Measurements of Volatile Organic Compounds (VOC) During POPCORN 1994: Applying a New On-Line GC–MS-Technique

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Abstract. Atmospheric concentrations of ca. 250 C_6–C_{15} hydrocarb on and C_4–C_{12} oxygenated volatile organic compounds (VOC) including alkanes, benzene and alkyl benzenes, monoterpenes and aldehydes were measured in August 1994 during the POPCORN campaign (POPCORN = Photo-Oxidant formation by Plant emitted Compounds and OH Radicals in North-Eastern Germany). About 80 substances together contributed 90% of the atmospheric carbon in this range of molecular weight. During this field campaign VOC-emissions from several crop and tree species and the ambient concentrations of CO, C_2–C_7 non-methane hydrocarbons (NMHC), C_1 and C_2 aldehydes, nitrogen oxides, ozone and hydroxyl-radicals (OH) were also measured. These data were used to interpret the VOC measurements presented here. The on-line GC–MS used for the VOC measurements combines adsorptive sampling with thermal desorption and GC–MS analysis in an automated system. Internal standards were used to quantify the measurements. Ozone was destroyed prior to the sample preconcentration through the gas phase reaction with NO. Aromatic compounds like benzene, toluene and xylenes were the most abundant compound class among the measured substances, α-pinene and Δ3-carene, most probably originating from pineforests ca. 1 km away from the measuring site, were the most abundant monoterpenes. The highest mixing ratios of most compounds were measured in nights with strong inversion situations. The toluene mixing ratios then reached 630 pptv; α-pinene mixing ratios went up to 430 pptv. The median of all toluene and α-pinene measurements during the campaign was 125 pptv or 22 pptv, respectively. These values are on the lower end of ambient measurements reported for continental sites. In most samples also n-pentanal, n-hexananl, n-nonanal and n-undecanal were present. Median mixing ratios were 9, 16, 14 and 8 pptv, respectively. Emission studies indicate that these highly reactive compounds are most probably emitted from maize. It is shown by a simple first order approach that the potential for ozone formation during the POPCORN campaign was roughly equal for anthropogenic and biogenic VOC. From measured concentrations of ozone, OH-radicals, methane, CO, C_2–C_{15} nonmethane hydrocarbons (NMHC) and C_5–C_{11} aldehydes a photochemical production of ozone in the order of 3.5 ppb/h can be estimated. Apart from formaldehyde and acetaldehyde, which are at least partly products of VOC oxidation, the substance group with the largest contribution to the VOC turnover are the monoterpenes. They contribute ca. 30%. However, the mechanism of terpene oxidation is very complex and presently only partly understood. Thus the actual contribution of monoterpenes to ozone formation is very uncertain. Other measured compound classes such as light alkenes, alkanes, aromatics, and C_5–C_{11} aldehydes contribute each between 10% and 15% to ozone formation. The measuring site was not influenced directly from strong biogenic or anthropogenic sources, and the results obtained during the POPCORN campaign can be regarded as a typical picture of a remote rural central European environment.

Key words: volatile organic compounds, C_5–C_{15} hydrocarbons, aldehydes, ozone formation, gas-chromatography, GC–MS.

1. Introduction

In the presence of NO and OH-radicals volatile organic compounds (VOC) act as precursors of ozone and other photo-oxidants in the troposphere (Warneck, 1988). Therefore understanding and possibly controlling the formation of these compounds critically depends on the knowledge of the sources, sinks and the atmospheric distribution of VOC. Currently the contribution of VOC from biogenic sources, especially plants, is under special consideration (Fehsenfeld *et al.*, 1992; Atlas *et al.*, 1993). This is mainly due to the fact that biogenic VOC sources are apparently ubiquitous and that many of the compounds emitted from plants are much more reactive than most anthropogenic VOC. In addition to monoterpenes and sesquiterpenes, oxygenated VOC, such as alcohols, aldehydes, ketones, ethers, acids, and esters, are thought to be biogenic emissions that are potentially important for the photochemical ozone production (cf. Arey *et al.*, 1991; Hewitt and Street, 1992; König *et al.*, 1995; Goldan *et al.*, 1995).

One purpose of the POPCORN campaign was the understanding of the photo-oxidant formation in a rural area. Therefore the ambient concentrations of VOC, nitrogen oxides (NO_x) and hydroxyl radicals (OH) and other trace species as well as meteorological parameters have been measured (cf. Plass-Dülmer *et al.*, this issue). Another purpose was to study how VOC affect the atmospheric photochemistry in a rural location. Since maize was thought to be a crop species which exhibits substantial VOC-emissions (Lamb *et al.*, 1993), an extended maize field near Pennewitt in Mecklenburg-Vorpommern was selected as the site for these measurements. Mecklenburg-Vorpommern in north-eastern Germany is a sparsely inhabited area with only scarce anthropogenic VOC sources (Plass-Dülmer *et al.*, this issue). The VOC-emissions of the most abundant tree and crop species in the vicinity of the field site were measured using mobile branch enclosure systems (Rudolph *et al.*, 1995).

In this paper the results of the ambient measurements of C_6–C_{15} hydrocarbons and C_4–C_{12} oxygenated VOC will be presented and compared to the results of the emission studies performed during the campaign. A simple first order estimate of the ozone production from different VOC will be presented.

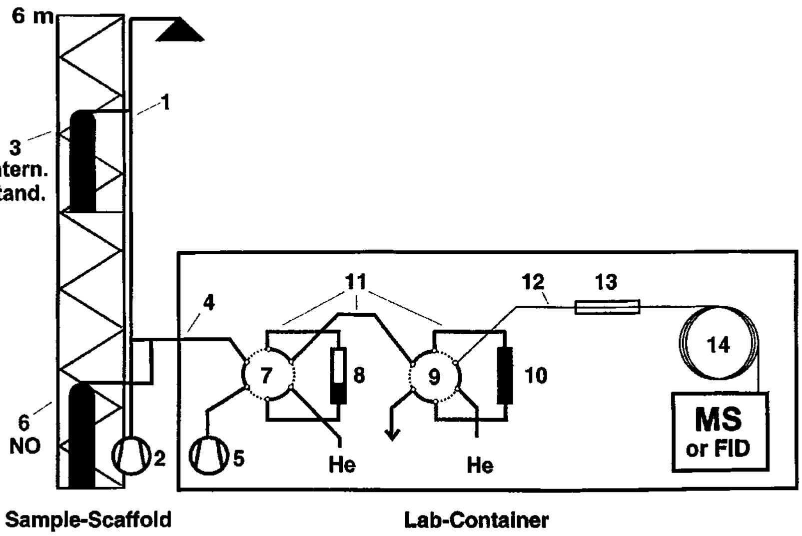

Figure 1. Set-up of the On-line GC–MS. (1)–(6) Inlet system: (1) inlet line (FEP, $l = 19$ m, o.d. = 6 mm, i.d. = 4!mm); (2) membrane pump with thermal mass flow controller; (3) gas cylinder with internal standard; (4) sample line (FEP, $l = 1.0$ m, o.d. = 6 mm, i.d. = 4 mm); (5) membrane pump with thermal mass flow controller; (6) gas cylinder with NO (250 ppmv in synthetic air). (7)–(13) Thermodesorption system (modified Tekmar 6000 with cryofocus module); (7) sample collection valve; (8) adsorption tube (silanized glass, $l = 180$ mm, o.d. = 6 mm, i.d. = 4 mm, filled with 100 mg Tenax TA, 60/80 mesh and 50 mg Carbotrap, 20/40 mesh, separated with small plugs of silanized glass wool); (9) trap desorption valve; (10) cryo-trap (glass lined stainless steel tube, i.d. = 2 mm, filled with silanized glass beads); (11) stainless lines (o.d. = 1/16″, i.d. = 1 mm). The two six-port valves (7 and 9) and the lines (11) are installed in a valve oven permanently heated to 200 °C. (12) Transfer line (deactivated fused silica, $l = 1.5$ m, i.d. = 0.32 mm); (13) cryofocus module. Sample desorption: 260 °C for 20 min; purge gas: helium (grade 6.0, Messer-Griesheim, 25 ml/min); low cryotrap temperature: −175 °C. Cryo-trap desorption: 260 °C for 10 min, purge gas = GC-carrier gas, see below; cryofocus temperature: −170 °C; injection temperature: 200 °C. (14) Gas chromatograph (CE 8000, Fisons Instruments), capillary column (DB-5ms, 30 m × 0.25 mm × 1 μm, J&W), carrier gas: helium (grade 6.0, Messer-Griesheim), flow rate app. 1 ml/min. Temperature program: 3 min 25 °C, 4 K/min from 25 °C to 130 °C, 10 K/min from 130 °C to 250 °C, 10 min at 250 °C. (15) Detector: quadrupole-MS (MD 800, VG-Masslab), full scan mode (18-210 amu in 1s) or FID (FID 80, Fisons Instruments).

2. Experiment

2.1. SAMPLING AND ANALYSIS

C_6–C_{15} hydrocarbons and C_4–C_{12} oxygenated VOC in the atmosphere were measured with an automated system that combines adsorptive sampling with thermal desorption and GC–MS analysis. Internal standards were used to quantify the measurements.

A schematic drawing of the experimental set-up is shown in Figure 1. The GC–MS system was installed in a container in the centre of a maize field of 35 ha. The sample inlet was located on a scaffold ca. 5 m away from the container (for details about the location and the positions of the other measuring instruments see Plass-Dülmer *et al.*, this issue). Continuous measurements were made during three phases (August 5–7, August 12–15, and August 16–22) which were characterised by different meteorological conditions. These phases will be referred to as phase 1, 2, and 3. During phase 1 the inlet was on the 2 m level of the scaffold, later on the 6 m level. From this inlet ambient air was drawn continuously through an FEP-line of 19 m length (1 in Figure 1). The flow-rate in this line was set to 5.0 l/min. It was controlled by a thermal mass flow controller. The resulting residence time in the inlet line was ca. 3 seconds.

4.5 m past the inlet a calibration gas from a cylinder was added to the sample at a flow rate of ca. 2 ml/min. This calibration gas contained synthetic air with perdeuterated hexane, perdeuterated toluene, 1,3,5-trimethylcyclohexane and *n*-undecane at mixing ratios of 2 ppmv each. Two such gas standards were prepared by injecting a gravimetrically prepared mixture of the pure substances into a stainless steel tube attached to an evacuated gas cylinder. The substances were transferred into the cylinder by heating the line with a heat gun and purging it with catalytically purified zero air until the pressure in the gas cylinder was 100 bar. Due to the dilution in the inlet line, the mixing ratios of the internal standards in the sample gas were about 800 pptv.

From the total sample flow 100 ml/min were used for analysis. This flow was withdrawn from the inlet line in such a way that the direction of the gas flow was reversed. By this virtual impactor aerosols particles with a diameter $> 0.5\ \mu$m (calculated using the formula given by Hinds, 1982) were prevented from entering the analytical system. Air samples of 3 dm^3 were taken by switching a six-port valve and thus passing the sample flow for 30 min through an adsorption tube filled with 100 mg Tenax TA and 50 mg Carbotrap. This tube was built into a modified Tekmar 6000 thermodesorber and was thermostated at 33 ± 1 °C during the collection of the samples.

Before reaching the adsorption tube, 0.4 ml/min of a commercially available mixture of NO (250 ppmv) in synthetic air were added, resulting in a mixing ratio of 1 ppmv NO in the sample flow. Since ozone reacts rapidly with NO ($k = 1.82 * 10{-}14$ cm^3/molec $*$ s; Atkinson *et al.*, 1992) the ozone concentration was reduced to 10% of the initial value within the residence time of 8 seconds in this part of the sample line. The ozone concentration is further reduced by the use of heated stainless steel lines in the thermodesorption system (Koppmann *et al.*, 1995). Thus losses of unsaturated compounds due to the reaction with ozone on the adsorbent were avoided. A similar method of ozone removal has already been described for measurements of monoterpenes (Rudolph *et al.*, 1995). From the results shown in Table I, it can be seen that with this method losses of unsaturated compounds can be reduced dramatically. It is superior to the scrubber method

Table I. results of laboratory studies on the interference from ozone and its reduction. The sample gas was prepared with the permeation gas source is shown in Figure 1. This setup was modified by passing the dry dilution air through an ozone generator (Dasibi 1008 PC). In some experiments NO was added at the test gas outlet, allowing a reaction time of 8 s before sample collection. In other experiments a 'scrubber' (1 MnO_2 coated copper net of 3.5 cm diameter, Dasibi Inc.) was inserted in the sample line. VOC m.r. were between 50 and 600 pptV. The recoveries were calculated from five repetitions of each experiment and 15 measurements of the pure sample gas. Given is the mean and one standard deviation of the VOC recovery

Recover (%)	NO	NO + O_3	O_3	Scr. + O_3	Scr.
Ozone m.r. (ppbV)	0	100	100	100	0
NO m.r. (ppbV)	1000	1000	0	0	0
Scrubber inserted	No	No	No	Yes	Yes
Isoprene	93 ± 7	76 ± 2	92 ± 3	96 ± 3	103 ± 3
Methylvinylketone	110 ± 15	132 ± 40	134 ± 18	111 ± 12	65 ± 32
Benzene-D6	95 ± 4	98 ± 2	95 ± 2	104 ± 2	100 ± 4
Toluene-D8	94 ± 3	100 ± 1	94 ± 3	98 ± 3	101 ± 2
Z-3-Hexen-1-ol	86 ± 5	81 ± 29	83	0 ± 0	0 ± 0
α-Pinene	92 ± 1	84 ± 1	57 ± 7	95 ± 5	101 ± 2
Sabinene	145 ± 6	154 ± 17	64 ± 24	35 ± 8	34 ± 8
β-Pinene	105 ± 4	93 ± 5	75 ± 9	82 ± 6	90 ± 4
Myrcene	94 ± 1	80 ± 4	12 ± 5	56 ± 11	83 ± 12
Limonene	97 ± 2	75 ± 0	17 ± 3	73 ± 9	88 ± 5
Eucalyptol	106 ± 5	97 ± 2	101 ± 4	104 ± 2	101 ± 4
γ-Terpinene	58 ± 7	38 ± 4	15 ± 2	24 ± 4	33 ± 6
n-Undecane	93 ± 3	100 ± 5	92 ± 10	93 ± 6	92 ± 6
α-Cedrene	106 ± 40	72	0 ± 0	0 ± 0	72

described by Hoffmann (1992) and Calogirou *et al.* (1996). Systematic changes exceeding 30% occur for sabinene and γ-terpinene. It seems that γ-terpinene is isomerised to sabinene, although the mechanism is not yet understood. However, the mixing ratios observed for both compounds during POPCORN are extremely low, nearly always below the detection limit. Thus the uncertainty for these two compounds is of little consequence for the measurements made during POPCORN.

Thermal desorption was achieved through heating the adsorption tube to 260 °C. After two cryofocussing steps the sample was injected into the GC (Fisons CE 8000). It was separated on a methylphenylsilicone coated capillary column (DB 5 ms, 30 m x 0.25 mm x 1 μm, J &W) with helium as carrier gas. The temperature program was as follows: 3 min at 25 °C, 4 K/min from 25 °C to 130 °C, 10 K/min from 130 °C to 250 °C, 10 min at 250 °C.

In phase 1 and 2 a quadrupole-MS with electron impact ionisation (MD 800 by VG-Masslab) in a full scan mode (19–250 amu) was used for detection. For technical reasons in phase 3 a flame ionisation detector (FID 80, Fisons Instruments) was used instead. The GC-analysis required ca. 50 min. The enrichment of the subsequent sample was performed during the run of the chromatogram. One complete measuring cycle required about 1.5 hours. Since the pressure of the liquid nitrogen was occasionally too low for fast cooling of the cryo-focussing unit, the measuring intervals were sometimes longer. A personal computer was used for the control of the gas-chromatograph and the mass spectrometer as well as for the data acquisition and evaluation.

2.2. LABORATORY TESTS

Extensive laboratory tests have been performed to check the recovery of individual substances, the linearity and the reproducibility of the measurements. These tests were performed with a permeation gas source (Figure 2) equipped for benzene, several alkanes, monoterpenes, and sesquiterpenes, as well as oxygenated compounds known to be biogenic emissions, e.g. hexanal and Z-3-hexen-1-ol. Most of the tests were performed at mixing ratios ca. 1 ppbv. However, for a number of tests the mixing ratios were varied between 2 pptv and 30 ppb. The mixing ratios were calculated from the weight loss of the diffusion vials and the flow rates through the dilution system. The set-up of the GC–MS system during these experiments was identical to the set-up described above. A shorter inlet line ($l = 4$ m) was used to connect the permeation gas source with the virtual impactor but since the flow in this line was reduced to 1 dm^3/min the residence time in this line was 3 seconds as it was during the field measurements. No internal standards were added to the sample lines. Instead, perdeuterated toluene was introduced into the permeation source and served as an internal standard. The sampling time was varied between 1 and 80 minutes, resulting in sampling volumes between 100 ml and 8 l.

For these tests FID and MSD were used in parallel by splitting the flow at the end of the analytical column. Based on a recovery for perdeuterated toluene of 100% and an FID response proportional to the amount of carbon entering the detector, the recovery of other compounds was calculated. It was found to be between 80% and 100% for all tested C_6–C_{11} hydrocarbons with the exception of some of the monoterpenes (see Table II). Lower recoveries (probably due to wall losses or incomplete desorption) between 40% and 70% were found for methacrolein, *n*-hexanal, Z-3-hexen-1-ol, and caryophyllen. For isoprene an even lower recovery (ca. 50%) and a dependence of the response on sampling volume was found. The tests showed that sampling of such highly volatile substances is only sufficiently effective with sample volumes below roughly 1 dm^3 (STP). Since during the field campaign the sample volume was 3 dm^3, hydrocarbons lighter than hexane and oxygenated compounds lighter than methacrolein could not be evaluated quantitatively.

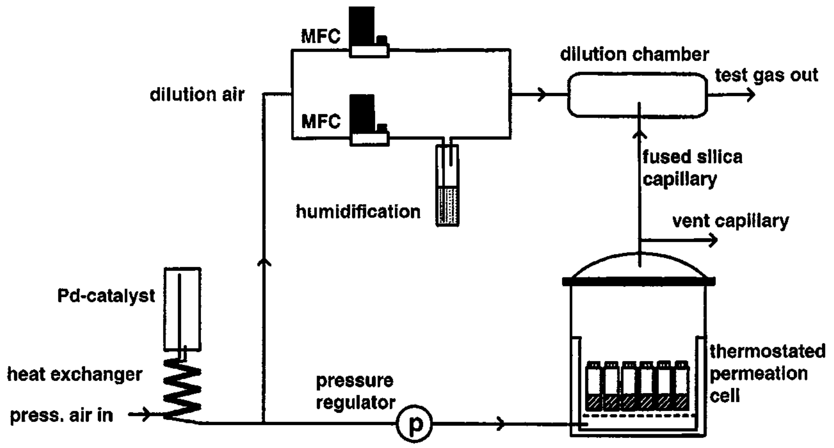

Figure 2. Permeation gas source used for laboratory tests. The permeation cell (volume ca. 1 dm^3) is made from silanized glass and is thermostated at 25 °C. Small vials filled with pure substances and sealed with PTFE membranes are placed inside. The compounds permeate through the membranes and are mixed into a flow of zero air that is prepared from pressurised air by catalytic oxidation on a Pd-catalyst at 500 °C. This mixture is split using different fused silica capillaries and the smaller fraction is further diluted in the dilution chamber (silanized glass, vol. ca. 0.5 l). The relative humidity of the dilution air is varied by passing a part of it through deionized water. The VOC-mixing ratios at the outlet are calculated from the weight loss of the vials and the flow rates through the dilution system. Mixing ratios between some pptv and some ten ppbv can be realised with this set-up.

The comparison of the FID and the TIC-response of the tested compounds showed an increasing sensitivity of the MS compared to the FID with increasing carbon number (see Figure 3). Assuming that the TIC-response of the mass spectrometer was proportional to n^2 (n being the number of the carbon and oxygen atoms in the molecule) a better description of the observed sensitivity could be obtained than with a calibration being simply proportional to the number of carbon atoms. This reduces the difference between FID-response and TIC response to typically 10–20%. It should be noted that there is no principal theoretical explanation for this behavior. The TIC response of a mass spectrometer is definitely substance specific. The observation that for the substances tested a quadratic dependence on the TIC response (per mole of substance) and the number of oxygen and carbon atoms in the molecule is found cannot be generalised. However, the laboratory tests were made for substances observed during the field study and most of the substances observed were homologues of the tested compounds. Consequently this calibration is the best choice for the quantitation of the measurements made by mass spectrometric detection. Moreover, the compounds used as internal standards during POPCORN showed the same behaviour (cf. Figure 4). Nevertheless, the absolute calibration for the measurements made with MS-detection (phase 1 and 2) is lower (on average between 10% and 20% but for compounds with structures

Table II. Results of laboratory studies using a permeation gas source. The recovery given here was calculated from the FID-signal based on a recovery for toluene-D8 of 100%. The variability of the response was calculated from measurements at four different concentrations between 2 pptv and 30 ppbv (cf. Figure 5)

	Recovery (%)	Variability for different mixing ratios (%)
Isoprene	46 ± 4	23
Methacrolein	43 ± 5	18
Hexane	86 ± 19	21
Toluene-D8	100 ± 0	22
Hexanal	74 ± 17	29
cis-Hexenol	62 ± 7	22
Trimethylcyclohexane	90 ± 8	n.m.
α-Pinene	83 ± 12	12
β-Pinene	59 ± 4	14
Δ3-Carene	72 ± 3	26
Limonene	106 ± 8	44
Eucalyptol	68 ± 5	28
γ-Terpinene	66 ± 5	20
Undecane	99 ± 15	20

n.m. = not measured.

not related to the tested compounds the uncertainty may be substantially higher) than for the measurements with flame ionisation detection.

The linearity of the measurement system was tested by varying the gas flows at the permeation gas source. Thus VOC-mixing ratios ranging from a few pptv to several ten ppbv were obtained. As an example the dependence of the specific FID-peak area (peak area/ng) is shown in Figure 5. A similar behaviour is seen for all tested compounds. They vary randomly around their mean by 10–30% (only exception is limonene) but exhibit no detectable systematic variations. The variability is included in Table II. It should be noted that this variability includes not only all variations due to the analytical procedure, but also all uncertainties, instabilities and variations of the permeation system used to generate the diluted test gases. Thus the variation given in Table II is an upper limit.

2.3. IDENTIFICATION AND QUANTIFICATION

Identification was performed by comparing retention times and mass spectra with those given by Adams (1989). Substances for which no such information was

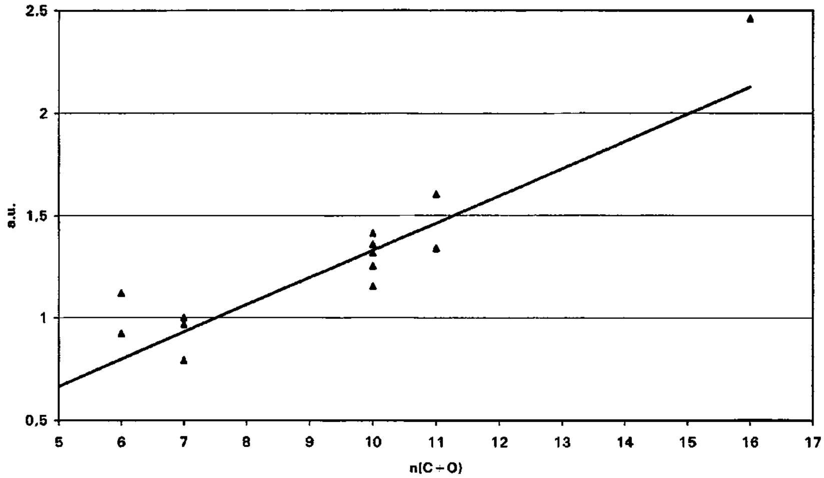

Figure 3. Results of laboratory test on the dependence of the TIC-response on the structure of the molecule. Here the ratio of TIC and FID response (a.u.) is plotted versus the number of carbon and oxygen atoms for 13 compounds ranging from C6 through C16. The coefficient of determination for the indicated linear least square fit is 0.75.

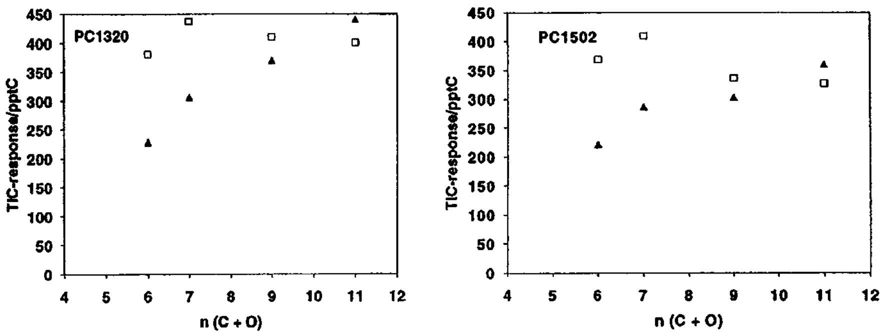

Figure 4. Dependence of the MS-response on the number of carbon atoms in the molecules in four chromatograms recorded during the field campaign (August 13 and 15). The triangles represent the TIC-peak area per pptC of the internal standards. It rises linearily with the number of carbon atoms in the molecules. If the TIC peak area is divided by this number the functional relationship is eliminated (open squares).

available were tentatively identified by comparison of their mass spectra with the 62K-NIST library (U.S. Department of Commerce, 1992). Isomers with similar mass spectra were tentatively identified using boiling point information. Quantification was performed by comparison of the peak areas with the peak areas of the four internal standards added to the inlet line. The peak areas of the substances tested in the laboratory were corrected for their experimentally determined recovery (Table II). Oxygenated compounds not tested were corrected for their not

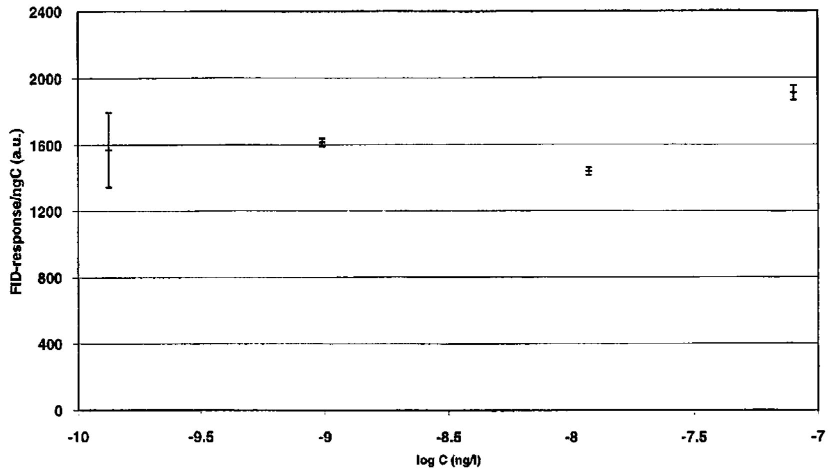

Figure 5. Variation of the FID-responsefactor of α-pinene at concentrations between 18 pptV and 20 ppbV. The wide range of different concentrations was obtained by varying the gas flows of the permeation gas source (Sigure 2).

quantitative recovery by applying a factor of 1.4, corresponding to the average recovery of oxygenated compounds in the range of 60–75%. For hydrocarbons not tested in the laboratory no corrected was applied. Except for some of the terpenes, the recovery of hydrocarbons is sufficiently close to 100% to justify this assumption (cf. Table II).

From FID-chromatograms the carbon response factors (peak area per pptC) of the internal standards were calculated by dividing the peak areas by the calculated mixing ratios and the number of carbon atoms. In all chromatograms detected with the FID these response factors differed by only 10–20% from their mean. This variation reflects not only the FID-response itself, but all uncertainties of the analytical procedure and variations due of the procedure used to spike the sample air with the internal standards.

During phase 1 (August 5–7) a calibration gas cylinder was used which proved to be leaky. The response of *n*-undecane was much lower than that of the other standard substances. Although *n*-undecane was excluded from the calculation of the mean response factors in this period the error of the response factors was typically 40–60% in these measurements, probably the consequence of the leaky cylinder. The measurements made during phase 1 therefore have a larger uncertainty than those during phase 2 and 3.

The mixing ratios of the analytes were calculated by dividing the peak areas by the number of carbon atoms in the molecule and the mean carbon response factor calculated for the chromatogram. In chromatograms recorded with MS-detection the peak areas in the total ion current (TIC) chromatograms were used for quantification. Due to the dependence of the TIC for mass-spectrometric detection (see above) from the number of carbon and oxygen atoms in the detected compound, the mean carbon response factors (per pptC) were calculated by dividing the peak areas of the internal standards by their mixing ratios and by n^2 (n being the number of carbon atoms per molecule).

In cases when the TIC-peak was not significant (i.e. smaller than three times the baseline noise) the peak area in the extracted ion chromatogram (EIC) of the most important fragment was used for quantification. From chromatograms in which the TIC peak of the considered substance was significant, the mean ratio of the TIC peak area compared to the EIC peak area was calculated and used to calculate the TIC peak areas from the EIC peak areas in other chromatograms. In cases when coelution of two major substances with different characteristic fragments occurred, the TIC peak area of both substances was calculated by addition of the peak areas of all known fragments seen in the extracted ion chromatograms.

2.4. BLANK VALUES, DETECTION LIMITS, AND UNCERTAINTIES

The blank values of the system were determined in the field by performing all steps of the analytical procedure without collecting an air sample. This was usually done once each day. From the peak areas in the blank chromatograms the corresponding mixing ratios of the analytes were calculated. The mean mixing ratio calculated from all blank chromatograms was subtracted from the measured values in the samples.

The 1 σ detection limits for the individual compounds for nearly all compounds is dominated by the variability of the blank values. The standard deviations of the blank values therefore are identical to the lower limit of detection. They are included in Table III. Since one and the same adsorption tube was used for all measurements, the blank peaks were generally small and well reproducible. The resulting detection limits are below 5 pptv for many of the compounds. Only for some aromatic compounds (namely benzene, toluene, the xylenes, benzaldehyde, and phenol, which are all known as contaminants from Tenax) the detection limits were significantly higher due to elevated and scattering blank values.

The precision of the measurements is determined by the error of the peak integration, the error of the mass response factors, the error of the recovery efficiencies, and the error of the blank values. The error of the peak integration is small compared to the other errors. The error of the mass response factors is different for each chromatogram. As discussed earlier, it was typically 40–60% for the chromatograms recorded in phase 1 and 10–20% in phases 2 and 3. In contrast, the error of the blank values is specific for each substance, but the same for the whole campaign. As a result of its definition it is identical with the detection limits given in Table III. The error of the recovery efficiencies was found in laboratory experiments to be between 5% and 17% (see above).

Depending on the measuring phase, the substance, and its concentration, the precision of the individual measurements was normally governed by one of the

Table III. Overview over the VOC measurements during the POPCORN campaign. Given are the method of identification, the lower limits of detection, maximum, mean, and median as well as the inner quartiles of the measured mixing ratios (in pptv) for the most abundant VOC

pptv	Iden-tification[a]	Limit of detection	Max. m.r.	Mean m.r.	Median m.r.	1st Quartile	3rd Quartile
n-Hexane	MS, L	24	274	52	35	b.l.	64
Sum other Hexanes	MS	10	90	31	25	15	46
n-Heptane	MS	6	86	26	22	16	32
Sum other Heptanes	MS	15	139	37	28	20	49
n-Octane	MS	17	91	b.l.[b]	b.l.	b.l.	b.l.
Sum other Octanes	MS	13	61	26	27	16	35
n-Nonane	MS, A	4	84	9	5	b.l.	9
n-Decane	MS	12	70	b.l.	b.l.	b.l.	17
n-Dodecane	MS	1	13	1	b.l.	b.l.	b.l.
Benzene	MS, L	43	345	127	58	93	157
Toluene	MS, L	39	629	150	125	73	170
Xylenes (sum)	MS	156	1445	207	b.l.	b.l.	292
Ethylbenzene	MS	17	158	34	25	b.l.	41
Styrene	MS	11	181	14	b.l.	b.l.	13
Ethinylbenzene	MS	4	33	5	4	b.l.	7
Propylbenz.-isom. (sum)	MS	63	332	102	96	b.l.	147
Butylbenz.-isom. (sum)	MS	15	73	26	22	b.l.	42
Naphtalene	MS	1	26	6	5	3	7
n-Pentanal	MS	3	45	11	9	2	15
n-Hexanal	MS, L	1	185	23	15	11	26
n-Heptanal	MS	1	27	2	b.l.	b.l.	b.l.
n-Oktanal	MS	1	38	6	b.l.	b.l.	9
n-Nonanal	MS, L	1	110	17	14	9	19
n-Decanal	MS	1	52	4	b.l.	b.l.	5
n-Undecanal	MS	2	50	9	8	b.l.	12
n-Dodecanal	MS	1	11	1	b.l.	b.l.	2
n-Tridecanal	MS	1	16	2	b.l.	b.l.	3
Methylvinylketone	MS, L	1	109	17	11	4	21
2-Butanone	MS	3	153	47	39	27	56
2-Pentanone	MS	1	119	18	12	6	22
2-Hexanone	MS	2	19	b.l.	b.l.	b.l.	3
2-Ethyl-1-hexanol	MS, L	4	419	36	8	b.l.	18
Ethylacetate	MS, A	1	104	23	14	7	34
Tricyclene	MS, L, A	1	9	2	2	b.l.	3
α-Thujene	MS, A	1	7	1	b.l.	b.l.	1
α-Pinene	MS, L, A	1	433	33	22	13	35
Camphene	MS, L, A	1	41	16	14	10	24
Sabinene	MS, L, A	1	b.l.	b.l.	b.l.	b.l.	b.l.
β-Pinene	MS, L, A	2	30	10	9	6	14
β-Myrcene	MS, L, A	1	40	1	b.l.	b.l.	b.l.
Δ3-Carene	MS, L, A	1	215	19	15	8	22
D-Limonene	MS, L, A	1	19	1	b.l.	b.l.	b.l.
β-Phellandrene	MS, L, A	1	8	1	b.l.	b.l.	2
Eucallyptol	MS, L, A	1	22	2	b.l.	b.l.	4
γ-Terpinene	MS, L, A	2	9	b.l.	b.l.	b.l.	b.l.

[a] Methods of identification: MS = comparison of mass spectrum with NIST-62K-library; L = mass spectrum and retention time known from laboratory experiments; A = comparison of mass spectrum and retention index with values given by Adams (1989).

[b] b.l.: below limit of detection.

listed errors. For most measurements during phase 1 the error of the response factors was the most important error. Only for measurements of aromatic compounds at low mixing ratios did the error of the blank value exceed this error. During phases 2 and 3 the error of the response factors was much smaller. Therefore the precision was usually limited by the error of the blank values.

The accuracy of the measurements is determined by the uncertainty of the internal calibration, the uncertainty of the function used to describe the substance specific response of the detection system and systematic errors of the recovery. Since the gas cylinders used for calibration contained gravimetrically prepared standards (see above) and the flow rates of the internal standard and the sample gas proved to be constant within 5% the error of its concentration in the inlet line can be estimated to be ca. 10%. Unfortunately the gas cylinder used during phase 1 proved to be leaky. As a result, it apparently did not contain the four standard substances in equal amounts and evidently not in correct amounts. Since the gas cylinder ran empty before it could be compared to another standard, it was not possible to determine its true composition. It is therefore assumed that the accuracy of the measurements in phase 1 is in the order of magnitude of the error of the response factors discussed above, that is ca. 50%. During phases 2 and 3 the accuracy of the internal calibration is estimated to be 10–30%.

For FID measurements (phase 3) the use of carbon response factors results in only small errors, for molecules with six or more carbon atoms the effect of functional groups is very small (cf. Dietz, 1967; Scanlon and Willis, 1985). The use of the carbon response factor determined from the internal standards for quantification of other VOC therefore only causes marginal systematic errors of a few percent or less. For phases 1 and 2 generally the TIC of the mass spectrometric detection is used to quantify the measurements. This has little consequences for the accuracy of the measurements made during phase 1; in this phase the errors resulting from the leaky cylinder dominate. However, for phase 2 the systematic uncertainty of the empirical function used to estimate the TIC response for individual compounds (see above) introduces an additional systematic error, on average 10%–20%.

For compounds not tested in the laboratory the estimated recovery efficiency can have a systematic error. However, for most hydrocarbons, except the terpenes, the test results indicate that the assumption of a quantitative recovery is justified within the reproducibility of the measurements. Moreover, the use of hydrocarbons with different structure and molecular weight as internal standards inherently includes the recovery correction for structurally similar compounds.

For terpenes the situation is more complicated. The recovery depends on the individual compound and from the measured recoveries it seems possible that for some terpenes mixing ratios calculated on the basis of 100% recovery may occasionally be up to 30–40% to low. However, on average the experimentally determined monoterpe recovery is ca. 80% and therefore for most terpenes the resulting systematic error should be below the reproducibility of the measurements. Moreover, most of the terpenes found in significant mixing ratios during POPCORN have been tested in the laboratory.

The recovery of the tested oxygenated compound is very similar and the variability observed for mixing ratios ranging from 2 pptv to 30 ppbv is below 30%. Therefore we estimate that the systematic error for oxygenated compounds resulting from the assumption of a general applicable recovery correction does not exceed 30%.

The accuracy of the measurements was also checked by comparing the results with parallel hydrocarbon measurements with an in-situ GC–FID system (cf. Koppmann *et al.*, this issue). This instrument used an independent external calibration. The compounds that were measured by both instruments include *n*-hexane, *n*-heptane, benzene and toluene. However, due to different sampling and measuring intervals there were only a few samples taken simultaneously by the two instruments. Since all these samples were collected when the mixing ratios of the compounds were comparatively low, the error of the measurements was relatively high. For *n*-hexane and *n*-heptane the measurements of both instruments agreed within the errors which were typically 25 pptv for hexane and 10 pptv for heptane. The mean ratio hexane(MS)/hexane(FID) was 0.8 ± 0.15 and the mean ratio heptane(MS)/heptane(FID) was 1.2 ± 0.5.

For toluene the mixing ratios measured with the on-line GC–MS were always higher than those measured with the GC–FID-system. The difference was 47 ± 30 pptv. Still, this difference is comparable to the standard deviation of the blank value of toluene (39 pptv), which determines the error of the measurement in this concentration range. For benzene the picture is more complicated. Measurements on August 6 and 7 indicate an underestimate of benzene by the MS-system by 36 ± 45 pptv, whereas parallel measurements on August 13–16 imply an overestimation by 115 ± 45 pptv. The calculated error of the benzene measurements with the GC–MS is 43 pptv. These findings underline that the precision of the measurements of aromatics at low mixing ratios is limited by apparently random variations of the blank values. In agreement with general analytical experience for reliance quantitation, a 3 σ level is more adequate than the 1 σ detection limits given in Table III. For most of the hydrocarbons and the oxygenated VOC the 1 σ detection limit is a few pptv or even less. Thus the levels for reliable quantitative evaluation are well below 10 pptv. For *n*-alkanes the detection limits are somewhat higher, but the agreement between the two techniques in the measurements of *n*-hexane and *n*-heptane shows that the different calibration and measuring techniques give comparable results even at low ambient mixing ratios. For benzene and several alkylbenzenes the situation is less favourable. The four most abundant aromatic compounds have detection limits of 40 pptv or more. Thus the uncertainties of measurements even for mixing ratios of some 100 pptv will be substantial.

3. Results and Discussion

A total of 65 VOC measurements were made during the POPCORN campaign. The three different measuring phases cover different meteorological situations (for details of the meteorological situation during the POPCORN campaign see Plass-Dülmer *et al.*, this issue, and Brauers *et al.*, this issue).

The measurements of phase 1 (August 5–7) reflect the warmer part of the campaign with daytime temperatures up to 35 °C and low wind velocities at night. This period is covered by 13 samples. Phase 2 (August 12–15), which was characterised by a low pressure system over the eastern Baltic Sea and strong westerly winds, is covered with 21 measurements. During phase 3 (August 16–21), which was characterised by lower wind velocities and the formation of strong night-time inversion layers, 31 measurements were made.

250 different compounds were detected and identified by their retention times and mass spectra. Among these are alkanes, alkenes, alcohols, aldehydes, ketones, esters, halocarbons, arenes, and monoterpenes. The isomers of propylbenzene, butylbenzene, and of some higher alkanes could not be assigned unambiguously. Two substances with characteristic fragments of $m/z = 79$ were tentatively identified as methylchlorosulfone and dimethylsulfone. The most abundant compounds are listed in Table III. Also given ar the 1 σ detection limits, the mean, median and maximum mixing ratios and the inner quartiles of the measurements (25% of the measurements are below the first quartile, 25% are above the third quartile). Together the compounds listed in Table III accounted for about 90% of the total amount of detected carbon.

3.1. VOC-PATTERNS

3.1.1. *Alkanes and Aromatic Compounds*

The median mixing ratios of typical anthropogenic hydrocarbons such as *n*-hexane, benzene and toluene were 30, 127, and 125 respectively. These mixing are on the lower end of reported measurements from continental sites (cf. Warneck (1988), and Atlas *et al.* (1995), and references therein). The abundance of *n*-alkanes generally decreased with increasing carbon number; *n*-hexane was the most abundant alkane in most samples. Among the aromatic hydrocarbons, benzene and toluene were almost always the most abundant compounds, followed by the xylenes and ethylbenzene. Figures 6 and 7 show the time series of selected alkanes and aromatic hydrocarbons, respectively. The comparison of the two figures clearly shows that the mixing ratios of these substances exhibited a very similar relative variation during all measuring phases. This behaviour was typical for all predominantly man-made VOC. In the following only two representatives, *n*-hexane and toluene, will be discussed.

In phase 1 the large day/night variations are striking. The mixing ratios of all compounds were usually higher at night, as decreasing wind speed and the for-

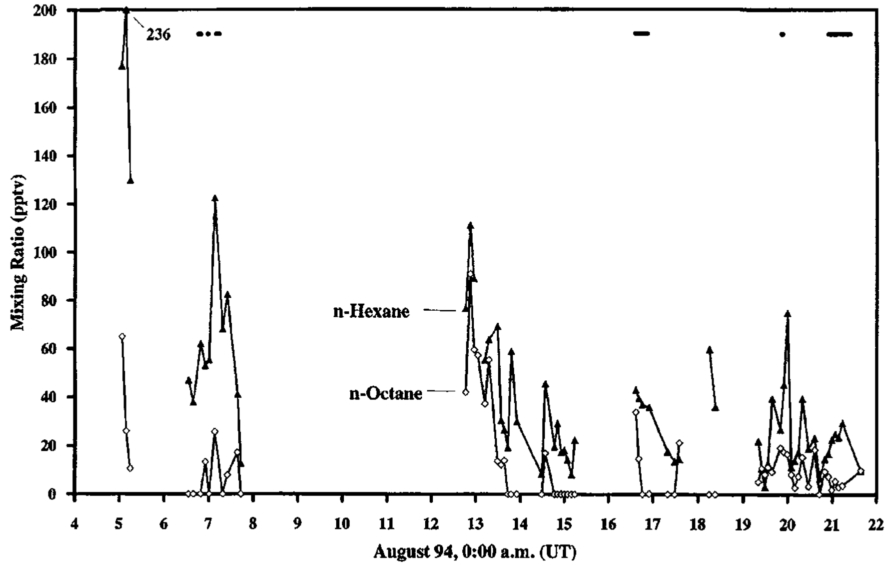

Figure 6. Time series of VOC mixing ratios during POPCORN. The solid bars in the upper part of the diagrams indicate periods of wind velocities < 2 m/s. Alkanes (*n*-hexane and *n*-octane).

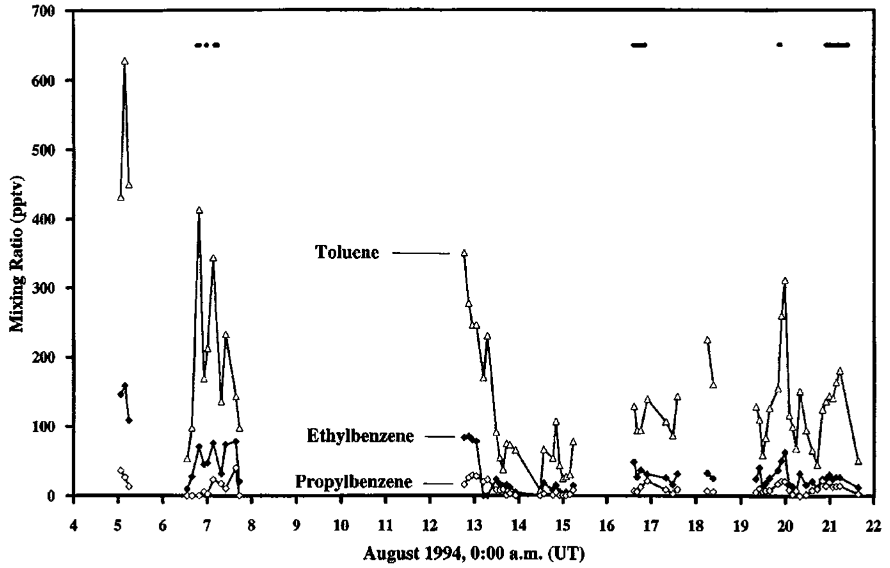

Figure 7. Time series of VOC mixing ratios during POPCORN. The solid bars in the upper part of the diagrams indicate periods of wind velocities < 2 m/s. Aromatics (toluene, ethylbenzene, and propylbenzene).

mation of an inversion layer resulted in a lower dilution of both anthropogenic and biogenic emissions with background air. The daytime mixing ratios of toluene were between 50 and 230 pptv and those of *n*-hexane varied between 20 and 80 pptv. In contrast, the night-time mixing ratios of toluene were between 170 pptv and 630 pptv, those of *n*-hexane between 55 and 235 pptv.

The measurements of phase 2 started when a cold front approached the site from the west. Before this cold front passed the site around 12 UT on August 13, elevated mixing ratios of all man-made hydrocarbons were measured. Toluene mixing ratios ranged between 250 and 350 pptv and *n*-hexane between 75 and 165 pptv. After the frontal passage westerly winds with high velocities were encountered and the mixing ratios of all anthropogenic compounds were low. Most values were close to or below the detection limits (i.e. 20 pptv for *n*-hexane, 40 pptv for toluene) until the end of this measuring series on August 15.

Phase 3 starts on August 16 after the wind had slowed down and turned to southerly directions. It includes two days under weak anticyclonic influence (August 16 and 17). On these two days typical mixing ratios of toluene were between 90 and 140 pptv; *n*-hexane mixing ratios were only ca. 30 pptv. After a cold front with rain crossed the site on August 18 the air masses changed again, but the mixing ratios changed only slightly. They were again ca. 100 pptv for toluene and ca. 25 pptv for *n*-hexane. In the night of August 19 and in the early morning of August 21 again low wind speeds were observed. The mixing ratios of toluene climbed to 310 pptv or 180 respectively in these nights; *n*-hexane peaked at 75 pptv and 30 pptv.

3.1.2. *Monoterpenes*

With median mixing ratios of 22 and 15 pptv respectively, α-pinene and Δ3-carene were the most abundant monoterpenes. Mixing ratios above 100 pptv were only found in two samples. The measured monoterpene mixing ratios are lower than most measurements reported from rural locations in summer so far (cf. Warneck, 1988, and references therein; Yokoushi and Ambe, 1988; Hoffmann *et al.*, 1993; Simon *et al.*, 1994; Goldan *et al.*, 1995).

Figure 8 shows the time series of three monoterpenes. In phase 1 the relatively high mixing ratios of α-pinene and Δ3-carene in the night of August 6 are striking. During the entire day the wind was from the north-west where an extended pine-forest is located (cf. Plass-Dülmer *et al.*, this issue). As indicated in Figure 8, the high night-time mixing ratios of α-pinene and Δ3-carene coincide with low wind velocities. Thus these elevated mixing ratios can be explained by the lower dilution of pine-emissions with ambient air in these samples. In contrast to this, the mixing ratios were below 30 pptv in the afternoon of August 6, when the wind velocity was much higher. During phase 3 similar patterns can be seen on August 16 and 17 and August 20 and 21, when the mixing ratios increased as soon as the wind calmed down. In contrast, during phase 2 no wind velocities below 2 m/s and no significant day/night differences in the terpene mixing ratios were observed.

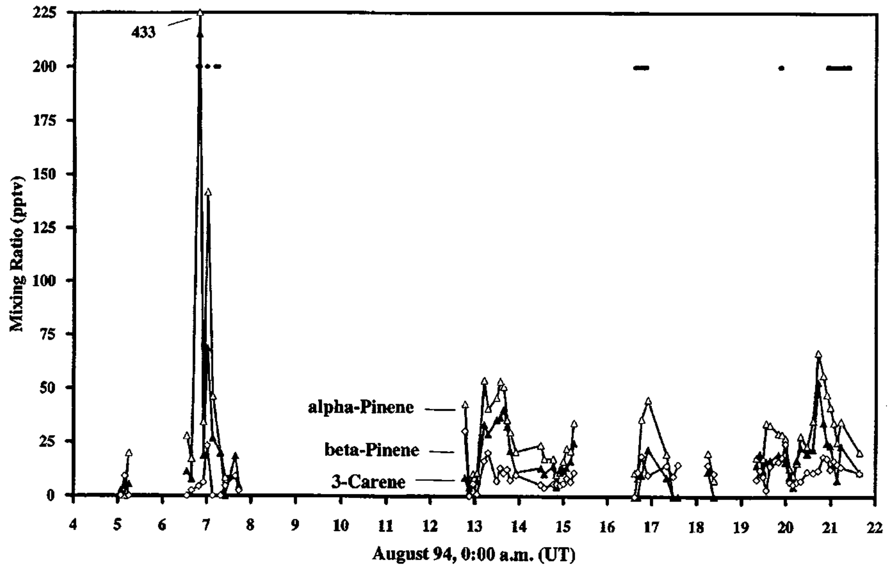

Figure 8. Time series of VOC mixing ratios during POPCORN. The solid bars in the upper part of the diagrams indicate periods of wind velocities < 2 m/s. Monoterpenes (α-pinene, β-pinene, and $\Delta 3$-carene).

3.1.3. *Aldehydes and Ketones*

With median mixing ratios of 9, 16, 14 and 8 pptv respectively, *n*-pentanal, *n*-hexanal, *n*-nonanal and *n*-undecanal were the most abundant measured aldehydes. *n*-Butanal coeluted with *n*-pentane and therefore could not be evaluated quantitatively.

Figure 9 shows the time series of *n*-pentanal and *n*-hexanal. Some of the features discussed before can also be seen here, especially the elevated night-time mixing ratios in phases 1 and 3. In contrast to the alkanes, the abundance of individual aldehydes does not strictly decrease with increasing carbon number: *n*-hexanal was usually more abundant than *n*-pentanal and both *n*-nonanal and *n*-undecanal generally were more abundant than *n*-heptanal, *n*-octanal, and *n*-decanal.

In phase 1 the daytime mixing ratios of *n*-hexanal were between 10 and 40 pptv with night-time values of up to 191 pptv on August 5 and up to 76 pptv in the night of August 6. The differences between daytime and night-time mixing ratios were less significant during phase 2 and 3. In these measuring phases *n*-hexanal and *n*-nonanal mixing ratios were typically between 15 and 25 pptv. *n*-Pentanal and *n*-undecanal mixing ratios were slightly lower, and *n*-heptanal, *n*-octanal, and *n*-decanal were often below their detection limits of ca. 1 pptv.

The measured ketones show basically the same time dependence as alkanes and aromatics. Figure 10 shows the time series of butanone and methylvinylke-

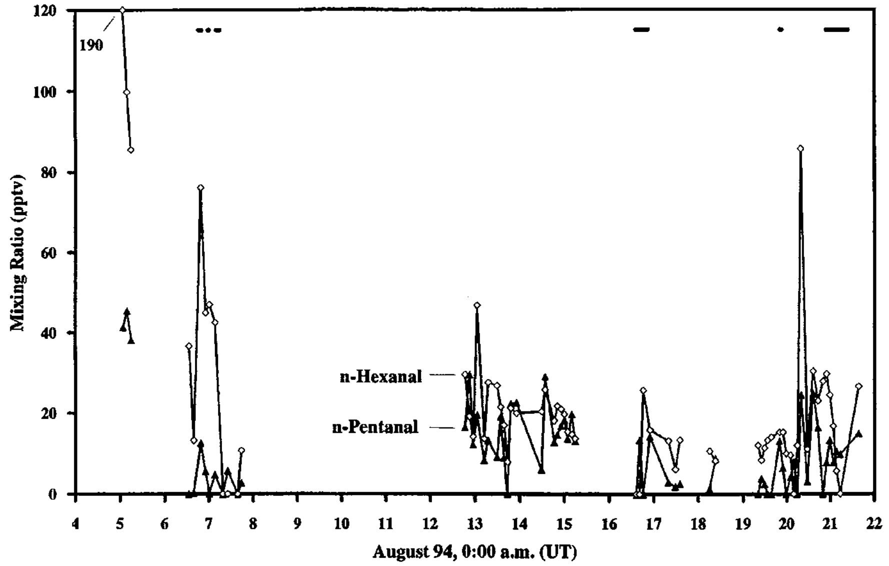

Figure 9. Time series of VOC mixing ratios during POPCORN. The solid bars in the upper part of the diagrams indicate periods of wind velocities < 2 m/s. Aldehydes (*n*-pentanal, *n*-hexanal).

tone. Normally butanone was the most abundant detected ketone followed by 2-pentanone and methylvinylketone. The mixing ratios of butanone were typically between 30 and 60 pptv, those of 2-pentanone and methylvinylketone between 5 and 20 pptv. The mixing ratios of 2-hexanone and higher ketones were often below their detection limits. They never exceeded 20 pptv.

3.1.4. *Other Compound Classes*

The mixing ratios of hexene and higher alkenes were always below the detection limits of ca. 2 pptv. Isooctanol (2-ethyl-1-hexanol) was the most abundant alcohol measured during the POPCORN-campaign. Its mixing ratios were typically between 4 and 18 pptv. However, mixing ratios of ca. 420 pptv were measured at the beginning of phase 2. No other alcohols (including Z-3-hexen-1-ol with a detection limit of 4 pptv) were detected. The most abundant ester was ethylacetate with mixing ratios between 5 and 100 pptv. Two sulfones, tentatively identified as methylchlorosulfone and dimethylsulfone, were present in many samples, but since no reference substances were available they were not evaluated quantitatively.

Despite detection limits as low as 1 pptv no sesquiterpenes were detected.

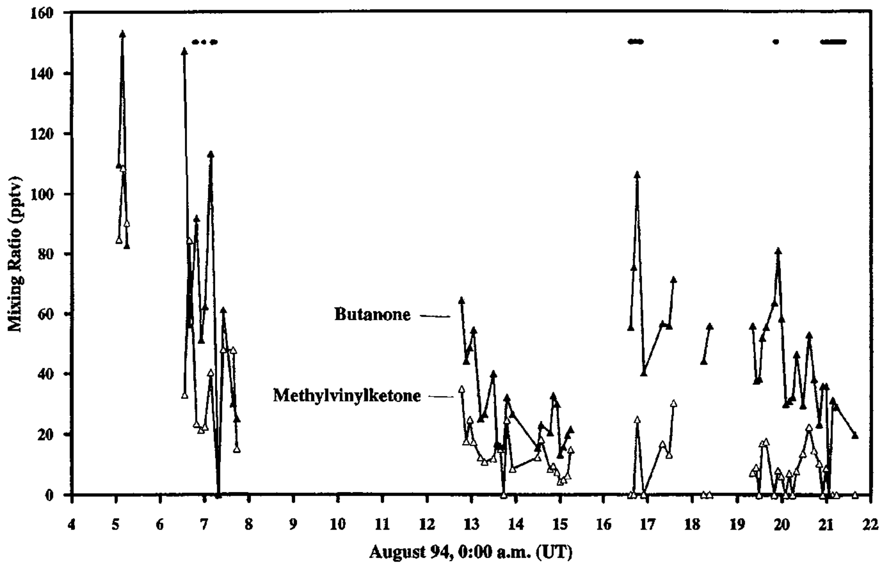

Figure 10. Time series of VOC mixing ratios during POPCORN. The solid bars in the upper part of the diagrams indicate periods of wind velocities < 2 m/s. Ketones (butanaone and methylvinylketone).

3.2. CORRELATIONS

In order to elucidate the sources and possible other factors affecting the atmospheric mixing ratios of the different substances, the correlations of several measured compounds with toluene and with α-pinene were examined. The correlation coefficients were calculted for the complete data set as well for three sub-sets representing different episodes of the campaign. If the atmospheric concentration of two compounds is determined by the same factors, significant correlations should be observed regardless of the meteorological situation. In Table IV the coefficients of determination (R^2) are given. These coefficients indicate to what extent the variability of the measured mixing ratios of both compounds can be explained by the same factors.

However, significant correlations do not necessarily mean that these substances originate from a common source. For example, methylvinylketone exhibits a significant correlation with toluene during the first and second episodes, although the major source of methylvinylketone is the photo-oxidation of isoprene (Graedel *et al*, 1993) whereas the major toluene source is car emissions. Instead, correlations in phase 1 and phase 3 can arise from similar dilution effects caused by the formation and the break-up of nightly inversion layers and by the impact of changing wind velocities.

Table IV. Coefficients of determination (R^2) of the correlation of some VOC mixing ratios with those of toluene and α-pinene, calculated for all measurements and for different episodes. Coefficients indicating significant correlations are printed in bold type. The significance criteria (5% error probability) were taken from Sachs (1992)

Correlation with toluene mixing ratios

R^2	*n*-Hexane	Butanone	Isooctanol	*n*-Hexanal	*n*-Nonanal	α-Pinene	Methylvinyl-ketone
All data ($n = 65$)	0.71	0.39	0.48	0.36	0.14	0.05	0.39
Aug. 5–7 ($n = 13$)	0.79	0.33	0.56	0.52	0.16	0.04	0.39
Aug. 12–15 ($n = 21$)	0.64	0.73	0.67	0.16	0.63	0.00	0.41
Aug. 18–21 ($n = 24$)	0.77	0.18	0.00	0.01	0.01	0.01	0.06

Correlation with α-pinene mixing ratios

R^2	3-Carene	Butanone	Isooctanol	*n*-Hexanal	*n*-Nonanal	β-Pinene	Methylvinyl-ketone
All data ($n = 65$)	0.96	0.02	0.02	0.05	0.00	0.01	0.00
Aug. 5–7 ($n = 13$)	0.99	0.01	0.06	0.01	0.02	0.06	0.10
Aug. 12–15 ($n = 21$)	0.78	0.04	0.08	0.02	0.02	0.49	0.02
Aug. 18–21 ($n = 24$)	0.80	0.01	0.45	0.10	0.19	0.16	0.16

As expected, *n*-hexane is significantly correlated with toluene throughout the whole campaign and in the three individual episodes. From all data a linear least square fit with a correlation coefficient (R) of 0.85 has been calculated. The calculated slope if 0.32 ± 0.02, the y-axis intercept is practically zero (4 ± 5 pptv). The R^2 value of 0.73 indicates that 73% of the variability of the hexane mixing ratios may be explained by the factors which also determine the variability of the toluene mixing ratios. This reflects the well-known fact that toluene and *n*-hexane have the same major sources (mainly emissions from cars) and similar atmospheric life-times.

Butanone and isooctanol showed significant correlations with toluene if all data are considered. However, the factors determining the mixing ratios of toluene account for only 32% and 48%, respectively, of the variability of butanone and isooctanol. Moreover, the existence and the extent of a correlation with toluene obviously depends on the episode, i.e. on the meteorological situation. This suggests that compared to toluene additional factors determine the atmospheric mixing ratios of butanone and isooctanol. Nevertheless, the correlation of both substances with α-pinene is usually much poorer, indicating that there are fewer common factors with this compound. Corresponding results were obtained for *n*-hexanal and *n*-nonanal.

As expected, α-pinene shows no significant correlation with toluene in any of the phases. However, throughout the whole campaign the strong positive correlation between the two most abundant monoterpenes (α-pinene and Δ3-carene) is striking. In Figure 11 the measured mixing ratios of Δ3-carene are plotted against the measured α-pinene mixing ratios. The calculated linear least square fit is $[\Delta 3\text{-carene}] = 0.50\ (\pm 0.01)\ [\alpha\text{-pinene}] + 2.8\ (\pm 0.9)$ pptv with a correlation coefficient (R^2) of 0.98. It is obvious that this correlation is dominated by the two outlying measurements of phase 1. However, even if these measurements are not considered the correlation coefficient is still 0.88 and the calculated slope only slightly changes to 0.63 ± 0.05.

To check for factors controlling the ratio of the α-pinene and Δ3-carene concentrations it was tested for correlations with the wind velocity and with the time of the day. During daytime the major sink for both substances is the reaction with the hydroxyl radical. Since Δ3-carene reacts by a factor of 1.5 faster with OH than α-pinene (Atkinson *et al.*, 1990), high OH concentrations as found around noon should reduce the Δ3-carene to α-pinene ratio. During night-time the reaction with the nitrate radical (NO_3) was the major loss process for both compounds. Again Δ3-carene reacts by a factor of 1.5 faster than α-pinene (Wayne *et al.*, 1991). However, the Δ3-carene to α-pinene ratios found at night and between 10:00 and 13:00 UT do not differ significantly from those measured during the morning and the afternoon hours. Lower wind velocities resulting in longer reaction times during the transport to the measuring site are supposed to lower this ratio in both cases. However, no significant correlations with the wind velocity were found, indicating

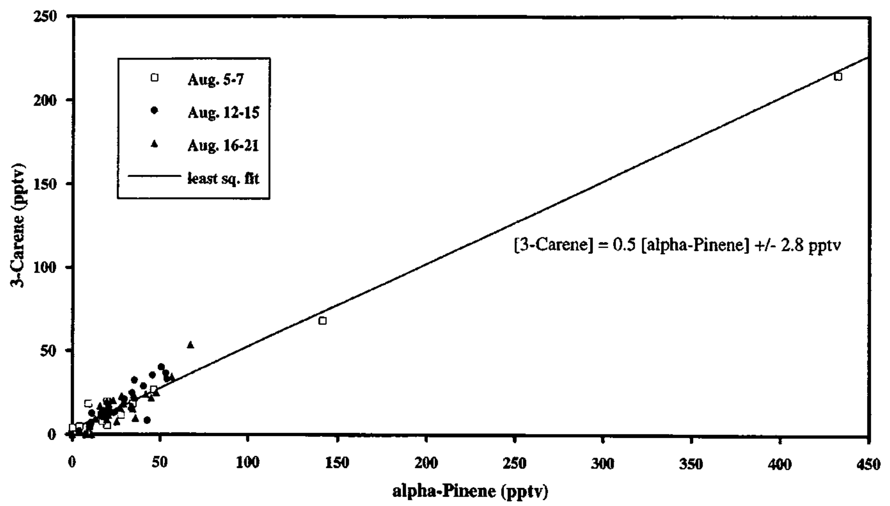

Figure 11. Plot of Δ3-caren mixing ratios versus α-pinene mixing ratios. For data obtained during different measuring series different symbols are used. Included in this figure is also the linear least square fit obtianed from all data ($R = 0.98$).

that the transport times were short compared to typical reaction times or that other factors (such as changing emission patterns) controlled this ratio.

3.3. COMPARISON OF THE AMBIENT MEASUREMENTS WITH EMISSION STUDIES

During the POPCORN campaign VOC-emission studies with mobile branch enclosures were performed on the most abundant crop and tree species around the measuring site by two groups (Rudolph *et al.*, 1995; Parusel, 1996). Both studies found that pine-trees were by far the most important terpene emitters in the vicinity of the POPCORN measuring site. α-Pinene and Δ3-carene were the predominantly emitted compounds. In fact, the Δ3-carene to α-pinene ratio of 0.50 in the ambient measurements reflects very well the ratio of 0.47 ± 0.11 which was found in the emission studies during the campaign. This, as well as the marginal intercept of the linear fit (see above), indicates that no other major source for these two compounds existed around the measuring site. The emission studies showed that the emission rate of β-pinene from pine-trees was much lower than for α-pinene and Δ3-carene. However, beech, which also belongs to the vegetation in the vicinity of the POPCORN field site, was found to emit substantial amounts of β-pinene along with sabinene and limonene. These findings explain the relatively high abundance of β-pinene in ambient air as well as its poor correlation with α-pinene.

In contrast to the literature (Lamb *et al.*, 1993) no significant monoterpene emissions from maize were measured in the emission studies performed during the

POPCORN-campaign (Rudolph *et al.*, 1995). This is supported by our observations of relatively low and scattering ambient monoterpene mixing ratios.

n-Hexanal, *n*-heptanal and *n*-nonanal were identified as emissions from maize (Rudolph *et al.*, 1995). The emission rates were 0.09 ± 0.22 μg/g(dry weight)h for *n*-hexanal, 0.09 ± 0.47 μg/g(dry weight)h for *n*-heptanal and 0.43 ± 0.31 μg/g(dry weight)h for *n*-nonanal. *n*-Nonanal emissions were also found in night-time experiments. Although the reported emission rates have large uncertainties they indicate that higher *n*-aldehydes observed in the atmosphere during the POPCORN-campaign were at least partly due to local emissions from maize.

3.4. RELATIVE IMPORTANCE OF THE DIFFERENT COMPOUND CLASSES FOR ATMOSPHERIC CHEMISTRY DURING POPCORN

In addition to the C_6–C_{15} VOC-measurements presented in this paper, also light non-methane hydrocarbons (NMHC) and CO (Koppmann *et al.*, this issue) as well as light aldehydes (Benning and Wahner, this issue) were measured in the atmosphere during the POPCORN campaign. Furthermore the OH-radical concentrations were measured by two different methods (Brandenburger *et al.*, this issue; Holland *et al.*, this issue; Hofzumahaus *et al.*, this issue). This allows to compare the atmospheric abundance of the different compound groups as well as their atmospheric turnover.

Table V and Figure 12 display the contribution of the most abundant measured VOC to the atmospheric carbon content. The light alkanes (C_2–C_5) and the light aldehydes (formaldehyde and acetaldehyde only) contributed most to the atmospheric content of non-methane VOC during the POPCORN campaign, followed by the C_6–C_8 aromatics whereas isoprene, higher aldehydes and monoterpenes contributed only marginally.

However, the importance of the different compound classes is mainly determined by their potential to build photo-oxidants like ozone, which is a by-product of their atmospheric oxidation. All VOC react more or less rapidly with OH radicals; unsaturated compounds can also exhibit a substantial turnover with ozone and with NO_3 radicals. The products of the initial oxidation again react with OH and often have much shorter life-times than their precursors. Therefore the atmospheric VOC-turnover is mainly determined by the velocity of their initial reactions with the hydroxyl radical, with ozone and with NO_3 radicals. Formaldehyde and acetaldehyde represent less reactive intermediates in the oxidation chain of higher molecular VOC. Under conditions where the formation of ozone is not limited by the abundance of nitrogen oxides at least two ozone molecules per carbon atom can be formed (Warneck, 1988) per carbon atom in the precursor. Since due to soil emissions high NO_x/VOC-ratios were encountered during POPCORN (cf. Rohrer *et al.*, this issue) the potential for ozone formation can roughly be estimated from the VOC turnover (in ppbC/h) by applying a factor of 2.

Table V. Atmospheric carbon content and turnover of various VOC calculated from the medians of the day-time measurements during POPCORN. CO and C_2–C_5 NMHC data were taken from Koppmann *et al.* (this issue), formaldehyde and acetaldehyde data from Benning and Wahner (this issue), the median OH concentration of $4 * 10^6$ molec/cm^3 from Brandenburger *et al.* (this issue), the median day-time ozone mixing ratio of 40 ppbv was taken from Brauers *et al.* (this issue). Available reaction rate constants were taken from the NIST kinetic database (Mallard *et al.*, 1994), those of C_6–C_{11} aldehydes were estimated as suggested by Kwok and Atkinson (1995)

Substance	Atm. carbon content (ppbC)	% (1)	Turnover (ppbC/h)	% (2)
CO	**113**		**0.21**	**11**
Methane	**1700**		**0.17**	**9**
Formaldehyde	1.6	13	0.22	
Acetaldehyde	2.1	17	0.50	
C_1–C_2 Aldehydes	3.7	29	0.72	
Ethane	1.4	11	0.01	0
Propane	0.8	7	0.01	1
i-Butane	0.3	2	0.01	1
n-Butane	0.5	4	0.02	1
Pentane	0.4	3	0.02	1
Sum C_2–C_5 Alkanes	3.3	26	0.07	4
Ethene	0.7	5	0.03	1
Ethyne	0.6	5	0.01	0
Propene	0.1	1	0.06	3
1-Butene	0.2	1	0.08	5
Sum C_2–C_4 Alkenes	1.6	13	0.18	10
Isoprene	0.1	1	0.21	11
Hexanes	0.4	3	0.03	2
Heptanes	0.4	3	0.04	2
Oktanes	0.3	2	0.03	2
n-Nonane	0.0	0	0.01	0
n-Decane	0.1	0	0.01	0
Sum C_6–C_{10} Alkanes	1.1	9	0.12	6
Benzene	0.8	6	0.01	1
Toluene	0.7	5	0.06	3
p-Xylene	0.1	1	0.03	2
m-Xylene	0.1	1	0.03	2
o-Xylene	0.2	2	0.05	3
Ethylbenzene	0.2	1	0.02	1

Table V. (Continued)

Substance	Atm. carbon content (ppbC)	% (1)	Turnover (ppbC/h)	% (2)
Sum C_6–C_8 Aromatics	2.0	16	0.20	11
Pentanal	0.0	0	0.01	0
Hexanal	0.1	1	0.03	2
Nonanal	0.1	1	0.05	3
Undekanal	0.1	1	0.03	2
Sum C_5–C_{11} Aldehydes	0.3	2	0.12	7
α-Pinene	0.2	2	0.23	12
β-Pinene	0.1	1	0.14	7
Δ3-Carene	0.1	1	0.19	11
Sum Monoterpenes	0.5	4	0.56	30
Sum all mes. VOC	12.7 (1)	100	1.8 (2)	100

(1) CO and methane not included.
(2) Formaldehyde and acetaldehyde not included.

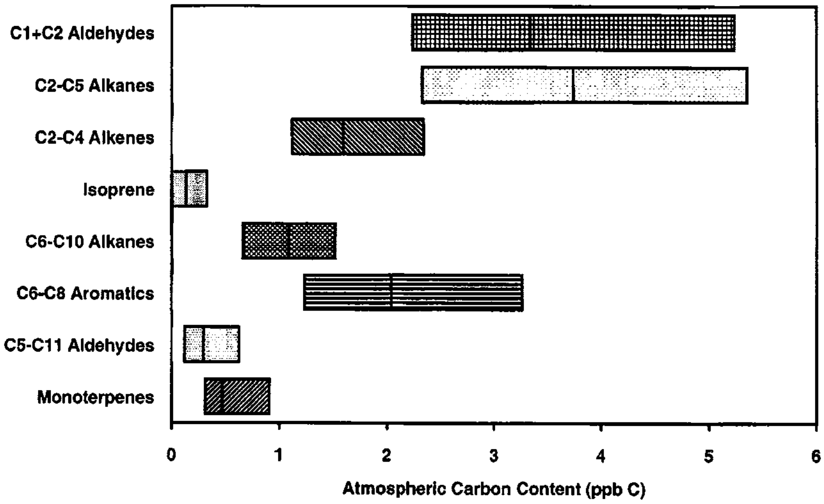

Figure 12. Atmospheric carbon content during the POPCORN campaign. The bars represent the inner quartiles of the day-time measurements of the most abundant compound classes.

In a simple first order approach the daytime VOC turnover can be calculated from the measured VOC, ozone, and OH concentrations and the respective reaction rate constants. For the most abundant VOC the turnover was calculated using the median of the measured OH concentrations of $4 * 10^6$ molecules/cm^3 (Brandenburger *et al.*, this issue). For alkenes, isoprene and monoterpenes also the reaction with ozone was considered. The median day-time ozone mixing ratio of

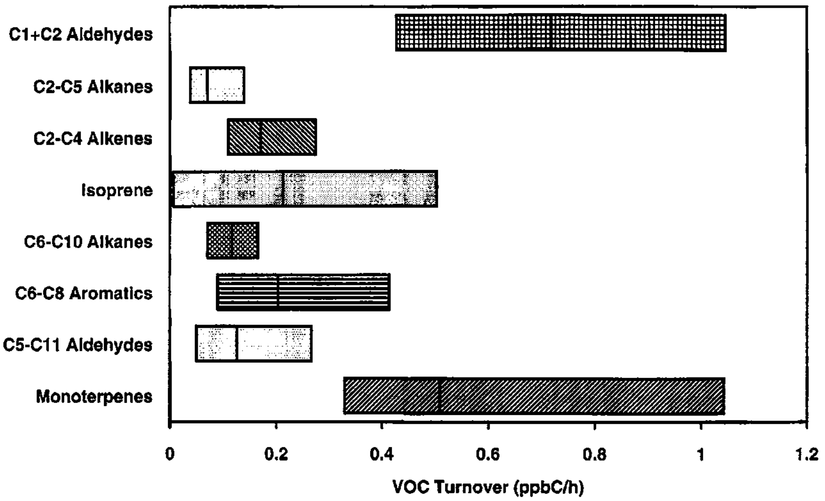

Figure 13. Turnover of the most abundant VOC during POPCORN calculated from the median daytime concentrations ([OH]) = 4∗10^6 molec./cm^3, [O$_3$] = 40 ppbv). The bars represent the inner quartiles of the VOC measurements.

40 ppbv was taken from Brauers *et al.* (this issue). Known rate constants for the reaction with OH were taken from the NIST chemical kinetics database (Mallard *et al.*, 1994), the rate constants of the C_6–C_{11} *n*-aldehydes were estimated using the approach suggested by Kwok and Atkinson (1995).

The day-time turnover of the individual compounds is included in Table V, the summarised turnover of the different compound classes is displayed in Figure 13. The compound class with the largest atmospheric turnover besides the light aldehydes (formaldehyde and acetaldehyde) were the monoterpenes, followed by isoprene, C_6–C_8 aromatics, light alkenes, and higher aldehydes. Alkanes apparently played a minor role during the POPCORN campaign. The contribution from the reaction of unsaturated compounds with ozone to the VOC-turnover is about 0.1 ppbC/h, corresponding to ca. 15% of the turnover of these compounds with the OH-radical.

The turnover of CO, methane, C_2–C_{15} NMHC and C_5–C_{11} aldehydes adds to about 1.8 ppbC/h. The NO_x levels during POPCORN were primarily due to substantial soil emissions, surprisingly high for a remote rural area. Noontime average values are in the range of 1.8 ppbv, night-time averages exceed 3 ppbv (Rohrer *et al.*, this issue). Considering the low VOC levels, this results in NO_x/VOC ratios untypically high for rural areas. This strongly suggests that ozone formation during POPCORN is VOC limited. With the ozone production factors given by Warneck (1988) for light hydrocarbon and the assumption that each carbon atom in the heavier VOCs contributes 2 molecules of potential ozone, an ozone production of ca. 3.5 ppb/h can be estimated from this turnover. However, ca. 30% of this production would result from the turnover of monoterpenes.

Losses of partially oxidised terpenes to the aerosol phase might lower the ozone yield. For the relatively clean air conditions encountered during POPCORN these losses might be quite small. However, presently there are no kinetic data available that would allow a realistic estimate of such losses for the conditions of the POPCORN campaign. We therefore have to accept a rather large range of uncertainty for the average terpene contribution to ozone formation with an upper limit of 30%. None of the other measured compound classes contributed more than 15%. The contribution of the predominantly biogenic substances isoprene, monoterpenes and higher aldehydes adds to ca. 50% of the total turnover.

The abundance of formaldehyde and acetaldehyde in the atmosphere during POPCORN was to some extent due to the photo-oxidation of the other VOC. However, there is evidence that formaldehyde and acetaldehyde were also directly emitted from maize (Rudolph *et al.*, 1995; Benning and Wahner, this issue) so an additional contribution to the ozone formation from these substances can be assumed. Also there are some compounds which were not measured during the POPCORN campaign but have recently been reported to exhibit high mixing ratios in rural areas like methanol, ethanol and acetone (Goldan *et al.*, 1995).

Since practically no OH is present at night, the reactions of unsaturated compounds with ozone and NO_3 are then the most important reactions. As the slightly higher night-time VOC mixing ratios are compensated by the lower night-time ozone mixing ratios of ca. 25 ppbv (Brauers *et al.*, this issue), the night-time VOC-turnover with ozone is about the same as during day-time (0.1 ppbC/h). NO_3 concentrations were not measured during POPCORN. The upper limit of its concentration can be estimated from a steady state between its formation by the reaction of NO_2 with ozone and its loss due to its reaction with NO. From the median of the night-time NO and NO_2 mixing ratios of 34 pptv and 3.05 ppbv respectively (Rohrer *et al.*, this issue) and the rate constants given by Atkinson *et al.* (1992) we calculated a steady-state NO_3-mixing ratio of 2.8 pptv. If also the formation of N_2O_5 is regarded as a loss process for NO_3, a mixing ratio of only 0.4 pptv results. This NO_3 concentration drives a turnover of monoterpenes of about 0.1 ppbC/h which is about twice as high as the night-time turnover of these compounds with ozone. The turnover of other compounds with NO_3 is negligible.

4. Conclusion

The ambient VOC measured during the POPCORN campaign present a quite complicated picture. Many compounds, especially typically biogenic VOC, were only present in mixing ratios of some 10 pptv or even lower. Despite their low mixing ratios, monoterpenes and higher aldehydes as well as isoprene contributed substantially to the atmospheric VOC-turnover and thus to the production of photo-oxidants. The contribution of these predominantly biogenic compounds and that of predominantly anthropogenic compounds (CO, alkanes, alkenes and aromatics) was roughly equal.

The POPCORN measuring site normally was not directly influenced by strong local VOC-sources and may be regarded as typical for remote rural sites in mid northern latitudes. Major anthropogenic sources like industrial areas and major highways were at least 20 km away. Monoterpenes emitted from a pine forest at least 1 km away were the predominant biogenic VOC. The maize field in the centre of which the measurements were made proved not to be a major VOC source, except for possible emissions of formaldehyde and acetaldehyde. This finding is in contrast to the current literature.

The measurements presented in this paper show that in this situation the local formation of photo-oxidants was not governed by a single compound or compound class but by a complex mixture of a variety of minor compounds originating from both anthropogenic and biogenic sources.

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