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Description and characterization of an on-line system for long-term measurements of isoprene, methyl vinyl ketone, and methacrolein in ambient air

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Abstract

In this work we present a detailed technical description of the system that was set up for long-term on-line measurements of isoprene and two of its major degradation products, methyl vinyl ketone and methacrolein in order to provide a better understanding of the role of forest stands as a complex source of reactive trace gases into the troposphere and to elucidate the role of forests as chemical reactors. Volatile organic compounds (VOCs) are preconcentrated on cartridges containing a package of two solid adsorbents (Tenax TA and Carbopack X). Ozone removal is performed prior to sampling by titration with nitrogen monoxide. For the calibration and characterization of the system, a diffusion source was built to produce standard gas mixtures of up to 16 different compounds with mixing ratios at tens ppt (parts per trillion) level mixing ratios and high accuracy. The developed system allows a reliable quantification of these VOCs (detection limit ~10 ppt, reproducibility ~5%) with a high temporal resolution (~30 min) and has proven to be stable and run automatically without major maintainence.

Keywords: Calibration; Volatile organic compounds; Isoprene; Methyl vinyl ketone; Methacrolein

1. Introduction

Biogenic volatile organic compounds (VOCs) are emitted in large quantities from vegetation. With estimated emission rates of 1150 Tg year^{-1}, biogenic emissions dominate over those from anthropogenic sources by one order of magnitude on a global scale [1,2]. Due to their emission in large quantities and their high reactivity biogenic VOCs have a significant impact on the photochemical processes that lead to the formation of ozone and other photooxidants in the planetary boundary layer [2,3].

The compounds released from vegetation include isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$), sesquiterpenes ($C_{15}H_{24}$), and several oxygenated species [4–7]. Isoprene emissions (500 Tg year^{-1}) represent the largest source of a single VOC into the troposphere [1]. Once emitted into the troposphere, VOC degradation is initiated by reaction with the OH radical at daytime, with NO_3 at night and for unsaturated VOCs by reaction with O_3 at day and night (e.g., Ref. [8], and references therein). Isoprene may react with all three oxidants in the troposphere. During the day, OH radicals initiate the majority of isoprene

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degradation, due to its fast reaction. At night, OH concentrations are reduced to low levels and the OH-initiated reaction plays only a minor role. Here, O_3 processing becomes more important than OH. If sufficient levels of NO_x and O_3 are present, also NO_3 chemistry can play a significant role in the nighttime isoprene degradation. Two of the major isoprene degradation products are methyl vinyl ketone (MVK) and methacrolein (MACR), which are formed at different yields depending on the oxidant. MVK is the main product of the reaction of isoprene with OH, whereas MACR is favored by the O_3 initiated degradation of isoprene. Both products are only formed at minor yields from the NO_3 chemistry. Although the importance of biogenic VOCs has been recognized, there is still a large uncertainty about the exact amount of biogenic VOC emissions and their contribution to tropospheric ozone production [9,10]. A significant lack of knowledge exists in the question how much of the emitted biogenic VOCs are already chemically processed within the canopy of a forest.

VOC concentrations are typically quantified by gas chromatographic (GC) techniques. Samples are either taken off-line in metal canisters [11–13] or on adsorption tubes [14–16] and analyzed later in the laboratory. VOC concentrations can also be measured on-line with in situ GC systems in the field. Here, VOCs are usually sampled cryogenically [17–19] or on adsorption tubes [20–22]. Whereas by off-line sampling the time resolution of measurements is usually restricted by the number of available containers or cartridges, the total number of on-line measurements is given by the time resolution of a single measurement and the duration of the on-line measurements.

The time resolution of GC measurements is usually on the order of 30 to 60 min. Some systems like the AirmoVOC HC1010 (Airmotec, Illnau, Switzerland) even reach a time resolution of 10–20 min [23]. Much higher time resolutions are unlikely to be achieved with GC systems and a further reduction of measurement time is restricted by the time necessary for sampling, focusing, and separation of VOCs. Time resolutions on the order of seconds can be achieved by using relatively new techniques like the PTR-MS (proton transfer reaction mass spectrometry) technique [24]. The disadvantage of the higher temporal resolution is a lower detection limit (because of omitting a sample preconcentration) and the loss of information. PTR-MS gives a signal corresponding to all compounds of identical molecular mass. Therefore, it is not possible to quantify, for example, single monoterpenes (all having the same molecular mass of 136 u) and also MVK and MACR (70 u) cannot be separated [25]. Therefore, valuable information on the relative abundance of the two major isoprene degradation products is only accessible with GC measurements.

On-line systems are usually operated only episodically during the few weeks of intensive field campaigns (e.g., Refs. [18–20]). The results are valuable and can be taken for the interpretation of the emissions and chemistry under these conditions, but usually no information is gained on seasonality of biogenic VOC emissions, for example. Unfortunately, only limited data are available for long-term measurements of biogenic VOCs (e.g., Ref. [26]).

Therefore, it is important to measure biogenic VOC emissions throughout a complete vegetation cycle. In this work we present a detailed technical description of the system that was set up for on-line long-term measurements of isoprene and two of its major degradation products, MVK, and MACR. The system began operation in June 2002 and is planned to be operated continuously until October 2003. The results will offer insight into the seasonal cycle of isoprene emissions and into the isoprene oxidation mechanisms at the field site.

2. Experimental

2.1. Gas chromatography

The system used to quantify VOC concentrations (Fig. 1) is composed of a gas chromatograph (GC 8000, Fisons Instruments, Mainz, Germany) equipped with a flame ionization detection (FID) system (MD 800, Fisons Instruments), a thermal desorption device (Aerotrap 6000, Tekmar, Cincinnati, OH, USA), and a cryo focus module (Cryo 820, Fisons Instruments).

The VOCs are sampled on a glass tube containing two solid adsorbents. The tube has a length of 180 mm and an outer diameter of 6 mm, and is fixed

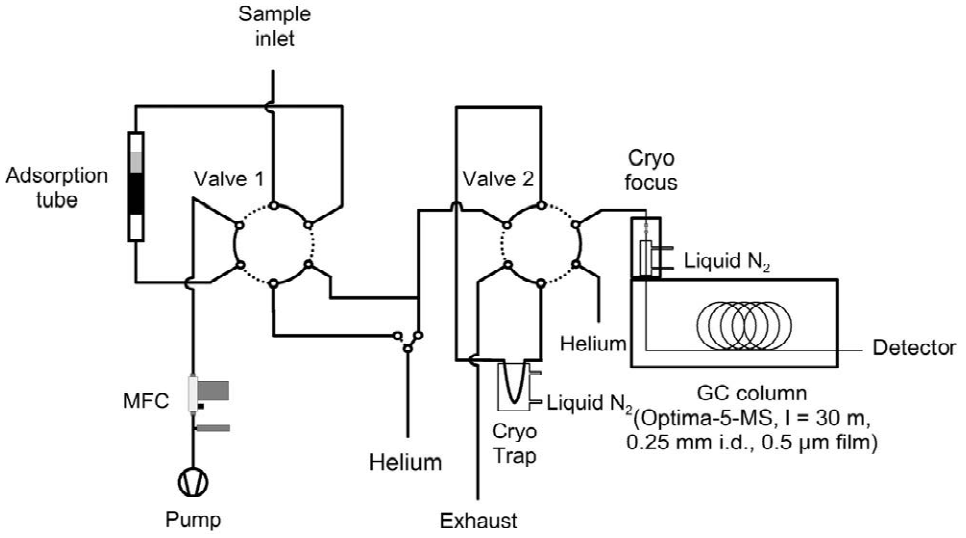

Fig. 1. Schematic drawing of the gas chromatographic system.

inside the thermal desorption device. The tube is filled with 50 mg Tenax TA (60–80 mesh, Macherey-Nagel, Dueren, Germany) and 150 mg Carbopack X (20–40 mesh, Supelco, Bellefonte, PA, USA), fixed with silanized glass wool. During sampling, air is pulled through the tube at a constant temperature of 30 °C and the VOCs are trapped on the adsorbents. The gas flow is kept constant at 100 ml min^{-1} with a mass flow controller. A schematic drawing of the system is shown in Fig. 1.

For analysis, valve 1 (Fig. 1) is switched and the tube is purged at room temperature for 0.5 min with 25 ml min^{-1} of helium (99.9999% purity). The VOCs are then thermally desorbed by flushing the heated tube (220 °C) for 8 min with helium. The desorbed VOCs are trapped at −130 °C in a stainless steel column (6×1/8 in. I.D.) packed with deactivated glass beads (1 in.=2.54 cm). By switching valve 2 and heating up the trap to 220 °C, the VOCs are then transferred to the gas chromatograph via a heated (200 °C) deactivated fused-silica column for 6 min. They are preconcentrated a second time at −130 °C on the gas chromatographic column inside the cryo focus device to reduce peak width. Subsequently, valve 2 is switched again, the cryo focus module is heated up to 200 °C, and the sample is injected. Peak separation is performed on a chromatographic column (Optima-5-MS, 30 m×0.25 mm I.D., 0.5 μm film thickness, Macherey-Nagel). The initial temperature of the GC oven is held at 40 °C for 3 min and then ramped to 160 °C at a rate of 15 °C min^{-1}. Helium is used as carrier gas at a flow-rate of 2.1 ml min^{-1}.

2.2. Preparation of calibration gas mixtures

Fig. 2 shows a schematic drawing of the diffusion system used for the preparation of the standard mixtures to calibrate the GC system. The system is described in detail by Gautrois and Koppmann [27] and Komenda et al. [28]. Only minor modifications have been made to the diffusion device to calibrate isoprene and its oxidation products. It was found essential to be able to humidify the nitrogen used for dilution with pure water in order to eliminate losses of oxygenated VOCs on surfaces. The humidifier was temperature controlled with water from an external thermostat (F20-HC, Julabo, Seelbach, Germany) to adjust different dew points. For the experiments described here, the flow-rates of the flows j_1 and j_2 were 4.4±0.2 l min^{-1} and 12.6±0.5 ml min^{-1}, respectively. The dilution flow could be adjusted between 1 and 20 l min^{-1}.

The different hydrocarbons used for preparing the gaseous standard mixtures are listed in Table 1. In total, 16 different VOCs from C_4 to C_8 have been

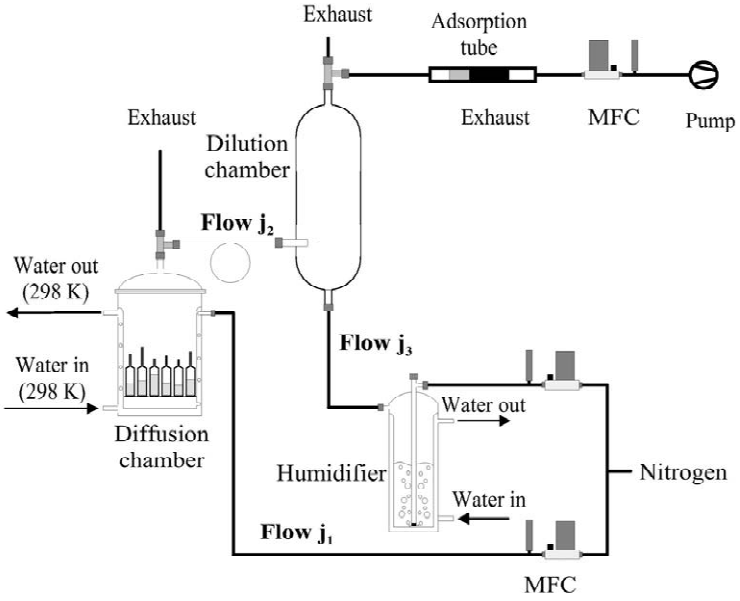

Fig. 2. Schematic drawing of the calibration system.

tested. The diffusion rates of the VOCs were determined by measuring the mass loss of the compound in the glass vials on a microbalance (R 160 P, Sartorius Research, Goettingen, Germany). The temporal stability of the diffusion rates was monitored by weighing the diffusion vials in regular intervals of 1–2 weeks over a period of 3 months. Table 2 lists the number of weighings, the mean diffusion rates and their variabilities for all investigated compounds. The maximum number of weighings was 11, other VOCs were placed into the diffusion chamber later or changes were made at the capillaries and therefore fewer data are available. The standard deviation of the diffusion rates ranged between 0.8 and 9.9%. The diffusion rates of isoprene, MVK, and MACR showed reproducibilities of 1.3, 1.1, and 9.9%, respectively. The diffusion rate of MACR showed a temporal trend with a decreasing mass loss of approx. 2% per week. A possible reason for this decrease could be a polymerization of the compound in the diffusion vial. The decreasing diffusion rate was accompanied by an increase in viscosity and by a darkening of the light orange color of the compound.

Table 1
Compounds used for the diffusion device

Compound	Purity (%)	Molecular mass (g mol^{-1})	Vapor pressure at 298 K (kPa)
i-Pentane	≥99.7	72.15	91.7
1-Pentene	≥99.5	70.14	85.0
Isoprene	≥99.7	68.12	73.4
n-Pentane	>99.5	72.15	68.3
cis-2-Pentene	~98	70.14	66.0
Cyclopentene	~99	68.12	50.7
1-Hexene	≥99.8	84.16	24.8
trans-2-Hexene	≥98	84.16	20.7
n-Hexane	≥99.8	86.18	20.2
Methacrolein	~95	70.09	16.0*
Benzene	≥99.5	78.12	12.7
2-Butanone	≥99.9	72.11	12.6
Methyl vinyl ketone	≥95	70.09	12.0
trans-2-Heptene	~99	98.19	6.6
n-Heptane	≥99.5	100.21	6.1
1-Octene	≥99.8	112.22	2.3

All compounds have been supplied by Fluka.
* At 293 K.

2.3. Calculation of mixing ratios of the calibration gas mixture

The mixing ratios of a VOC, c_i, in the calibration

Table 2
Mean value and reproducibility of diffusion rates

Compound	Number of weighing intervals (n)	Diffusion rate, r_i (ng min^{-1})	1σ of diffusion rate (%)
i-Pentane	4	19 408	2.4
1-Pentene	6	25 237	2.5
Isoprene	4	26 643	1.3
n-Pentane	10	17 012	4.1
cis-2-Pentene	9	19 247	2.1
Cyclopentene	11	7637	2.8
1-Hexene	10	3643	2.1
2-Butanone	7	12 777	0.8
trans-2-Hexene	11	3433	1.7
n-Hexane	11	5967	1.4
Benzene	11	6798	1.1
Methacrolein	11	3993	9.9*
Methyl vinyl ketone	4	8674	1.1
trans-2-Heptene	11	4932	1.2
n-Heptane	11	4732	1.0
1-Octene	11	1886	1.5

* The diffusion rate of MACR showed a long term decreasing trend of ~2% per week.

gas mixture can be calculated with the following equation:

$$c_i = \frac{r_i j_2 N_A}{j_1 j_3 M_i N} \quad (1)$$

where c_i = mixing ratio of compound i (ppb); r_i = diffusion rate of compound i (ng min^{-1}); j_2 = flow through fused-silica column (ml min^{-1}); N_A = Avogadro's number ($6.022 \cdot 10^{23}$ mol^{-1}); j_1 = flow through diffusion chamber (ml min^{-1}); j_3 = dilution flow (ml min^{-1}); M_i = molecular mass of compound i (g mol^{-1}); N = number density at $T = 298$ K and 1013 hPa ($2.4651 \cdot 10^{19}$ ml^{-1}).

Different VOC concentrations were adjusted by varying the dilution flow (Fig. 2, flow j_3) only. The flows through the diffusion chamber and the fused-silica column were always kept constant. This is necessary to assure a constant pressure inside the diffusion chamber which has an influence on the stability of the diffusion rates.

3. Gas chromatographic test of the system

Several tests were run with the system to assure a quantitative trapping of the VOCs of interest on the adsorbents, to achieve separation of the sampled VOCs on the chromatographic column, to test the reproducibility, linearity, and long-term stability of the system, and to investigate possible influences due to cross sensitivities.

3.1. Sampling

As described in Section 2.1, we used a combination of 50 mg Tenax TA and 150 mg Carbopack X for trapping the VOCs of interest. Carbopack X is a graphitized black carbon, specifically designed for sampling low boiling hydrocarbons (C_3 to C_5). An extensive test of this adsorbent and a comparison with several carbon molecular sieves (Carboxen 569, Carboxen 1003, and Carbosieve SIII) is given by Dettmer et al. [29] and Dettmer and Engwald [30], who reported superior recovery and storage properties of Carbopack X compared to other adsorbents.

In the system described here, the sampling flow-rate is kept constant at 100 ml min^{-1}. During sampling, the temperature of the adsorbents is kept at 30 °C, by cooling the adsorption tube with cold nitrogen or by heating the tube. We run several tests at different temperatures and found that the trapping of isoprene, MVK, and MACR is quantitative at 30 °C and not reduced in comparison to lower temperatures. We chose such a comparatively high temperature to reduce the effect of water condensa-

tion on the adsorbents, which could be a problem when cooling the adsorption tube to temperatures lower than ambient.

The breakthrough volume of several VOCs on the adsorption tubes was determined at conditions typical for the planned measurements of ambient air ($T = 30\,°C$, sampling flow = 100 ml min^{-1}, dew point = 10 °C). Between 0.2 and 4 l of air with VOC mixing ratios between 50 ppt and 2.7 ppb were sampled (equivalent to a sampling time of 2 to 40 min). For the tested VOCs listed in Table 1 no breakthrough was observed up to a sampling volume of 4 l. Higher sampling volumes were not tested, because some peaks already exceeded the recordable detector voltage of 1 V. Typical volumes of sampling ambient air are between 0.5 and 1 l, and thus lower than the breakthrough volume.

3.2. Separation

Fig. 3 shows a chromatogram of the calibration gas mixture, containing the VOCs listed in Table 1. As can be seen, the peaks are very narrow and usually have peak widths of 1–2 s. The separation of all compounds of the calibration mixture is sufficient for reliable quantification. None of the peaks are coeluting in a way that makes the quantification impossible. Especially the peaks of interest with regard to biogenic emissions and tropospheric degradation (i.e., isoprene, MVK, and MACR) are clearly separated, not only for measurements of the calibration gas mixture as shown in Fig. 3 but also for measurements of ambient air samples.

3.3. Precision

The precision of both the dynamic preparation of the calibration gas mixture and the measurement with the gas chromatographic system was tested by continuously measuring the calibration gas mixture over a time period of 3 days. The sampling frequency of approx. 30 min allowed 135 consecutive measurements during that period. VOC concentrations ranged between 60 ppt and 1.8 ppb (isoprene: 1.8 ppb, MVK: 580 ppt, MACR: 240 ppt). Fig. 4 shows the result of the peak quantification of isoprene, MVK, and MACR. Average peak areas were 118 500, 13 200, and 9700 μV s, with 1σ variations

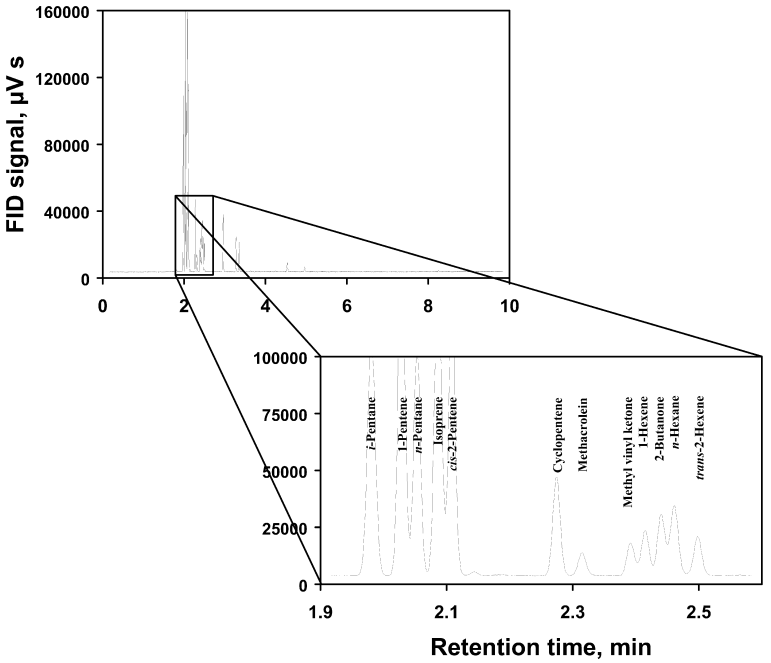

Fig. 3. Chromatogram of the calibration gas mixture.

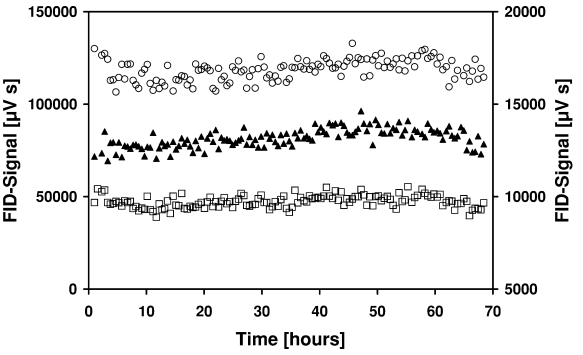

Fig. 4. Test of the reproducibility of the gas chromatographic system and the calibration system. Peak areas of isoprene (open circles, left scale), MVK (filled triangles, right scale), and MACR (open squares, right scale) for 130 consecutive measurements of the calibration gas mixture (sample volume = 0.5 l, concentrations: isoprene = 1850 ppt, MVK = 580 ppt, and MACR = 240 ppt).

of 5, 3, and 4%, respectively. The results of the other tested VOCs are listed in Table 3. All compounds [with the exceptions of *i*-pentane (9%) and 1-pentene (6%)] have a reproducibility of 5% or better. It has to be pointed out that this reproducibility is a combination of both the preparation of the calibration gas mixture (which might also be subject to variations) and of the chromatographic quantification. Therefore, these values must be regarded as upper limits for the reproducibility of the quantification.

3.4. Linearity of the detector response

The linearity of the system was tested by sampling different volumes (and different concentrations) of the calibration gas mixture. Different concentrations were adjusted by varying the dilution flow (Fig. 2, flow j_3) only. Since we use FID for quantification, the signal of the detector should only dependent on the mass of the sampled VOC. The sample mass of a VOC preconcentrated on the adsorbents is calculated by multiplication of the sample volume and the diffusion rate with the dilution:

$$m_i = Vr_i \cdot \frac{j_2}{j_1 j_3} \quad (2)$$

where m_i = sample mass of compound i (ng); V = sample volume (ml); r_i = diffusion rate of compound i (ng min^{-1}); j_2 = flow through fused-silica column (ml min^{-1}); j_1 = flow through diffusion chamber (ml min^{-1}); j_3 = dilution flow (ml min^{-1}).

Table 3
Summary of the reproducibility of measurements and calibration details

Compound	Formula	Concentration range (ppt)*	Reproducibility		Number of different sampled masses (n)	FID correction factor	FID response, (µs ng^{-1})	Correlation coefficient (r^2)
			At ppt	1σ ** (%)				
i-Pentane	C_5H_{12}	250–10 700	1240	9	31	1.03	52 610	0.997
1-Pentene	C_5H_{10}	340–11 700	1660	6	30	1.02	53 966	0.997
Isoprene	C_5H_8	370–12 700	1770	5	30	1.01	50 767	0.998
n-Pentane	C_5H_{12}	220–9400	1100	5	98	1.03	53 017	0.996
cis-2-Pentene	C_5H_{10}	260–10 900	1280	3	98	1.02	51 107	0.998
Cyclopentene	C_5H_8	110–5900	520	5	79	0.99	50 892	0.999
1-Hexene	C_6H_{12}	40–2300	200	3	99	1.02	52 446	0.998
2-Butanone	C_4H_8O	170–9400	820	4	54	1.71	39 386	0.997
trans-2-Hexene	C_6H_{12}	40–2200	190	4	99	1.02	51 001	0.999
n-Hexane	C_6H_{14}	70–3700	320	4	99	1.02	53 133	0.998
Benzene	C_6H_6	80–4600	410	3	99	0.93	52 952	0.995
Methacrolein	C_4H_6O	50–2700	220	3	32	1.72	47 207	0.999
Methyl vinyl ketone	C_4H_6O	120–6600	570	4	32	1.72	29 730	0.998
trans-2-Heptene	C_7H_{14}	50–2700	230	3	99	1.01	49 237	0.999
n-Heptane	C_7H_{16}	40–2500	220	3	99	1.02	58 764	0.992
1-Octene	C_8H_{16}	20–900	60	4	99	1.01	48 741	0.997

* Calculated from the diffusion rate and the dilution flow-rates.

** 1σ variation of 135 consecutive measurements of the calibration gas mixture at the given concentration.

Fig. 5 shows the observed peak area of isoprene (upper plot), MVK (middle plot), and MACR (lower plot) as a function of sample mass. Different symbols denominate different mixing ratios. The error bars give the 1σ variance and thus show the reproducibility of measurements. The results for all compounds in the calibration gas mixture are summarized in Table 3. The linearities of the detector response are very good, with squared correlation coefficients between 0.992 and 0.999. As expected, measurements of different concentrations did not result in changes in the slopes of peak ares versus sample mass. Also, for no compound a significant regression line intercept was observed.

3.5. Calibration

The FID response for the different VOCs is calculated from the slope of linear regressions of the peak area versus sample mass (for all measurements). From these fits the individual response factor of each VOC (RF_i) is calculated by Eq. (3):

$$RF_i = F_i \cdot \frac{A_i}{m_i} \quad (3)$$

where RF_i = individual response factor ($\mu V\ s\ ng^{-1}$); F = correction factor of compound i (dimensionless); A_i = peak area of compound i ($\mu V\ s$); m_i = sampled mass of compound i (ng).

In Eq. (3), F_i denominates the correction factor that accounts for the theoretical differences in sensitivities of VOCs (especially the oxygenated VOCs) in FID and is based on the effective carbon number concept. We use the procedure described in detail in Ref. [28] to derive the correction factors for VOCs. Table 3 lists the correction factors, F_i, and the individual response factors, RF_i, for all compounds in the calibration gas mixture. For the hydrocarbons, the correction factors are about unity. The (corrected) individual response factors of all hydrocarbons range between 49 200 $\mu V\ s\ ng^{-1}$ (*trans*-2-heptene) and 58 800 $\mu V\ s\ ng^{-1}$ (*n*-heptane). The oxygenated VOCs have higher correction factors of about 1.7. Applying this FID correction factor should result in values within the range of the results of hydrocarbons. But only for MACR, F_i is close to that range with a value of 47 200 $\mu V\ s\ ng^{-1}$. The individual response factors of MVK (29 700 $\mu V\ s\ ng^{-1}$) and of 2-butanone (39 400 $\mu V\ s\ ng^{-1}$) are still significantly lower. It is not clear whether these deviations from the expected values are due to a different detector response other than calculated from theoretical values or due to problems with the diffusion source to produce the calibration gas mixture. The latter is supported by the observation that both compounds in the diffusion vials showed a darkening in color and an increase in viscosity. Therefore, we conclude that (although not visible in the diffusion rate itself) an unknown chemical reaction occurred in the diffusion vial and that the lower response factors of MVK and 2-butanone are the result of problems in the preparation of the calibration gas mixture.

3.6. Detection limit and accuracy of VOC measurements

The detection limit is given by the smallest peak area that can be distinguished from the noise of the baseline of the detector signal. For the measurements presented here, this value is ~500 $\mu V\ s$. For a response factor of about 50 000 $\mu V\ s\ ng^{-1}$ this corresponds to a minimum sample mass of 0.01 ng that has to be sampled in order to get a signal to be differed from the noise of the baseline. The detection limit in terms of mixing ratio then also depends on the molecular mass of the VOC of interest and the sample volume. For isoprene ($M = 68\ g\ mol^{-1}$) and a sample volume of 0.5 l, a detection limit of ~7 ppt can be calculated. Compounds that have a smaller response factor (or higher FID correction factors) inevitably have a higher detection limit. For MVK and MACR, this detection limit is calculated to be ~12 ppt.

The accuracy of VOC quantification is not as easily accessable. Since the quantification with FID is not an absolute method and requires calibration, the accuracy of VOC quantification is depending on the accuracy of the preparation of the calibration gas mixture and on the accuracy of the GC measurements. The accuracy of the preparation of the calibration gas mixture with the method described here can be estimated from the error of the different gas flows and from the error of the diffusion rate. The error of the nitrogen flow through the diffusion chamber, of the flow from the diffusion chamber into

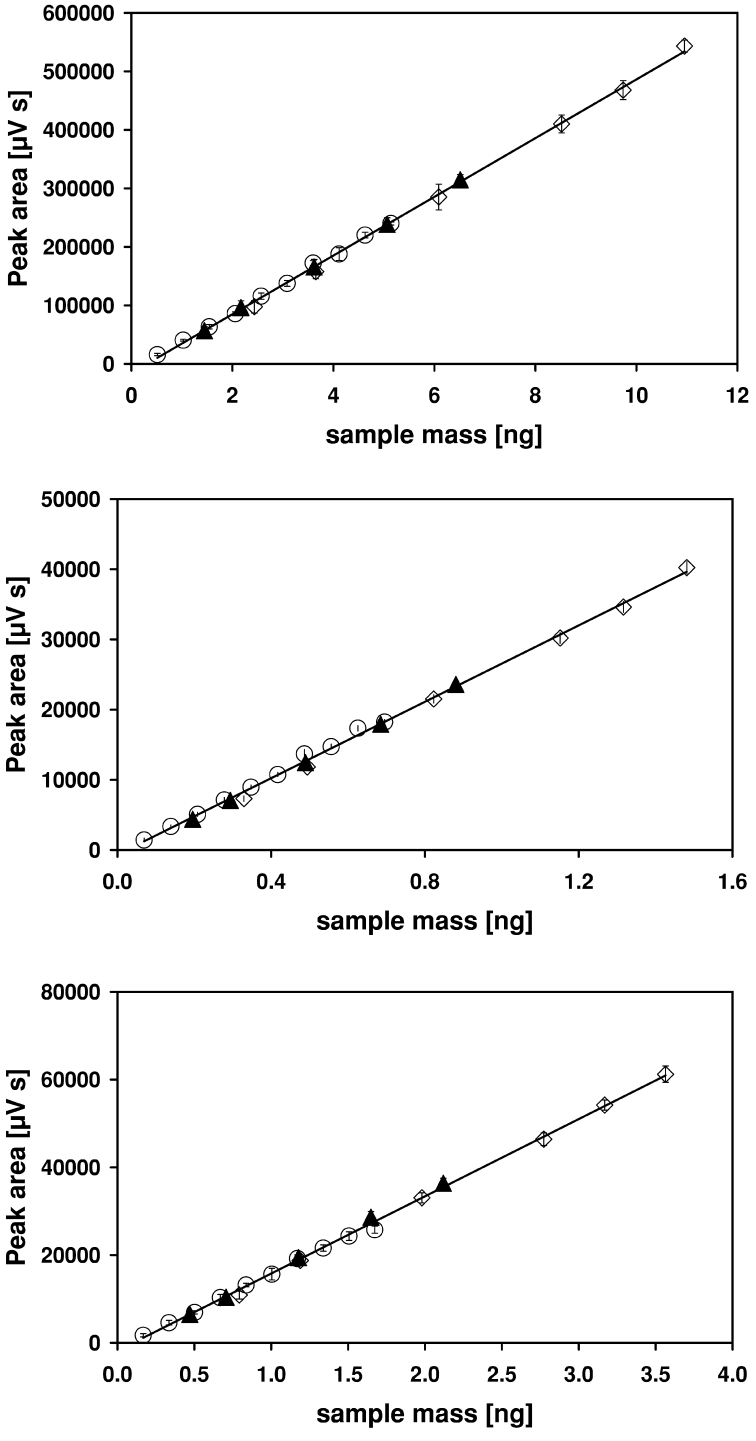

Fig. 5. Peak area of isoprene (upper graph), MVK (middle graph), and MACR (lower graph) versus sample mass for measurements with different mixing ratios (isoprene: open circles = 1850 ppt, filled triangles = 2600 ppt; open diamonds = 4370 ppt; MVK: open circles = 580 ppt, filled triangles = 820 ppt; open diamonds = 1380 ppt; MACR: open circles = 240 ppt, filled triangles = 570 ppt; open diamonds = 340 ppt) and different sample volumes (between 0.1 and 1.0 l).

the dilution chamber, and of the dilution flow is ~4% each (see Section 2.2). The precision of the diffusion rate is different for each compound. Values are given in Table 2 and vary between 1 and 10%. Using a Gaussian addition of the individual errors, the accuracy of the composition of the calibration gas mixture can be calculated to be between 7 and 12%. The accuracy of the GC measurements is at best determined by an intercalibration experiment and can only be estimated at this point. The precision of the FID responses for the different VOCs presented in Table 3 can be taken as a first approximation to this accuracy. The different response factors show a standard deviation of 13% of their mean value. Combined with the accuracy of the preparation of the calibration gas, the overall accuracy of VOC quantification can be estimated to be between 15 and 20%.

3.7. Cross sensitivities

3.7.1. Humidity

The calibration measurements were usually performed with the calibration gas mixture at a fixed humidity (dew point 10 °C). As shown in Fig. 2, a temperature controlled humidifier was used to humidify the dilution gas flow. By varying the water temperature, we adjusted different dew points and tested the influence of different humidities on quantifying VOC concentrations. In this experiment, we tested our calibration gas mixture at dew points of 5, 10, 13, 16, and 19 °C, and of dry nitrogen (evaporated liquid nitrogen). Fig. 6 shows, as examples, the peak areas of isoprene, MVK, and MACR for measurements of the calibration gas mixture at different humidities normalized to the measurements under dry conditions. The error bars give the 1σ variation of the measurements. Variations in the dew point between 5 and 19 °C did not result in changes in the peak areas. Only the measurement under dry conditions show slightly smaller peak areas. A possible explanation for this observation could be wall effects which might play a role under these dry conditions, which never occur under ambient conditions. For the range of humidities under ambient conditions, we observed no influence of humidity on the quantification of VOCs.

3.7.2. Ozone

When measuring the VOC content of ambient air, ozone will always be present at concentrations on the order of 10 to 100 ppb. It has been shown in several

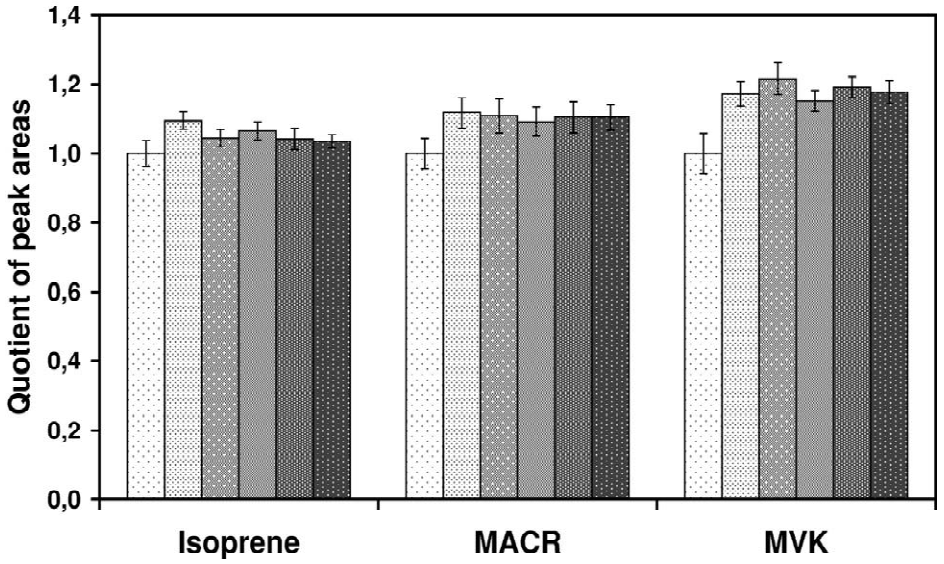

Fig. 6. Effect of humidity of the calibration gas mixture on the measurements (dew point for bars from left to right: dry, 5, 10, 13, 16 and 19 °C), measured at isoprene = 1770 ppt, MVK = 570 ppt, and MACR = 220 ppt. Peak areas at different humidities are normalized to peak areas under dry conditions. Error bars are 1σ variation in the measurements.

publications (Ref. [31], and references therein), that the sampling of VOCs on solid adsorbents in ozone containing air leads to degradation of VOCs on the adsorbents, artefact formation, and several other problems. Therefore, it is essential that ozone is removed prior to sampling. In the literature, several ozone scrubbing techniques are described (Ref. [30], and references therein). We chose the titration with nitrogen monoxide as the appropriate method, because for the solid ozone scrubbers (e.g., manganese dioxide coated copper nets) reports in the literature are contradicting and in some studies losses of the sampled VOCs were observed. Since neither of the VOCs react with NO or with NO_2, no cross sensitivities should be observed.

For the ozone removal, a mixture of approx. 20 ppm nitrogen monoxide in pure nitrogen was used. Ozone titration was performed by adding 6 ml min^{-1} of the NO mixture to the sampling air stream. To compensate this addition, the sampling air flow was increased from 100 ml min^{-1} to 106 ml min^{-1}, therefore still sampling 100 ml min^{-1} of ambient air. Thus, a concentration of 1.1 ppm NO in the sampling air is adjusted. With a rate constant of $1.82 \cdot 10^{-14}$ cm^3 s^{-1} (at $T = 298$ K) [32] for the reaction:

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (4)$$

and a concentration of 1.1 ppm, the lifetime of O_3 is about 2 s. NO is added approx. 1 m upstream of the adsorption tube into the inlet line (length = 1 m; inner diameter = 4 mm). The residence time and thus the reaction time is about 8 s, which is sufficient for a quantitative removal of ozone prior to sampling.

The effect of NO addition to the sampled air and a possible influence on the quantification of isoprene, MACR, and MVK has been tested and the result is shown in Fig. 7. No influence could be observed and hence it was shown that NO titration is an applicable and artefact free method for ozone scrubbing during measurements of these VOCs.

4. Measurements of ambient air

4.1. Performance of measurements

A schematic overview of the tower based measurements at the forest site is given in Fig. 8. Sampling lines are placed at four different heights, in and above the forest canopy. All sampling lines are made of PFA (perfluoroalkoxy copolymer), have a length of 40 m, and an inner diameter of 4 mm (Bohlender, Lauda-Koenigshofen, Germany). The lines are placed inside aluminium tubes which are

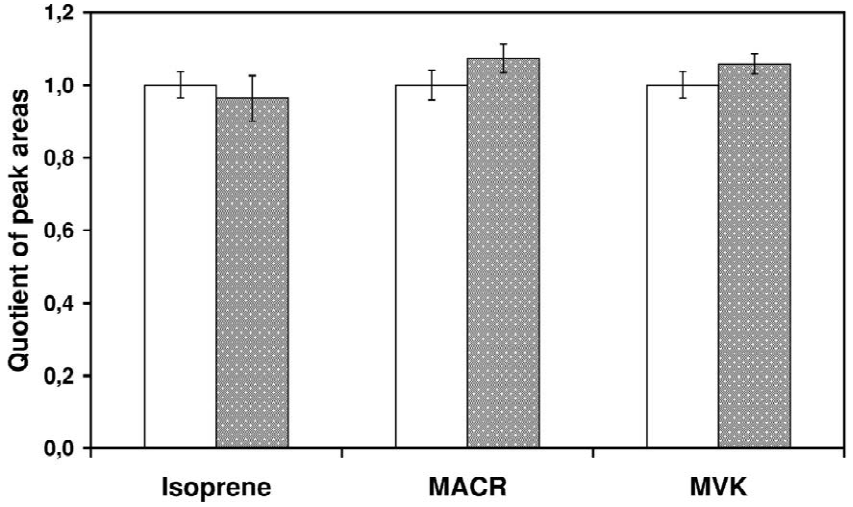

Fig. 7. Effect of the NO titration on the measurements (left bars: without NO titration, right bars: with NO titration), measured at isoprene = 1770 ppt, MVK = 570 ppt, and MACR = 220 ppt. Peak areas are normalized to peak areas without NO titration. Error bars are 1σ variation in the measurements.

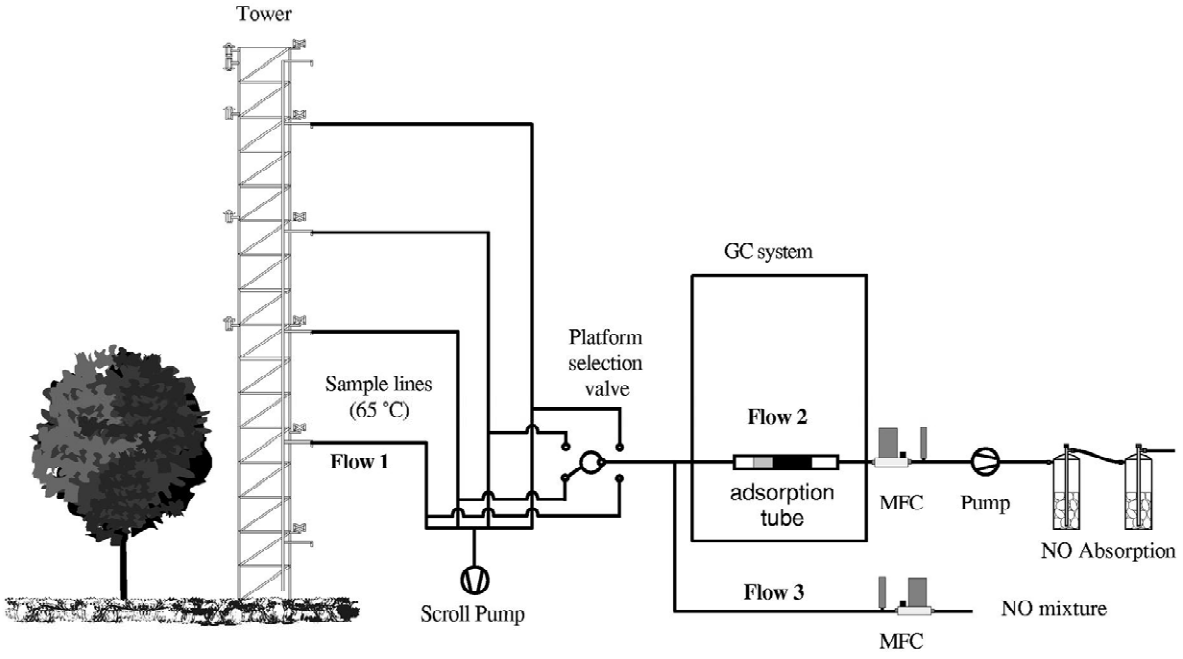

Fig. 8. Flow diagram of the sampling system set up for measurements of ambient air at different heights.

insulated with Armaflex pipe insulations (Armacell, Muenster, Germany). Inside the aluminium tube, the sampling lines are heated to 65 °C with a self-limiting heating hose (Horst, Lorsch, Germany) to ensure constant temperature inside the sampling line and to avoid condensation. At the inlet, the line is connected to a custom-made PTFE filter holder. PTFE filters (45 mm diameter, 0.2 μm pore size) are used to filter aerosols, pollen, insects, and any other condensed material. Ambient air is continuously pumped through all lines using an oil-free scroll pump (XDS10-S, BOC Edwards, Kirchheim, Germany). The air flow through the sampling lines is kept at 3.5 l min^{-1}, and is continuously checked with a rotameter. The residence time of the air inside the inlet line is about 10 s. From these sampling lines, several instruments take a fraction of the total air flow for their analysis.

For VOC quantification, the four sampling lines are connected to a four way dead-end flowpath valve (Valco Instruments, Schenkon, Switzerland). From the total air flow of 3.5 l min^{-1} a fraction of 100 ml min^{-1} is pulled over the adsorption tube via a sampling line which is connected to the common outlet of this valve. Desorption and analysis of the sampled VOCs is performed as described in Section 2.3. VOC mixing ratios are calculated with the following equation:

$$c_i = \frac{F_i A_i}{V \mathrm{RF_m}} \quad (5)$$

where c_i = concentration of compound i (ng l^{-1}); F_i = FID correction factor of compound i (dimensionless); A_i = peak area of compound i (μV s); V = sample volume (l); $\mathrm{RF_m}$ = mean response factor (μV s ng^{-1}).

As described above, ozone titration is performed in the last sampling line by adding NO to the sampling air flow. It has to be noted that ozone removal is performed at the end of the sampling line at ground level and not directly at sample inlet on top of the tower. The losses of isoprene due to its reaction with ozone in the 40 m inlet line prior to the NO addition can be estimated as follows: the reaction of isoprene with ozone is relatively slow with a rate constant of $1.28 \cdot 10^{-17}$ cm^3 s^{-1} (at $T = 298$ K and $2.61 \cdot 10^{-17}$ cm^3 s^{-1} at $T = 338$ K [33]). Even for

high ambient ozone concentrations of 100 ppb, the lifetime of isoprene is on the order of several hours. With a residence time prior to the NO titration of only 10 s, losses due to ozonolysis of isoprene inside the inlet line are negligible.

Since NO belongs to the numerous trace gases which are monitored during the complex field experiments at the forest site, the exhaust gas must not be released to the ambient air without purification. To remove NO from the exhaust gas, a combination of two adsorbents (Sofnofil and Sofnocarb) is used. Sofnofil (Molecular Products, Essex, UK) is an impregnated activated aluminia containing potassium permanganate which oxidizes all remaining NO to NO_2. The second adsorbent, Sofnocarb (Molecular Products), which is mainly activated carbon, then absorbs the nitrogen dioxide. The conversion and absorption efficiency was tested by measuring the concentrations of NO and NO_2 prior and behind the two adsorbents with a chemiluminescence NO-detection system (ECO PHYSICS CLD 770) equipped with a photolytic converter for the measurement of NO_2 [34]. An initial NO concentration of 1 ppm prior to the adsorbents was reduced to a mixing ratio below the detection limit of 13 ppt. Therefore, a contamination of the air due to the NO titration can be excluded.

4.2. First results of ambient measurements

The continuous measurements of isoprene and its oxidation products started on 6 June 2002. Until the end of August, almost 3000 samples (35 samples per day on average) were measured. Isoprene and MACR were quantified in 2850 of these samples, MVK which sometimes had too small mixing ratios was quantified 2650 times. Detailed results of these measurements and intensive interpretations will be presented elsewhere.

Here, only the mixing ratios of isoprene, MACR, and MVK measured on the first 12 days in June 2002 are shown (Fig. 9). Isoprene showed the most pronounced diurnal cycle. Measured mixing ratios ranged from ~20 ppt during nighttime to ~1.3 ppb during the day. Daytime maximum values varied strongly depending on temperature and solar radiation. On warm sunny days the maximum values exceeded 1 ppb whereas on colder, cloudy days the maximum isoprene mixing ratio was as low as 200 ppt. The nighttime minima showed smaller variations. At night, isoprene mixing ratios always had lowest values between 20 and 40 ppt.

The mixing ratios of MACR varied between 20 and 180 ppt, the mixing ratios of MVK between the detection limit of ~10 and 200 ppt. As products of the isoprene oxidation, the concentrations of MACR and MVK depend on the emission of isoprene and the concentration of the oxidants. It is visible that on the first 2 days shown here, MACR and MVK showed higher mixing ratios as a result of the higher isoprene concentrations and the more active isoprene chemistry. Between 6 and 13 June, daytime maximum mixing ratios of isoprene did not exceed 600 ppt. During that episode, MACR and MVK concentrations showed a trend over several days with decreasing concentrations. Beginning with the stronger increase in isoprene production on 14 June, also the mixing ratios of the oxidation products rose again.

5. Comparison with other systems

The quantification of isoprene, MACR, and MVK in ambient air with gas chromatographic systems is not a completely novel method and has been applied for several years. However, in most publications dealing with VOC quantification the description of the exact procedure of sampling, analysis, and calibration is scarce and sometime lacks several crucial details (e.g., the treatment of ozone scrubbing). Table 4 gives a compact overview of the main features of the instrument and methods described here in comparison with those described previously in the literature.

All instruments described in Table 4 are on-line GC systems. Sampling of VOCs is either performed cryogenically or on a cartridge containing one or two adsorbents. Typically, several hundred milliliters of air are required for VOC quantification. Ozone scrubbing is performed differently for each instrument. In contrast to the method described here, solid-phase scrubbers such as potassium iodide, sodium sulfite or thiosulfate are used [22,35,38,39]. In at least three procedures, ozone is not removed prior to sampling [36,37,41] and in two references no

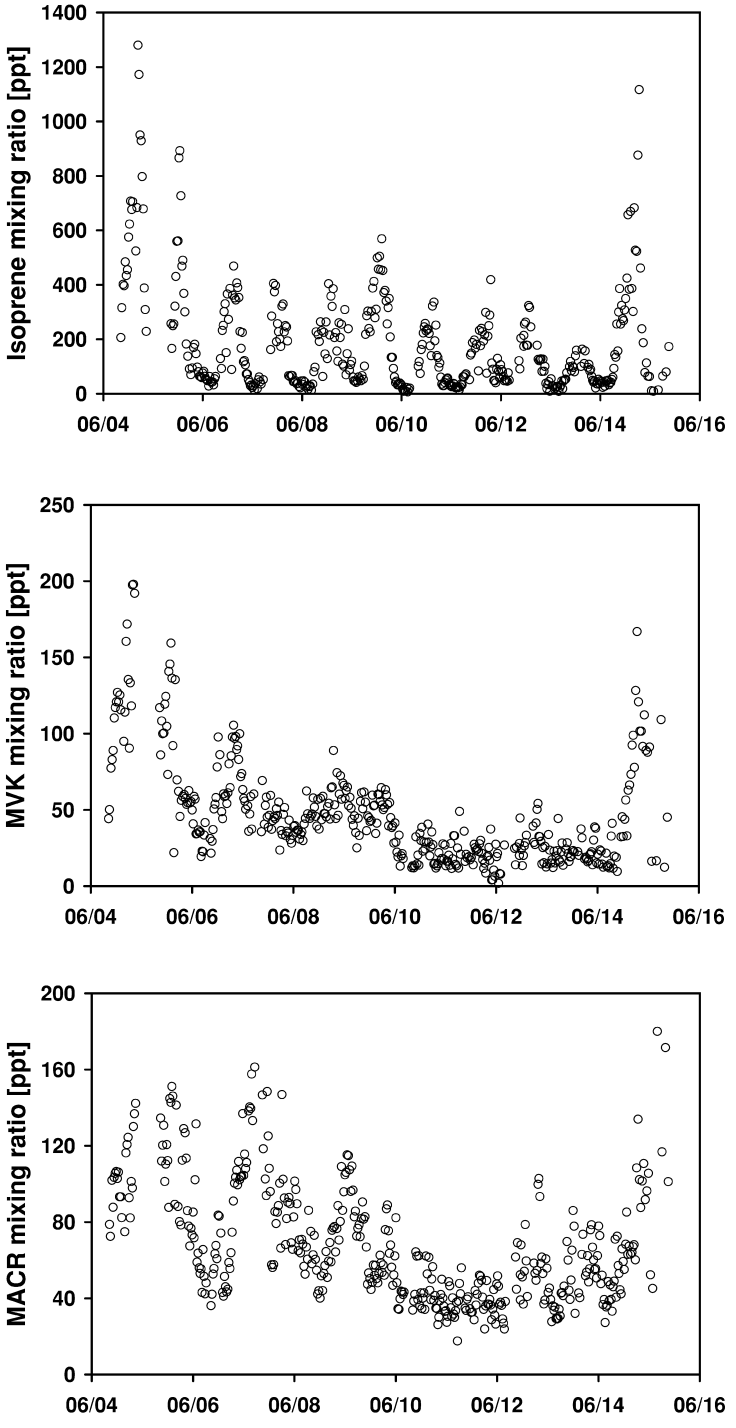

Fig. 9. Diurnal cycles of the mixing ratios of isoprene, MVK, and MACR (top to bottom) measured between 6 and 16 June.

Table 4
Comparison to on-line GC systems for measurements of ambient isoprene, MACR, and MVK previously described in the literature

Ref.	Sampling procedure	Sample volume	Ozone scrubber	Calibration	Temporal resolution	Duration of experiment	Detection limit
[35]	Cryogenic at −196 °C	250 ml	Anhydrous sodium sulfite	Dynamic diluted mixtures of gravimetric cylinder standards	1 h	5 weeks	10 ppt
[36]	Tenax TA	6 l	None	Gravimetric cylinder standard	75 min	6 weeks	10 ppt
[37]	Tenax TA at 15 °C	200 ml	None	Dimethyl sulfide, dibromomethane and bromoform at the ppb level	45 min	6 months	2 ppt
[38]	Cryogenic at −145 °C	200–300 ml	Anhydrous sodium sulfite	Static and dynamic diluted mixtures of gravimetric cylinder standards	1 h	3 weeks	Not specified
[39]	50 mg Tenax TA at 15 °C	300–800 ml	Crystalline potassium iodide	Acetone at 7 ppb and relative response factors of VOC against acetone	1 h	4 weeks	10 ppt for isoprene, 100 ppt for MACR and MVK
[40]	234 mg Tenax TA/ 200 mg Carboxen at 20 °C	500–750 ml	Not specified	Acetone at 7 ppb and relative response factors of VOC against acetone	1 h	4 weeks	Not specified
[22]	300 mg Carbotrap C/200 mg Carbotrap/100 mg Carbosieve S III at 30–35 °C	2.5–10 l	Sodium thiosulfate	Multicomponent cylinder standard at the ppb level	3 h	1 week	5–10 ppt
[41]	1500 mg Tenax TA	100–400 ml	None	Dynamic diluted mixtures of gravimetric cylinder standards	1 h	4 weeks	30 ppt for isoprene, 50 ppt for MACR and MVK
[19]	Cryogenic at −130 °C	300 ml	Not specified	Dynamic diluted mixtures of gravimetric cylinder standards	Not specified	8 days	5 ppt for all compounds
This paper	50 mg Tenax TA/ 150 mg Carbopack X at 30 °C	500 ml	Titration with NO	Custom-made diffusion source	30 min	>1 year	7 ppt for isoprene, 12 ppt for MACR and MVK

ozone removal procedure is described [19,40]. As already pointed out, ozone removal is essential to avoid sample losses and especially in combination with Tenax as adsorbent artefact formation has been observed when ozone is not removed prior to sampling (Ref. [30], and references therein). The detection limits of the different instruments differ significantly between 2 ppt [37] and 100 ppt [39], and typically the oxidation products have higher detection limits. Compared with the other methods the detection limit of the instrument described here (7 ppt for isoprene and 12 ppt for MACR and MVK each) is at the lower end of this range. This relatively low detection limit is combined with the highest temporal resolution of measurements. Typically, a complete cycle of sampling, desorption, and analysis requires 1 h whereas the system described here has a temporal resolution of only 30 min. The instrument described here has already been operated longer in the field than any of the mentioned instruments. In combination with the higher temporal resolution the data set obtained with this instrument can be expected to be the largest consecutive set of ambient isoprene, MACR, and MVK measurements and the data will provide new inside into seasonality in isoprene emissions and into isoprene oxidation under very different meteorological conditions.

6. Summary

The GC system described in this work was developed for long-term on-line measurements of isoprene and two of its major degradation products, MACR and MVK, in ambient air. The system combines a low detection limit (~10 ppt) with high precision (~5%) and high temporal resolution (~30 min). The overall accuracy of isoprene, MACR, and MVK quantification at ambient concentrations is estimated to be between 15 and 20%, but this error has to be validated in an intercalibration experiment.

The VOCs of interest are sampled on a glass tube containing a package of two adsorbents (Tenax TA and Carbopack X). The breakthrough volume of the VOCs of interest was tested and no breakthrough was observed up to a sampling volume of 4 l (at a sample flow-rate of 100 ml min^{-1}). Subsequent to sampling, the VOCs are thermally desorbed onto the GC system, separated on an Optima-5-MS column, and detected with FID.

Calibration of the system is performed with a custom-made diffusion system. Here, the high-purity liquid VOCs diffuse out of glass vials into the gas phase and their concentrations are dynamically diluted down to concentrations in the ppt range. The nitrogen used for dilution can be humidified to different dew points by a temperature-controlled humidifier. The accuracy of the preparation of the calibration gas mixture is calculated to be between 7 and 12%, depending on the precision of the diffusion rate of each individual VOC.

Cross interferences in the quantification of VOCs due to different humidities and ozone concentrations in the sample air as well as the temporal stability of the system have been tested thoroughly in laboratory studies. Variations in the dew point of the calibration gas mixture between 5 and 19 °C did not result in changes in the peak areas and so it was shown that humidity within that range has no influence on the quantification. Ozone removal prior to sampling is necessary to avoid VOC degradation on the adsorbent and artefact formation. The ozone removal by titration with NO was successfully deployed and it was shown that no cross interferences resulted due to the addition of NO to the sampled air.

The GC system is successfully being operated in the field. Measurements of ambient air started in June 2002 and are planned to run continuously until October 2003. Ambient isoprene concentrations ranged from ~20 ppt during nighttime to ~1.3 ppb during the day. The mixing ratios of MACR varied between 20 and 180 ppt, the mixing ratios of MVK between the detection limits of ~10 and 200 ppt. Detailed results and interpretations of these measurements will be described elsewhere.

Acknowledgements

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