). These findings possibly indicate a systematic error in the standard preparation technique by JRC. JRC used solutions of MTs in methanol for preparing standard tubes. Part of the solutions where injected onto the adsorption catridges and methanol was back-flushed by carrier gas. The process of preparing standard tubes on the base of MTs in solution consists of three steps: (1) preparing MT solutions (2) injection of standard solution onto the adsorption tubes, (3) back-flushing of the solvent (methanol). Every step is afflicted with systematic errors possibly leading to lower amounts of MTs on the cartridges than expected. Most likely is the unrecognized loss of MTs through the back-flushing procedure.

The time between standard preparation and analysis in the different laboratories was two to four weeks and should not have influenced recovery[14,23]. Janson[24], however, reported a 10% loss of limonene within 9 days storage time. As shown in Table 5 storage time may significantly influence the recovery of some terpenes. TUM found signifcant losses of up to 17% of β-pinene during the storage of standard tubes at 6°C over one month. Longer storage time had no measurable effect on the recovery. Therefore, the standard tubes used for calibration and samples should be kept under the same conditions and over the same time in order to achieve reliable results.

Field intercomparison

During the BIATEX joint experiments at the Schachtenau research site the three groups performed field intercomparison experiments.

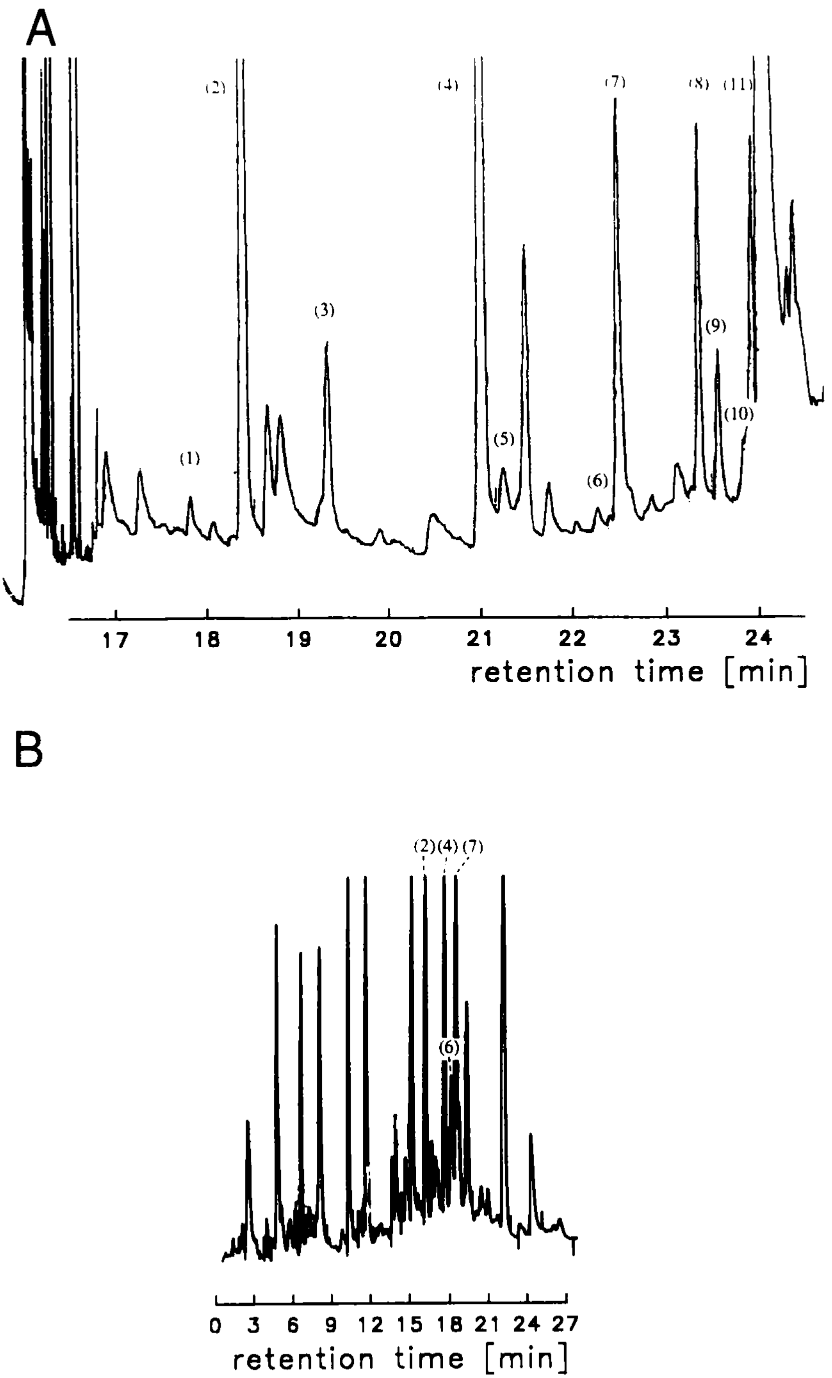


Figure 3 Chromatograms of night ambient air samples at 31 m height in a natural spruce forest at the Schachtenau research site in the Bayerischer Wald national park by TUM (A) and INP (B) on June 11–12, 1991. INP oven temperature program: Start temperature −20 °C, 5 °C min^{-1} to 85 °C which was held for 10 min. TUM oven temperature program see Figure 2. (1) tricyclene, (2) α-pinene, (3) camphene, (4) β-pinene, (5) sabinene, (6) myrcene, (7) Δ^3-carene, (8) limonene, (9) β-phellandrene, (10) *p*-cymene, (11) 1,8-cineole.

MT ambient air mixing ratio by INP and TUM INP built up an online system for monoterpene ambient air mixing ratio measurements at various levels within and above the spruce canopy. Air was transferred through heated teflon tubing from the height measured to the analytical device placed in a nearby shelter. Ambient air concentrations of α-pinene and β-pinene at 31 m height were compared. In Figure 3 chromatograms of ambient air samples from the upper edge of the spruce canopy are shown. α-pinene, β-pinene, myrcene, Δ^3-carene were identified by INP. TUM analyzed 10 monoterpenes (tricyclene, α-pinene, β-pinene, camphene, sabinene, myrcene, Δ^3-carene, limonene, β-phellandrene and 1,8 cineole).

In ambient air of the spruce canopy the main compounds were α-pinene and β-pinene. They showed a pronounced diurnal cycle with low values during the day and high values at night (Figure 4). Maximum concentrations up to 190 pptv α-pinene were found just before sunrise and after sunset. In general, β-pinene concentrations were somewhat lower than those of α-pinene.

The diurnal behavior of α-pinene and β-pinene mixing ratios with low values during the day, when emissions were high, and high values in the early morning and late evening, when emissions were low is typical for that site and have been recorded several times[14,19,20,21,22]. It has been shown by TUM[22] that these measurements reflect the real diurnal cycle of α-pinene and β-pinene mixing ratios in ambient air and cannot be ascribed to high levels of oxidizing species during the daylight periode degrading terpenes adsorbed on Tenax TA under the applied sampling conditions at that site. A similar observation was made by Hoffmann *et al.*[13] when testing the effect of scrubbers, removing oxidizing species in ambient air, on the recovery of monoterpenes on Tenax TA.

Comparable diurnal cycles of MT mixing ratios in and above canopies have also been reported by other authors[25,26,27]. This observation may be a result of both atmospheric chemistry (degradation of reactive MTs mainly through reaction with O_3 and OH) and turbulent transport[20,28].

In general, the α-pinene and β-pinene values of INP and TUM were in excellent agreement. Only two values of β-pinene mixing ratios in the late evening differed by 20% and 7% from the mean.

Emission rate measurements by JRC and TUM Terpene emission rates from an attached spruce twig were estimated by JRC and TUM. A twig of the upper sun crown was built into the TUM climate controlled gas exchange cuvette. TUM and JRC took air samples downstream of the cuvette using comparable sampling flows and sampling times. The resulting emission data for α-pinene, β-pinene, sabinene and limonene were in good agreement (Table 6) and usually differed by not more than 10% from the mean. The observed differences in calculated camphene emission rates may be explained by separation difficulties from other compounds on the CP-Sil 8 column.

The measured emission rates of the living spruce twig were in the same range as previously reported values[14,21,22].

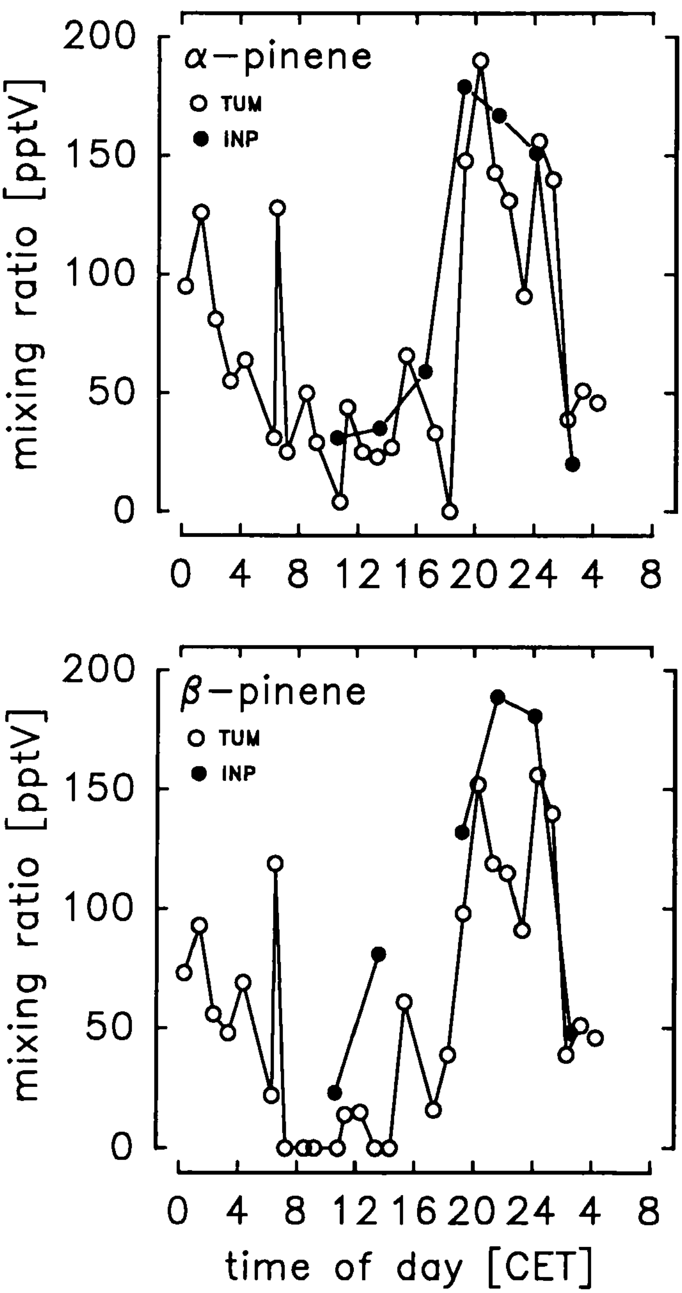


Figure 4 Field intercomparison experiment of α-pinene and β-pinene mixing ratios—the most prominent monoterpenes in ambient air samples at the Schachtenau research site in the Bayerischer Wald national park by INP and TUM. Air samples were taken at 31 m height at the upper edge of the canopy on June, 11–12, 1991.

Table 6 Field intercomparison of monoterpene emission rates from a twig (1 year old) in the upper sun crown of a spruce tree, by JRC and TUM using the TUM gas exchange cuvette system. The middle of sampling time is given, emission rates are based on total leaf area, leaf temperature was 21 °C.

Date	*Time [CET]*	*TUM Analysis*			*JRC Analysis*		
		α-pinene	*β-pinene*		*α-pinene*	*β-pinene*	
		[pmol m^{-2} s^{-1}]			*[pmol m^{-2} s^{-1}]*		
14.06.90	13.08	114.21	17.45				
14.06.90	13.19				133.25	33.05	
14.06.90	14.08	102.66	24.73				
14.06.90	14.13				124.80	29.35	
		camph.	*sabin.*	*limo.*	*camph.*	*sabin.*	*limo.*
		[pmol m^{-2} s^{-1}]			*[pmol m^{-2} s^{-1}]*		
14.06.90	13.08	3.13	17.08	26.24			
14.06.90	13.19				36.70	18.35	24.95
14.06.90	14.08	15.62	14.20	24.52			
14.06.90	14.13				36.70	20.55	24.95

camph. : camphene;
sabin. : sabinene;
limo. : limonene.

CONCLUSIONS

Three different analysis techniques of MTs present in air samples by INP, JRC and TUM revealed comparable results for most of the MTs tested both in intercomparison experiments performed with standard tubes and in field intercomparison experiments. Scatter in the data of some standard sets underline the difficulty of calibrating such hydrocarbons as MTs. To ensure a correct quantification of MTs in air samples it is suggested that intercomparison experiments should be performed during joint experiments.

Acknowledgements

This investigation was partly funded by the German Department of Research and Technology 07 EU 720 and the French committee EUROTRAC-BIATEX. We thank Dr. P. Borell and Dr. P. Naug for valuable comments on the manuscript.

References

1. L. D. Butler and M. F. Burke, *J. Chromatogr. Sci.* **14**, 117–122 (1976).
2. J. Namiesnik, L. Torres, E. Kozlowski and J. Mathieu, *J. Chromatogr.* **208**, 239–252 (1981).
3. M. E. McNally and R. L. Grob, *Amer. Lab.* **1**, 20–33 (1985a).
4. M. E. McNally and R. L. Grob, *Amer. Lab.* **2**, 106–118 (1985b).
5. K. Sakodyskii, L. Panina and N. Klinskaya, *Chromatographia* **7**, 339–344 (1974).
6. J. Janak, J. Ruzickova and J. Novak, *J. Chromatogr.* **99**, 689–696 (1974).

7. W. Averill and J. E. Purcell, *Chromatography Newsletter* **6**, 30–32 (1978).
8. M. W. Holdren, H. H. Westberg and P. R. Zimmerman, *J. Geophys. Res.* **84** (C8), 5083–5088 (1979).
9. M. L. Riba, E. Randrianalimanana, J. Mathieu., L. Torres and J. Namiesnik, *Intern. J. Environ. Anal. Chem.* **19**, 133–143 (1985).
10. E. D. Pellizzari, J. E. Bunch and B. H. Carpenter, *Environ. Sci. Technol.* **6**, 552–555 (1975).
11. J. F. Walling, J. E. Bumgarner, D. J. Driscoll, C. M. Morris, A. E. Riley and L. H. Wright, *Atmos. Environ.* **20** (1), 51–57 (1986).
12. F. Jüttner, *J. Chromatogr* **442**, 157–163 (1988).
13. T. Hoffmann, Linscheid M. and D. Klockow in: *Field Measurements and Interpretation of Species Derived from* NO_X, NH_3 and VOC Emissions in Europe (S. Beilke, M. Millan and G. Angeletti eds., Air Pollution Report 25, CEC-DG XII/E1, Brussels 1990) pp. 186–191.
14. R. Steinbrecher, Gehalt und Emission von Monoterpenen in oberirdischen Organen von Picea abies (L.) Karst. (Dissertation, TU-München, 1989), 199pp.
15. S. Nitz, F. Drawert and E. Jülich, *Chromatographia* **18**, 313–317 (1984).
16. D. C. Fenimore, J. H. Whitford, C. M. Davis and A. Zlatkis, *J. Chromatogr.* **140**, 9–15 (1977).
17. M. L. Riba, N. Tsiropoulos, B. Clement, A. Golfier and L. Torres, *J. Chromatogr.* **456**, 165–173 (1988).
18. B. Clement, M. L. Riba, V. Simon and L. Torres, *Intern. J. Environ. Anal. Chem.* (in press).
19. R. Steinbrecher, W. Schürmann, R. Schönwitz, G. Eichstädter and H. Ziegler, in: *Transport and Transformation of Pollutants in the Troposphere* (P. Borrell, P. M. Borrell and W. Seiler, eds. SPB Academic Publishing bv, The Hague 1991) pp. 205–208.
20. G. Enders, R. Dlugi, R. Steinbrecher, B. Clement, R. Daiber, J. V. Eijk, S. Gäb, M. Haziza, G. Helas, U. Herrman, M. Kessel, J. Kesselmeier, D. Kotzias, K. Kourtidis, H. -H. Kurth, R. T. McMillen, G. Roider, W. Schürmann and L. Torres, *Atmos. Environ.* **26**, 171–189 (1992).
21. R. Steinbrecher, W. Schürmann and H. Ziegler in: *Annalen der Meteorologie* **27** (Deutscher Wetterdienst, Offenbach, 1992) pp. 79–80.
22. W. Schürmann, Emission von Monoterpenen aus Nadeln von Picea abies L. Karst sowie deren Verhalten in der Atmosphäre (Dissertation TU-München, 1993) 192 pp.
23. J. M. Roberts, F. C. Fehsenfeld, D. L. Albritton and R. E. Sievers in: *Identification and Analysis of Organic Pollutants in Air* (L. A. Keith and H. Butterworth eds., Ann Arbor Science Publisher, Boston 1984) pp. 371–388.
24. R. Janson, Monoterpenes from the boreal coniferous forest and their role in atmospheric chemistry (Dissertation Stockholm University, Department of Meteorology, 1992) pp. 138.
25. R. R. Arnts and B. W. Gay, EPA-60/3-79-081 (1979).
26. J. M. Roberts, C. J. Hahn, F. C. Fehsenfeld, J. M. Warnock, D. L. Albritton and R. E. Sievers, *Environ. Sci. Technol.* **19**, 364–369 (1985).
27. M. L. Riba, J. P. Tathy, N. Tsiropoulos, B. Monsarrat and L. Torres, *Atmos. Environ.* **21**, 191–193 (1987).
28. T. E. Graedel, *Rev. Geophy. Space Phys.* **17**, 937–947 (1979).