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Volatile organic compounds and isoprene oxidation products at a temperate deciduous forest site

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Abstract. Biogenic volatile organic compounds (BVOCs) and their role in atmospheric oxidant formation were investigated at a forest site near Oak Ridge, Tennessee, as part of the Nashville Southern Oxidants Study (SOS) in July 1995. Of 98 VOCs detected, a major fraction were anthropogenic VOCs such as chlorofluorocarbons (CFCs), alkanes, alkenes and aromatic compounds. Isoprene was the dominant BVOC during daytime. Primary products from BVOC oxidation were methylvinylketone, methacrolein and 3-methylfuran. Other compounds studied include the BVOCs α-pinene, camphene, β-pinene, *p*-cymene, limonene and *cis*-3-hexenyl acetate and a series of light alkanes, aromatic hydrocarbons and seven of the CFCs. The correlation of meteorological parameters, with the mixing ratios of these different compounds, reveals information on atmospheric oxidation processes and transport. Long-lived VOCs show very steady mixing ratio time series. Regionally and anthropogenically emitted VOCs display distinct diurnal cycles with a strong mixing ratio decrease in the morning from the breakup of the nocturnal boundary layer. Nighttime mixing ratio increases of CFCs and anthropogenic VOCs are suspected to derive from emissions within the Knoxville urban area into the shallow nocturnal boundary layer. In contrast, the time series of BVOCs and their oxidation products are determined by a combination of emission control, atmospheric oxidation and deposition, and boundary layer dynamics. Mixing ratio time series data for monoterpenes and *cis*-3-hexenyl acetate suggest a temporarily emission rate increase during and after heavy rain events. The isoprene oxidation products demonstrate differences in the oxidation pathways during night and day and in their dry and wet deposition rates.

1. Introduction

The role of biogenic volatile organic compound (BVOC) emissions in atmospheric chemistry processes, in particular in the formation of tropospheric ozone, has been discussed extensively [*Lloyd et al.*, 1983; *Lopez et al.*, 1989; *Atherton and Penner*, 1990; *MacKenzie et al.*, 1991; *Fehsenfeld et al.*, 1992]. Regions where BVOC emissions have a particularly high impact on air quality are generally characterized by two features: Firstly, a high vegetation biomass density with a significant percentage of high BVOC emitting plant species, such as isoprene-emitting oak trees, and secondly, by sunny and warm climate conditions. BVOC emissions have been shown to increase exponentially with temperature [*Guenther et al.*, 1991, 1993]. Besides higher emissions in warm climates the formation of tropospheric pollutants such as ozone and other oxidants and aerosols is furthermore fostered by the high photochemical activity.

A problem region where BVOCs are suspected to play a major role in atmospheric processes and which recently has received fundamental research attention is the southeastern United States. The U.S. national ambient air quality standard (NAAQS) for ozone frequently is not attained in this region [*Chameides et al.*, 1988, 1992; *Aneja et al.*, 1990, 1992; *McKeen et al.*, 1991; *Roselle et al.*, 1991, 1994; *Rao et al.*, 1996]. Previous studies conducted include the Rural Oxidant in the Southern Environment (ROSE) [*Goldan et al.*, 1995] and the Atlanta Southern Oxidant Study (SOS). Our study was part of the Nashville Southern Oxidants Study [*Fehsenfeld et al.*, 1997] and the North American Regional Study on Tropospheric Ozone (NARSTO) in the summer of 1995.

BVOC emissions and their role in atmospheric oxidant formation were investigated by several research groups at Walker Branch Watershed, a mixed deciduous forest research site maintained by the Oak Ridge National Laboratory and located near Oak Ridge, Tennessee. BVOC emission rates from vegetation were studied on a variety of different experimental scales. Enclosure experiments were performed on individual leaves and branches. Other techniques for quantitative flux measurements were done at the canopy and landscape level and included indirect or direct eddy covariance methods, surface layer gradient techniques, and mixed layer gradient methods using a tethered balloon system for vertical profiling within the mixed boundary layer. These experiments and the results are described by *J. Greenberg et al.* (Tethered ballon measurements of biogenic VOCs in the atmosphere, submitted to *Atmospheric Environment*, 1998 hereinafter referred to as G98 and *B. Hall et al.* (Isoprene flux measurements, modeling and associated uncertainties at the canopy scale, submitted to *Journal of Applied Meteorology*,

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1998). Another part of the experiment was the monitoring of volatile organic compounds (VOCs) in ambient air at a clearing within the forest stand, which is described in this paper. The purpose of this study was to examine the contribution of individual compounds to the overall BVOC and VOC loading of the atmosphere and to look at the dependence of atmospheric VOCs and BVOC levels on environmental and meteorological parameters.

2. Experiment

2.1. Site

The Walker Branch research forest of the Oak Ridge National Laboratory, Tennessee, is a mixed hardwood forest with a mean canopy height of 24 m. Latitude and longitude of the site are 35° 57'30"N, 84° 17' 15" W; the elevation is 365 m. A 44 m walk-up tower is available for ambient measurements and to access the forest canopy. A more detailed description of the site and the area has been given by *Johnson and van Hook* [1989] and *Guenther et al.* [1996b]. A biomass survey for the Oak Ridge site was performed in 1995 [*Guenther et al.*, 1996b]. A forest clearing located about 600 m east of the tower site was used for the installation of a field laboratory. The clearing extended approximately 250 m in east-west direction and 100 m in north-south direction. The instrument trailer was parked about 15 m from the eastern end of the clearing and about 10 m from a meteorological monitoring station maintained by the Oak Ridge National Laboratory. A 10 m tall sampling tower was erected 5 m south of the trailer. Meteorological and ozone data were recorded at a nearby (≈ 10 m) monitoring station (sampling height ≈ 5 m, 15 min average data). The last day of ozone data is missing because of an instrument failure.

2.2. Sampling System

Ambient VOCs were analyzed by an in-situ technique, thereby eliminating sample storage time in sample containers or adsorbent cartridges and sample handling steps. This procedure also minimizes problems associated with storing labile compounds. Air was continuously pulled from the top of the sampling tower through an impregnated inlet filter for particulate and ozone removal. The scrubbing of ozone is essential to prevent potential losses of unsaturated compounds during the sampling step [*Helmig*, 1997]. The filter material used was Teflon-impregnated glass fiber (Pallflex T60A20, Putnam, Connecticut) which had been soaked in a 5% solution of sodium thiosulfate and then dried for 3 hours in an oven at 120°C. Ozone scrubbing efficiency of this filter was > 95% and was checked regularly. Air was pulled through the filter and a 0.4 cm inner diameter Teflon tubing sampling line at 5 L min^{-1} into the instrument trailer. Total length of the sampling line to the analytical instrument was approximately 12 m. Part of the sampling flow (2.5 L (for routine monitoring) to 10 L (for MS identification) sample volumes at 250 mL min^{-1} sampling rate) was directed onto a temperature-controlled multistage solid adsorbent trap for enrichment of VOCs. The analytical range covered VOCs in the volatility range of approximately C_3 to C_{15}. The adsorbent trap was filled with three layers of solid adsorbents arranged in order of increasing adsorbent strength (300 mg Carbotrap C, 200 mg Carbotrap, 100 mg Carbosieve S III (all adsorbents from Supelco, Bellefonte, Pennsylvania). This adsorbent combination has been extensively tested and used in numerous other studies and has been shown to allow analysis of a wide range of VOCs within the volatility range of ≈ C_2-C_{15} [Löfgren et al., 1991; *Ciccioli et al.*, 1992a, b; *Tang et al.*, 1993; *Dindal et al.*, 1995; *Oliver et al.*, 1996; *Helmig et al.*, 1996; D. Helmig et al. (Biogenic volatile organic compound emissions (BVOCs) I. Identifications from three continental sites in the U.S.), *Chemosphere*, in press, 1998, hereinafter referred to as H98].

2.3. Chemical Analysis

The concentrated VOCs were analyzed by thermal desorption and cryogenic freezeout with a custom-made inlet system [*Helmig*, 1996]. Schematics of the major components of this system have been given previously [*Helmig and Greenberg*, 1994; H98]. The whole analytical system was fully automated and computer controlled. The adsorbent trap temperature during the concentration step was ≈ 30°-35°C. After sampling, the adsorbent trap was moderately heated to 45°-50°C and purged with 1 L dry helium in the sampling flow direction to remove atmospheric water concurrently enriched on the adsorbent [*Helmig and Vierling*, 1995; *McClenny et al.*, 1995]. The adsorbent trap was then heated at a rate of 50°C min^{-1} to 250°C, and thermally desorbed VOCs were backflushed with 25 mL min^{-1}. He onto a cryogenic freeze-out trap (10 cm of 0.125 outer diameter stainless steel tubing filled with 80/100 mesh glass beads) which was temperature controlled at -175°C by blowing liquid nitrogen blow-off onto the outside wall of the stainless steel tubing. Prior to the transfer of the sample VOCs, deuterated benzene (≈ 25 ng) was added to the freeze-out trap as an internal standard by filling and injecting a sample loop with a gas-phase standard from a compressed gas cylinder. For GC injection the freeze-out trap was rapidly heated to 80°C by flowing an electrical current directly through the stainless steel tubing and VOCs were backflushed onto a 30 m by 0.32 mm inner diameter, 1 μm film thickness DB-1 column (J&W, Folsom, California). Separation and detection was achieved by temperature-programed gas chromatography with mass spectrometric (GC/MS) detection (Hewlett Packard 5890/5972). The MS was operated in the scan mode (m/z = 45-250 until July 17, and m/z = 33-250 from July 17 on) with electron impact ionization (70 eV). During the injection time the GC column was held at -60°C for 3 min and then programed to 150°C at a rate of 6°C min^{-1}. Between runs the GC column and adsorbent trap were baked at 250°C and 300°C, respectively.

2.4. Calibration

Two pressurized gas standards were used to establish response factors for quantitative measurements. (1) A *n*-butane/benzene (10.53/10.30 ppb) standard from the National Institute of Standards and Technology (Boulder, Colorado) and (2) a multicomponent standard containing isoprene (8.02 ppb), neohexane (5.99), α-pinene (4.63), β-pinene (3.58), and limonene (3.07) (H. Westberg, Washington State University, Washington). The concentrations for this standard were determined at the site with a calibrated GC/atomic emission detector (AED) instrument using the same sample introduction technique as used for the GC/MS. Standards were analyzed by filling Teflon bags with about 5 L calibration gas and connecting the bag to the adsorbent trap inlet. In previous experiments we have found precision and accuracy to be better than ≈ 5% for this procedure. For the multicomponent standard a comparison of the

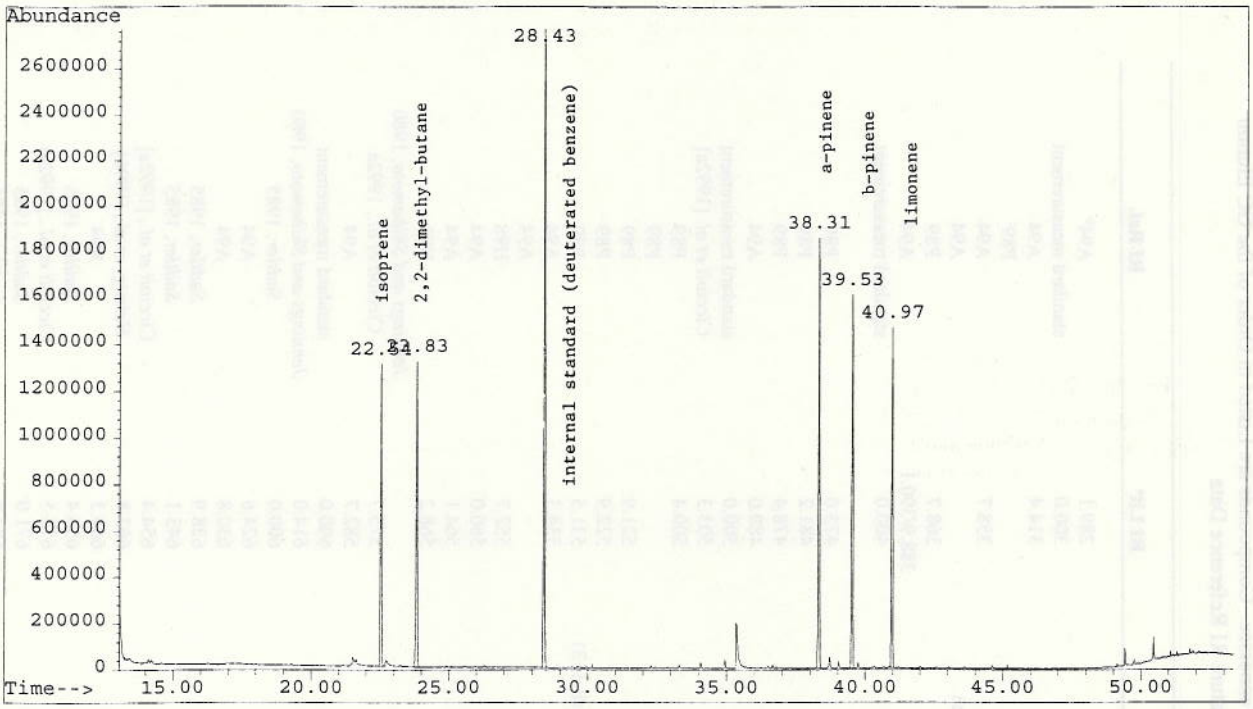

Figure 1. Chromatogram of a five component hydrocarbon standard sample (2.5 L) collected through the inlet filter and inlet line and analyzed in the same manner as ambient air samples. Peaks are labeled with their identifications. Deuterated benzene was added to the sample as an internal standard.

standard analysis between collection through the inlet filter and the whole sampling line and the collection right at the adsorbent trap did not show any significant differences, which indicates a quantitative transmission of these biogenic compounds through this part of the sampling system. A chromatogram showing the analysis of the multicomponent standard sampled from a Teflon bag attached to the inlet filter on top of the sampling tower and pulled through the whole analytical system is shown in Figure 1. It has previously been noted that certain BVOCs (such as 2-methyl-3-butene-2-ol and β-pinene) may undergo rearrangement reactions during adsorption/thermal desorption from carbon based solid adsorbents [*Cao and Hewitt*, 1993; *Arnts et al.*, 1995; *J. Greenberg*, unpublished results, 1995]. The mechanisms of these reactions are not well understood yet. From our analysis of the multicomponent standard we conclude that for the compounds tested here, such reactions did not occur. We also did extensive testing of isoprene recovery for sampling through the impregnated inlet filters and did not find any losses under our sampling conditions. This two stage trapping and desorption technique has also been shown to yield consistent identifications and relative quantities in the analysis of a 55 component hydrocarbon standard used in the international hydrocarbon intercomparison experiment [*Apel and Calvert*, 1994]. Other experiments describing the validation of the trapping and injection technique for analysis of methacrolein (MACR) and methylvinylketone (MVK) are described by G98. Blank experiments were conducted by attaching a VOC scrubber made of three activated charcoal tubes (Orbo-32, Supelco, Bellefonte, Pennsylvania) in series to the inlet side of the inlet filter and analyzing ambient air in the same manner as samples but with all VOCs being trapped by the charcoal adsorbent. Signals of the compounds of interest were generally within the range of "not detected" to "below 1%" of regular ambient air samples. The only exemptions were F-113 and benzene which had blanks in the 5-10% range. Average peak area counts from blank and standard runs were subtracted from the respective results of the sample runs. The MS sensitivity was optimized by a manual tune at the beginning of the experiment and again on July 17 and then maintained at the established tune parameters for the duration of the measurement period. Since calibrations were only performed once (two repeats each) to the beginning of the experiment and only at one concentration level, results for calibrated compounds should only be considered semiquantitative. Detection limits were in the range of 5-10 ppt for a 2.5 L sample volume. From the measurements of the internal standard and atmospheric tetrachloromethane (TCM) the precision of the measurements is estimated to be within the range of 3 - 10 %.

2.5. Data Analysis

Samples were collected and analyzed in ≈ 3 hour intervals over a 1 week period during the third week of July 1995. A total of 44 ambient tower samples were analyzed. Compound identification was achieved by comparison of the mass spectra and GC elution retention indices (RI) with literature data. Linear programed RI were calculated according to the relationship given by *Van den Dool and Kratz* [1963] and by analyzing an *n*-alkane test mixture as reference standard. Relative quantitative mixing ratios for individual compounds over the measurement period were derived from the GC/MS chromatograms by extracting selected characteristic ion chromatograms of the compounds of interest, integrating the peak areas and normalizing to the respective internal standard results. Fragment ions (m/z) used for quantification of the investigated compounds were propane (43), isobutane (43), *n*-butane (43), *n*-pentane (43), MVK (55), isoprene (67), *cis*-3-hexenyl acetate

Table 1. Volatile Organic Compounds Observed in Ambient Air at Walker Branch Site, Near Oak Ridge, Tennessee. Compounds are Listed in Order of the GC Elution with GC Retention Time (Rt), Retention Index on DB-1 (RI), Mass Fragmentation (M/Z) Pattern, and Literature RI Reference Data

Rt (min)	RI	M/Z (Percentage Abundance)	Identification	RI Lit[a]	RI Ref.
13.49	287.4	42(100),41(27),43(6)	ethenone		
13.84	296.6	41(100),39(81),42(67),38(20),40(17),37(14)	propene	289.1	A94[b]
13.97	300.0	43(100),44(86),39(71),41(55),38(21),42(17)	propane	300.0	standard measurement
14.45	312.6	85(100),87(32),50(17),101(8),35(8)	dichlorodifluoromethane (F-12)	314.4	A94
15.66	344.5	65(100),45(28),67(25),44(17),85(14),69(13)	1-chloro-1,1-difluoroethane		P89[c]
16.28	360.8	43(100),41(47),42(37),39(21),44(5)	isobutane	358.7	A94
16.60	369.2	85(100),135(42),87(22),33(6)	1,2-dichloro-1,1,2,2-tetrafluoroethane		A94
16.65	370.5	44(100),43(57),42(18)	acetaldehyde	368.7	P89
17.42	390.8	41(100),39(53),56(47),55(20),40(10),38(8)	1-butene/2-methylpropene	388.9/390.1	A94
17.81	400.9	43(100),41(35),42(15),39(15),58(12)	*n*-butane	400.0	standard measurement
21.09	471.0	41(100),56(57),40(42),55(39),39(29)	cyclobutane		
21.22	473.8	43(100),41(96),42(93),57(60),39(29),56(24)	2-methylbutane	473.0	P89
21.48	479.4	43(100),58(26),42(7)	acetone	481.2	P89
21.56	481.1	101(100),103(64),66(16),35(14),105(10),68(5)	trichlorofluoromethane (F-11)	478.4	P89
21.85	487.3	42(100),55(69),41(49),39(44),70(33),29(17)	1-pentene	489.0	A94
22.44	499.9	43(100),42(63),41(53),39(17),57(14),72(8)	*n*-pentane	500.0	standard measurement
22.63	504.3	67(100),53(77),68(67),39(67),40(31),51(16)	isoprene	503.3	*Ciccioli et al.* [1992a]
22.80	508.2	45(100),43(16),41(6),44(5)	isopropylalcohol	500.4	P89
23.09	514.9	76(100),44(20),78(10),38(6)	carbon disulfide		P89
23.31	520.0	49(100),84(61),86(38),51(31),47(18),35(10)	dichloromethane	521.9	P89
23.53	525.1	43(100),74(16),42(10),59(7)	acetic acid methyl ester	522.9	P89
23.85	532.5	101(100),151(67),103(64),85(45),153(43),55(18)	1,1,2-trichloro-1,2,2-trifluoroethane (F-113)	531.5	P89
23.89	533.4	57(100),43(91),71(76),41(60),56(37),39(24)	2,2-dimethylbutane	534.3	A94
24.32	543.4	43(100),41(76),72(38),39(36),44(12),42(8)	2-methylpropanal		A94
24.78	554.0	41(100),39(85),70(67),42(17),38(16),40(13)	methacrolein	552.7	H98
24.99	558.9	42(100),55(33),41(25),70(19),39(16)	cyclopentane	560.0	A94
25.18	563.2	43(100),42(94),41(36),71(20),39(16),55(7)	2,3-dimethyl-butane	564.1	A94
25.43	569.0	55(100),43(82),70(35),42(17),39(9)	methylvinylketone	568.2	H98
25.63	573.6	43(100),86(12),42(7),44(6)	3-methyl-2-butanone		*Jennings and Shibamoto*, 1980
25.89	579.7	43(100),72(18),57(6),42(6)	methylethylketone	575.7	*Ciccioli et al.*, 1992a
25.95	581.0	56(100),41(83),57(78),39(7),86(5),55(5)	3-methylpentane	582.7	A94
26.75	599.5	57(100),41(84),43(76),56(52),42(38),45(31)	*n*-hexane	600.0	standard measurement
26.88	602.8	82(100),53(83),81(54),39(42),51(21),50(21)	3-methylfuran	614.0	*Jennings and Shibamoto*, 1980
27.02	606.5	43(100),61(14),70(10),45(10),41(7),69(6)	ethylacetate	600.0	*Sadtler*, 1985
27.68	623.5	56(100),41(61),69(37),55(24),39(23),42(22)	methlylcyclopentane	624.6	A94
27.93	630.0	43(100),57(86),56(49),42(28),39(22),85(18)	2,4-dimethylpentane	630.8	A94
28.01	632.0	97(100),99(65),61(56),63(18),119(14),117(14)	methylchloroform	628.9	*Sadtler*, 1985
28.59	647.0	78(100),77(23),51(21),52(20),50(18),39(13)	benzene	643.1	*Sadtler*, 1985
28.79	652.2	117(100),119(97),121(32),47(29),82(26),35(21)	tetrachloromethane	654.4	*Ciccioli et al.*, [1992a]
29.17	662.0	43(100),46(83),41(22),55(18),90(10),42(10)	isopropylnitrate	663.8	*Helmig, et al.*, [1996]
29.39	667.7	43(100),41(55),56(44),57(41),42(38),85(27)	2,3-dimethylpentane	669.3	A94
29.44	669.0	43(100),41(16),86(12),71(10),56(8),39(8)	2-pentanone	659.4	*Sadtler*, 1985
29.71	676.0	44(100),43(96),41(72),57(57),58(34),71(31)	pentanal	675.5	*Ciccioli et al.*, [1992a]
29.82	678.8	57(100),86(16),42(5)	3-pentanone	671.0	*Sadtler*, 1985
30.06	685.0	95(100),130(98),97(62),60(60),134(33),35(18)	trichloroethylene	683.8	*Sadtler*, 1985

30.19	688.4	57(100),56(37),41(31),43(20),39(10),55(6)	2,2,4-trimethylpentane	689.0	A94
30.58	698.4	41(100),43(76),56(69),55(47),69(44),39(34)	3-heptene	697.9	*Ciccioli et al.*, 1992a
30.64	700.0	43(100),41(58),57(45),71(43),56(28),42(24)	*n*-heptane	700.0	standard measurement
31.28	718.2	41(100),43(88),69(84),55(65),39(52),83(47)	propylcyclopentane		
31.85	734.4	57(100),41(37),85(29),56(21),71(18),39(12)	2,4-dimethylhexane	735.1	*Ciccioli et al.*, 1992a
32.40	750.0	43(100),44(84),71(53),40(43),70(41),41(32)	2,3,4-trimethylpentane	751.0	A94
32.53	753.7	91(100),92(61),39(16),65(14),63(9),51(9)	toluene	750.1	*Sadtler*, [1985]
33.40	778.4	44(100),41(75),56(74),43(55),57(51),39(29)	hexanal	778.5	*Ciccioli et al.*, [1992a]
33.64	785.2	57(100),56(45),41(28),71(19),43(19),70(8)	trimethylhexane isomer		
33.77	788.9	41(100),43(98),55(87),56(79),42(64),70(55)	1-octene	786.6	*Sadtler*, [1985]
34.10	798.3	166(100),164(77),131(77),129(77),94(48),168(46)	tetrachloroethene	800.0	*Sadtler*, [1985]
34.16	800.0	43(100),57(57),85(46),41(33),71(31),56(23)	*n*-octane	800.0	standard measurement
34.17	800.3	43(100),56(38),61(14),41(14),73(10),42(9)	acetic acid butyl ester	796.6	*Sadtler*, [1985]
35.75	849.1	91(100),106(30),51(14),77(10),65(10),39(10)	ethyl benzene	846.1	*Sadtler*, [1985]
36.03	857.7	91(100),106(48),105(24),77(15),51(14),39(12)	*m*-xylene, *p*-xylene	853.8/855.5	*Sadtler*, [1985]
36.72	879.0	[44(100),41(84),43(82),91(77),70(75),55(55)][d]	*o*-xylene	876.7	*Sadtler*, [1985]
36.73	879.3	[44(100),41(84),43(82),91(77),70(75),55(55)][d]	heptanal	880.9	*Ciccioli et al.*, [1992a]
37.04	888.9	43(100),56(99),41(97),55(82),69(47),70(44)	1-nonene	887.9	*Sadtler*, [1985]
37.26	895.7	108(100),65(84),78(75),39(40),77(25),51(23)	methoxybenzene	893.9	*Sadtler*, [1985]
37.38	899.3	43(100),57(86),41(45),71(27),85(25),56(20)	*n*-nonane	900.0	standard measurement
38.07	922.5	93(100),91(30),92(25),79(22),121(18),41(18)	tricyclene	921.7	*Adams*, [1989]
38.32	930.9	77(100),106(89),105(89),51(54),50(34),78(16)	benzaldehyde	927.3	*Sadtler*, [1985]
38.41	933.9	93(100),91(41),92(38),77(32),79(26),41(23)	α-pinene	933.1	*Sadtler*, [1985]
38.69	943.3	91(100),120(22),65(14),43(14),92(12),57(10)	*n*-propylbenzene	945.8	A94
38.81	947.4	93(100),121(60),67(48),39(45),79(44),43(44)	camphene	946.5	*Adams*, [1989]
38.90	950.4	105(100),120(32),91(19),77(16),39(12),79(11)	ethyl-3-methyl-benzene	953.0	A94
39.08	956.5	105(100),120(48),39(18),77(17),91(14),51(13)	ethyl-4-methyl-benzene	955.3	A94
39.33	964.9	43(100),41(50),55(32),69(24),108(21),39(19)	6-methyl-5-hepten-2-one	963.0	*Sadtler*, [1985]
39.43	968.2	105(100),120(29),44(19),40(19),77(13),65(12)	ethyl-2-methyl-benzene	964.4	*Sadtler*, [1985]
39.46	969.2	93(100),91(39),77(37),41(31),79(28),39(19)	sabinene	971.3	*Adams*, [1989]
39.62	974.6	93(100),41(56),69(41),79(27),77(27),39(27)	β-pinene	970.3	*Sadtler*, [1985]
39.81	981.0	105(100),120(44),77(15),39(15),119(12),41(12)	1,2,4-trimethylbenzene	986.1	A94
39.82	981.3	43(100),41(97),44(81),57(68),56(63),55(56)	octanal	980.5	*Sadtler*, [1985]
40.00	987.3	43(100),67(50),82(30),41(27),55(18),70(13)	*cis*-3-hexene-1-ol acetate	987.0	*Jennings and Shibamoto*, [1980]
40.17	993.1	146(100),148(65),111(47),75(41),50(33),74(27)	*p*-dichlorobenzene	990.6	*Sadtler*, [1985]
40.38	1000.1	43(100),57(90),41(45),71(34),85(21),56(18)	*n*-decane	1000.0	standard measurement
40.61	1008.5	105(100),120(38),119(26),39(23),77(20),91(16)	1,2,3-trimethylbenzene	1015.6	*Ciccioli et al.*, [1992a]
40.67	1010.7	121(100),93(96),43(65),91(64),119(54),71(53)	3-carene	1009.4	*Adams*, [1989]
40.79	1015.1	119(100),134(24),91(24),117(14),120(10),39(10)	*p*-cymene	1022.2	*Adams*, [1989]
41.07	1025.2	68(100),67(74),93(73),43(38),39(37),79(33)	limonene	1026.9	*Adams*, [1989]
41.45	1039.1	93(100),79(56),91(52),77(49),105(37),80(36)	trans-ocimene	1045.6	H98
41.87	1054.4	93(100),91(45),77(39),136(30),121(29),92(28)	γ-terpinene	1056.6	H98
42.09	1062.5	43(100),57(36),71(31),121(26),85(15),41(15)	2-benzyl-2-propanol		
42.70	1084.7	57(100),41(99),43(72),56(62),44(55),55(50)	nonanal	1082.8	*Sadtler*, [1985]
43.13	1100.4	43(100),57(99),41(53),71(43),85(26),39(21)	*n*-undecane	1100.0	standard measurement
43.22	1103.9	43(100),57(68),71(64),41(43),85(38),70(24)	branched alkane		

[a] Identifications without RI confirmation should be considered tentative.
[b] A94: E. Apel, National Center for Atmospheric Research, Boulder, Colorado, unpublished data, 1994.
[c] P89: W. Pollock, National Center for Atmospheric Research, Boulder, Colorado, unpublished data, 1989.
[d] Coeluting peaks.

[$CH_3CH_2CH{:}CHCH_2CH_2OCOCH_3$] (67), MACR (70), benzene (78), 3-methylfuran (82), deuterated benzene (internal standard) (84), dichlorodifluoromethane [F-12] (85), toluene (91), ethyl benzene (91), *o*-xylene (91), tricyclene (93), α-pinene (93), camphene (93), β-pinene (93), limonene (93), 1,1,1-trichloroethane (97), trichlorofluoromethane [F-11] (101), 1,1,2-trichloro-1,2,2-trifluoroethane [F-113] (101), tetrachloromethane [TCM] (117), *p*-cymene (119), trichloroethene (130), and tetrachloroethene (166). Because of the higher scan range, data for compounds with quantification ions < 45 is only available from July 17 on.

Chromatographic peak areas were initially normalized by dividing through the peak area count of the internal standard and the sample volume. The data were then multiplied by the response factor from the calibration measurements. In cases where no calibration standard for the respective compound was available the average of all data was normalized to 1, and mixing ratio time series are reported as relative deviations from the mean. For the reasons detailed below, it became evident that the atmospheric levels of TCM deviated less than the readings for the internal standard. Therefore all data were recalculated and normalized to ambient TCM levels rather than solely to the deuterated benzene signal.

3. Results and Discussion

A list of the identified compounds is given in Table 1. This table includes the compound retention index (RI), mass spectral fragmentation data (average of approximately six scans around peak maxima after background subtraction and normalization to the base peak), and literature reference data for compound confirmation. A total of 98 VOCs were detected, structural identification was accomplished for 89 compounds (approximately 98% of the overall peak area), nine compounds remained unidentified. In a few instances, structural identification could not be achieved; however, characteristics of certain compound classes were evident. In those cases, tentative identifications are given.

A typical chromatogram obtained for an ambient air sample collected during noontime on July 17 is shown in Figure 2. An enlargement of a chromatogram section showing the monoterpene pattern is given in Figure 3.

The record of meteorological data (temperature, wind direction, wind speed, relative humidity, and rainfall (K. Birdwell, Oak Ridge National Laboratory, Oak Ridge, Tennessee), and ozone data during the study period from July 17 to 22 is illustrated in Figures 4a and 4b. Figure 5 shows the peak area counts for the internal standard over the 6 day measurement period. The sensitivity gain on July 17 resulted from a change of the MS tune parameters. An approximately 15% sensitivity decline over the last 4 days is observed. Relative standard deviations for the internal standard on the individual days were 6.6, 3.4, 4.8, 3.1, and 5.8%, respectively. A systematic decrease in the internal standard area counts during midday becomes evident during all days. We attribute this effect to the change in ambient temperature inside the trailer. Even though the trailer was air-conditioned, during daytimes, with three GC ovens operated inside the trailer and full sunlight exposure on the outside walls, temperatures inside the trailer increased from about 20°C to 35°C. The internal standard injection loop was neither temperature nor pressure controlled, and therefore these parameters varied with the conditions inside the trailer leading to lower internal standard injection amounts at the elevated temperatures. Since VOCs collected from ambient air were not

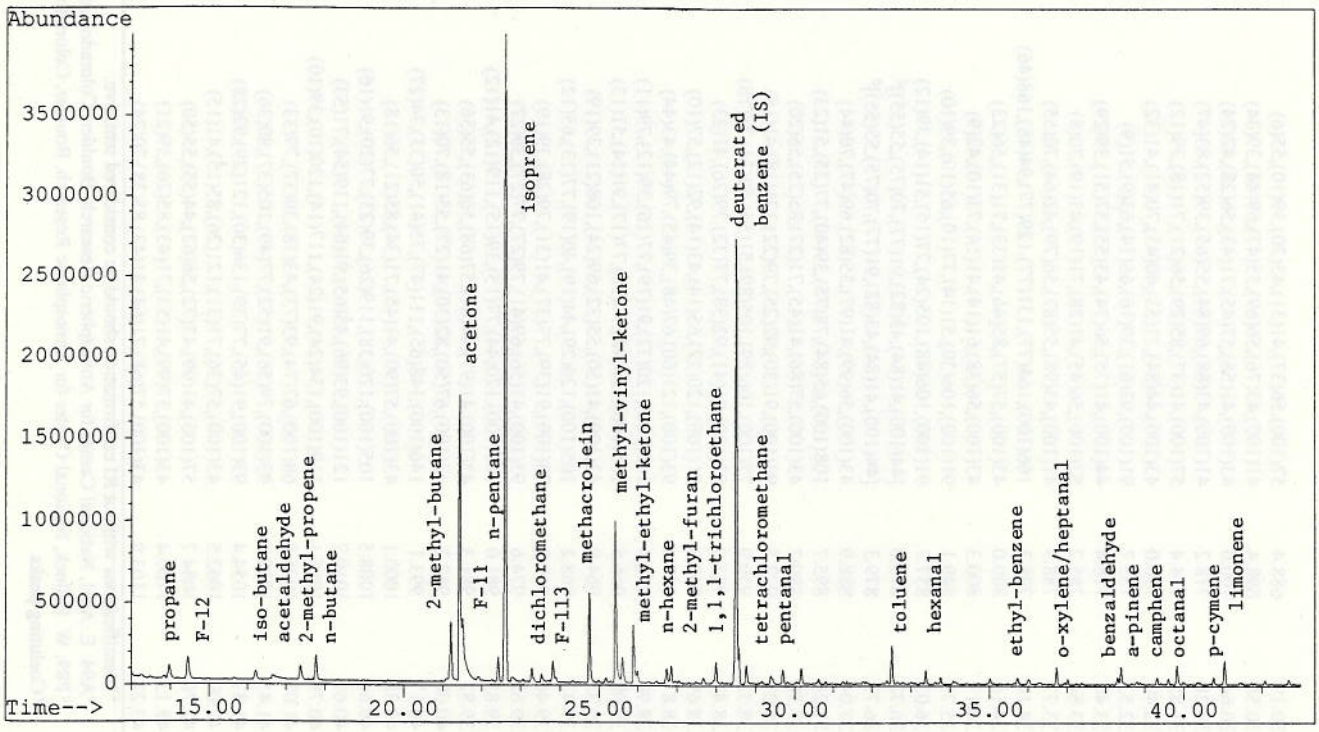

Figure 2. Gas chromatography/mass spectrometry chromatogram (total ion current) of a 10 L forest air sample collected in-situ at Oak Ridge,Tennessee, from 1255 to 1335 hrs on July 17, 1995. Major identified compounds are labeled on the chromatogram peaks. Deuterated benzene was added to the sample as an internal standard.

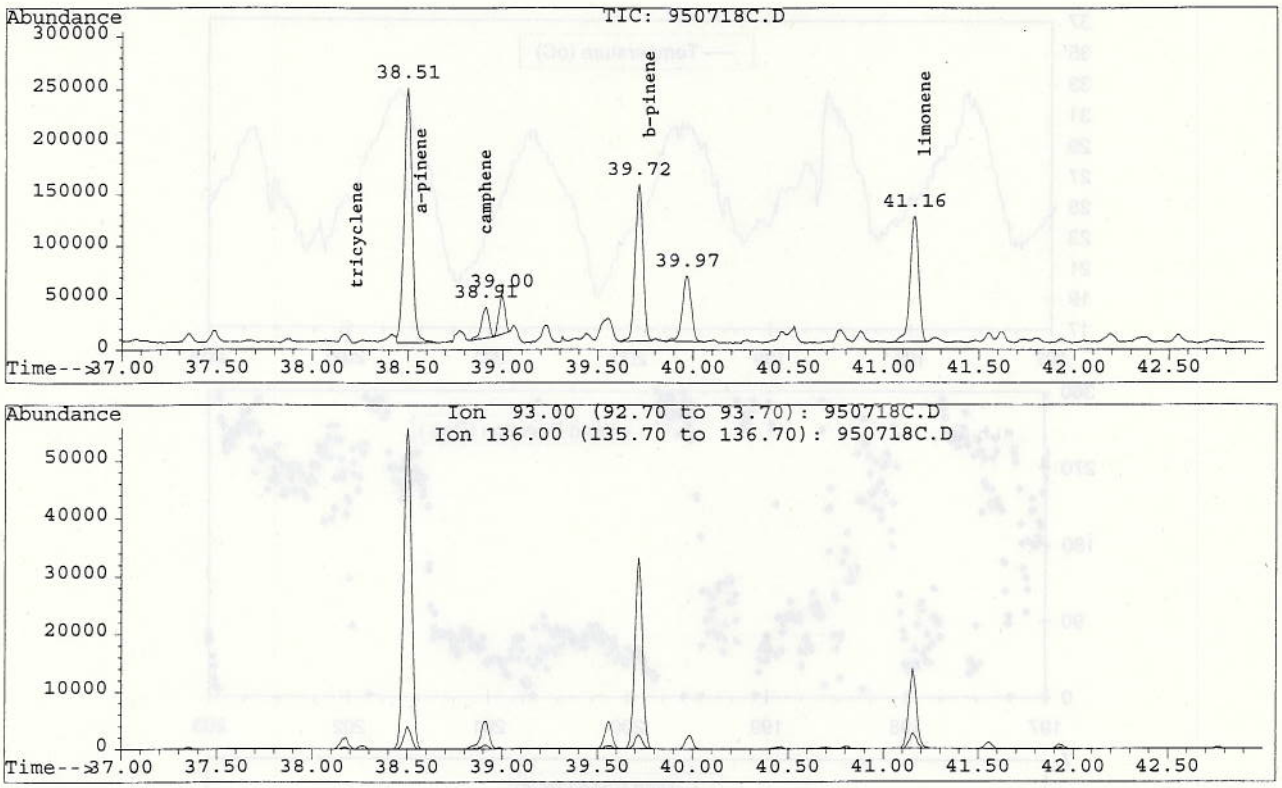

Figure 3. Chromatogram section showing the elution range of monoterpenes. This sample (2.5 L) was collected from 08.42 to 08.52 hrs on July 18, 1995. The top trace shows the chromatogram total ion current and the bottom trace the extracted ions at m/z = 93, 136 as indicator for monoterpenes. Identified monoterpene peaks are labeled in the chromatogram.

affected by the temperature variations inside the trailer, we explored an alternative approach for normalizing the data. Figure 6 illustrates the mixing ratio time series observed for TCM. TCM has an estimated atmospheric lifetime of approximately 45 years [*Solomon et al.*, 1992], and its release into the atmosphere has drastically declined after the ratification of the Montreal Protocol. As a consequence, ambient atmospheric levels of TCM have stabilized at about 104 ppt. A gradual decline of TCM is now being observed [*Montzka et al.*, 1996]; however, this decline is insignificant on the timescale of this study. Consequently, very small temporal fluctuations of atmospheric TCM levels are being observed [*Frank et al.*, 1991a, b]. The data in Figure 6 was obtained after adjustment to the sample volume and the instrument sensitivity drift. For the period of July 18 to 22 the overall relative standard deviation of this time series was 3.0 %. The higher deviations on July 16/17 are more likely from some instrument instabilities observed on this day rather than from changes in the TCM atmospheric mixing ratio. Therefore the TCM readings were used to normalize the other compounds.

Mixing ratio time series of other CFCs are plotted in Figure 7. Anthropogenic hydrocarbons are divided into light alkanes, benzene, and other aromatic compounds and are shown in Figure 8. Results for benzene are given in ppbv. Biogenic compounds are illustrated in Figure 9. Results for isoprene and α-pinene, β-pinene, and limonene are given in ppbv, and tricyclene, camphene, and *p*-cymene are plotted as relative mixing ratio time series around the overall normalized mean. Identified isoprene oxidation products are MACR, MVK, and 3-methylfuran. The mixing ratio time series of these compounds are given in Figure 10. Another BVOC identified in numerous samples is *cis*-3-hexenyl acetate. Figure 11 shows the chromatogram section with the MS peak identification. The normalized relative mixing ratio time series of this compound is plotted in Figure 12.

The list of compound identifications (Table 1) and the sample chromatogram (Figure 2) show typical characteristics for rural continental air with some anthropogenic influence. A major fraction of observed VOCs are anthropogenically emitted gases, such as the CFCs, alkanes, alkenes, and aromatic compounds. Identified BVOCs emitted from the forest vegetation include isoprene, alkenes, monoterpenes, and one oxygenated compound. Isoprene was the dominant VOC present in daytime air samples. A total of 11 terpenoid compounds were detected. The major monoterpenes were tricyclene, α-pinene, camphene, β-pinene, and limonene. Another abundant BVOC was *p*-cymene. Other monoterpenes identified include sabinene, 3-carene, *trans*-ocimene, and γ-terpinene. The major primary products from the oxidation of BVOCs identified were the isoprene products MACR, 3-methylfuran, and MVK. Other observed compounds that are potential oxidation products of both biogenic and anthropogenic VOCs include acetone and acetaldehyde.

3.1. Chlorofluorocarbons

As discussed in detail above, TCM shows little concentration changes over the study period. Among the other CFCs, F-11, F-12, and F-113 have estimated atmospheric lifetimes of 51, 111, and 90 years', respectively [*Solomon et al.*, 1992; *Cunnold et al.*, 1986], which are in excess of the TCM lifetime. However, the concentrations of these compounds (Figure 7) show higher variations than for TCM. This may indicate a more

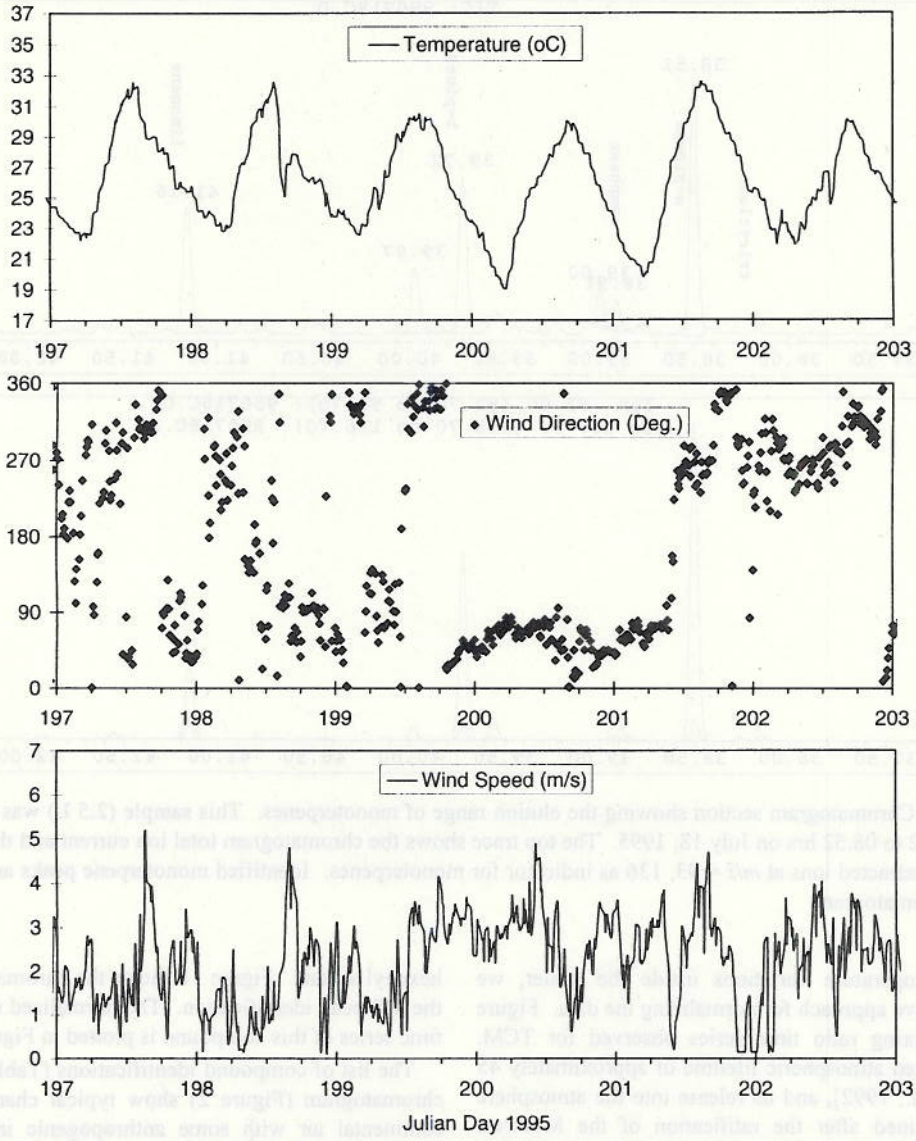

Figure 4a. Meteorological (temperature, wind direction, wind speed) data at the Walker Branch,Tennessee, site from July 16 to 21.

inhomogeneous atmospheric distribution and/or higher release rates of these compounds in the immediate surrounding area. The mixing ratio time series of 1,1,1-trichloroethane, tetrachloroethene and trichloroethene demonstrate the dependence of the degree of diurnal variations from the atmospheric lifetimes. Estimated atmospheric lifetimes of these three gases are 6.3 years [*Solomon et al.*, 1992], 107 days [*Helmig et al.*, 1996], and 7.6 days (using $K_{OH,\ 298K} = 2.36 \times 10^{-12}$ cm^3 $molecules^{-1}$ s^{-1} [*Atkinson*, 1989] and $[OH]_{24hours} = 6.5 \times 10^5$ molecules cm^{-3}). The level of diurnal variability increases with decrease of the atmospheric lifetime. The highest variations are found for trichloroethene. Shorter-lived CFCs are expected to have a less homogenous atmospheric distribution. Increases in CFC mixing ratios are typically seen during nighttime hours with maxima between midnight and sunrise. Mixing ratios drop after sunrise and the breakup of the nocturnal surface layer. This observation infers a surface source and release of the shorter-lived CFCs within the area. The typical lag time between the offset of vertical mixing (≈ 20.00 hrs) to when mixing ratio maxima are reached (≈ 03.00 hrs) is about 7 hours. The highest CFC nighttime levels were observed during east/southeasterly winds (Figure 4a). With an average wind speed of ≈ 2.5 m s^{-1}, one of the major source regions is therefore estimated to be within a range of 50-75 km to the east/southeast of the site. This corresponds to the location of the city of Knoxville, which has about 360,000 residents and is the biggest city within a 300 km radius of the site. Therefore it appears plausible that the Knoxville urban area can be identified as a major source region for the observed nighttime CFC maxima at the Walker Branch research site.

3.2. Anthropogenic VOCs

Another group of anthropogenic VOCs that was looked at closely are light hydrocarbons and aromatic compounds. All three mixing ratio plots in Figure 8 show similar characteristics. Concentrations increase during night with maxima being reached in the early morning hours before sunrise. After sunrise a rapid concentration drop occurs. Mixing ratios decline to ≈ 1/3 to 1/4 of their nighttime maxima within less than 3 to 5 hours. Similar

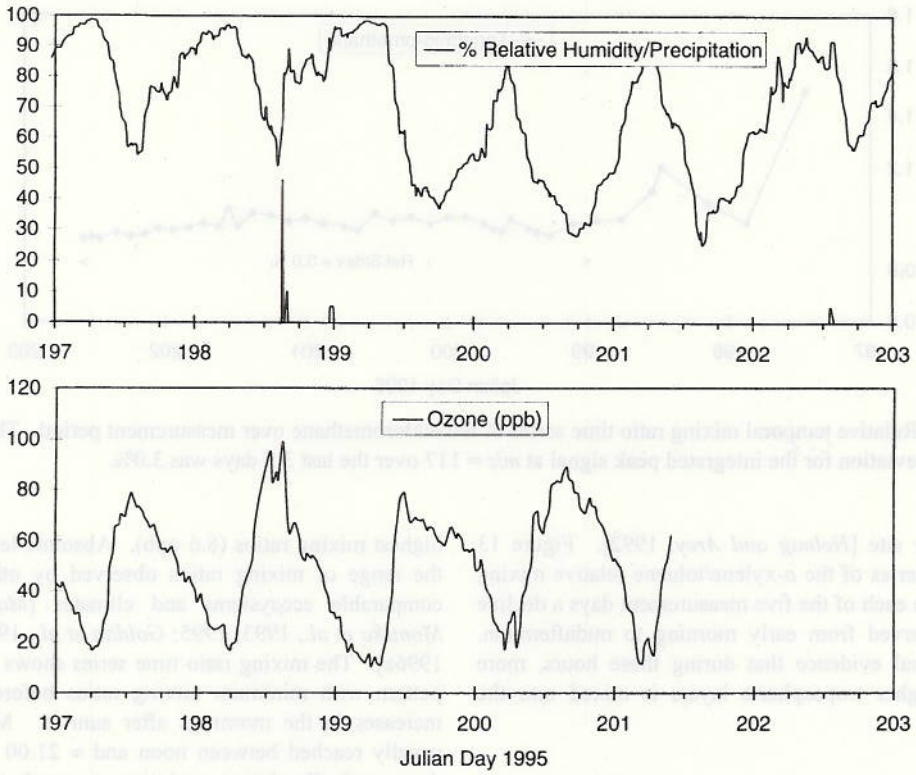

Figure 4b. Meteorological (relative humidity in percent, precipitation (divide *y*-axis scale by 25 to obtain mm in 15 min) and ozone data at the Walker Branch,Tennessee site from July 16 to 21.

mixing ratio time series for anthropogenic hydrocarbons were reported by *Goldan et al.* [1995] at a forest site in Alabama. Daytime atmospheric lifetimes of all of the hydrocarbons are expected to be shorter than at night, because the atmospheric depletion is mainly determined by reactions with the OH radical. However, considering their OH radical reaction rate constants and typical ambient OH mixing ratios leads to lifetimes of the order of 3-15 days for all of these hydrocarbons [*Helmig et al.*, 1996]. Therefore the daily concentration drops observed here are substantially larger than to be explained solely by the daytime loss from OH reactions. Similarly to the discussion of the CFCs (see above), an enrichment of hydrocarbons during night by emissions into the shallow nocturnal boundary layer from nearby sources appears the most plausible explanation. In the early morning hours with the onset of vertical mixing, much cleaner tropospheric air is mixed into ground layer air and results in the strong decrease of VOC mixing ratios. This explanation is confirmed by another observation: The atmospheric removal of both *o*-xylene and toluene is determined by OH reaction with reaction rate constants (298 K) of 13.7 x 10^{-12} and 5.96 x 10^{-12} molecules cm^{-3} s^{-1} [*Atkinson*, 1989]. Consequently, the atmospheric lifetime of toluene is about twice that of *o*-xylene. Both compounds derive from the same type of emission sources, mainly from the use and combustion of fossil fuel and are released into the atmosphere in a fairly constant ratio. The evolution of the ratio of their atmospheric mixing ratios can therefore be used as an indicator to gauge the "age" or atmospheric transport time of a given air parcel from an emission

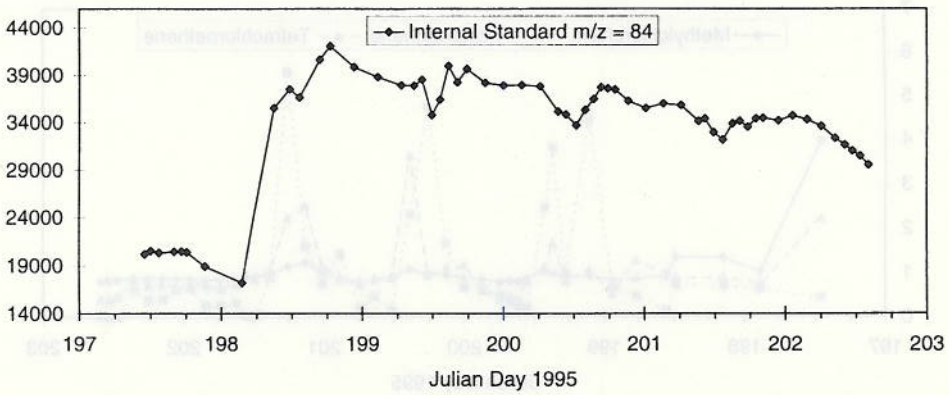

Figure 5. Peak area counts for internal standard (deuterated benzene) ion at *m/z* = 84 in each sample analyzed during the experimental period. The sensitivity change on July 17 resulted from a change in the mass spectrometer tune parameters.

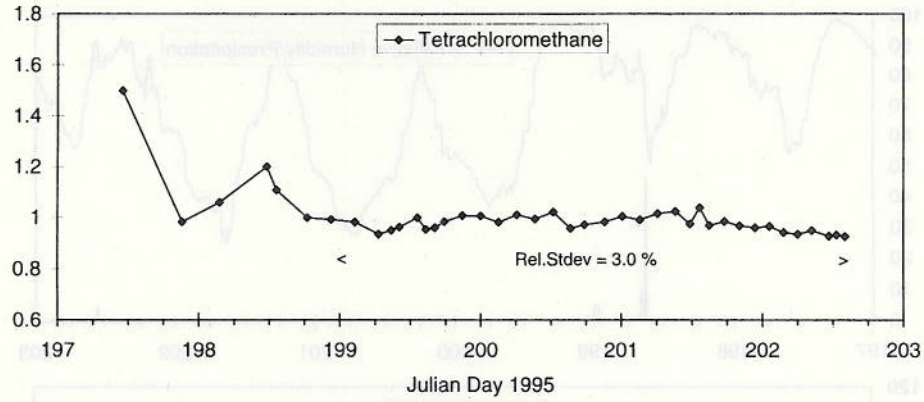

Figure 6. Relative temporal mixing ratio time series of tetrachloromethane over measurement period. The overall standard deviation for the integrated peak signal at $m/z = 117$ over the last 3.5 days was 3.0%.

source to a receptor site [*Helmig and Arey*, 1992]. Figure 13 illustrates the time series of the *o*-xylene/toluene relative mixing ratio time series. On each of the five measurement days a decline of this ratio is observed from early morning to midafternoon. This yields additional evidence that during these hours, more "aged" air from higher tropospheric layers is mixed into the surface layer.

3.3. Biogenic VOCs

Isoprene mixing ratios show the highest variability of all compounds analyzed (Figure 9). The mixing ratio variance spans about 2 orders of magnitude from the lowest (< 100 ppt) to the highest mixing ratios (8.6 ppb). Absolute levels are well within the range of mixing ratios observed by other investigators in comparable ecosystems and climates [*Martin et al.*, 1991; *Montzka et al.*, 1993, 1995; *Goldan et al.*, 1995; *Guenther et al.*, 1996a]. The mixing ratio time series shows a consistent diurnal pattern with minimum mixing ratios before sunrise and steep increases in the mornings after sunrise. Maximum levels are usually reached between noon and ≈ 21.00 hrs. Mixing ratios drop gradually during nighttime to reach their minima in the early morning. The isoprene diurnal mixing ratio cycle observed here agrees qualitatively with measurements from other deciduous forest sites [*Martin et al.*, 1991; *Montzka et al.*, 1993, 1995; *Goldan et al.*, 1995]. Isoprene emissions are controlled by

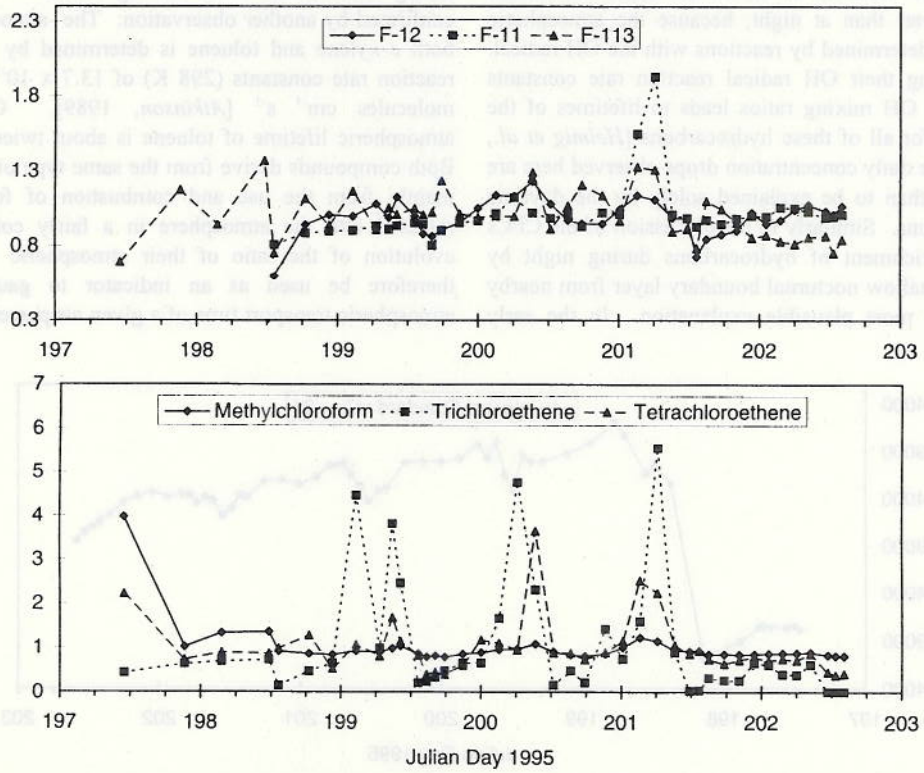

Figure 7. Relative mixing ratio time series for chlorofluorocarbons with top dichlorofluoromethane (F-12), trichlorofluoromethane (F-11), and 1,1,2-trichloro-1,2,2-trifluoroethane (F-113) and bottom 1,1,1-trichloromethane, (methylchloroform), trichlorethene and tetrachloroethene.

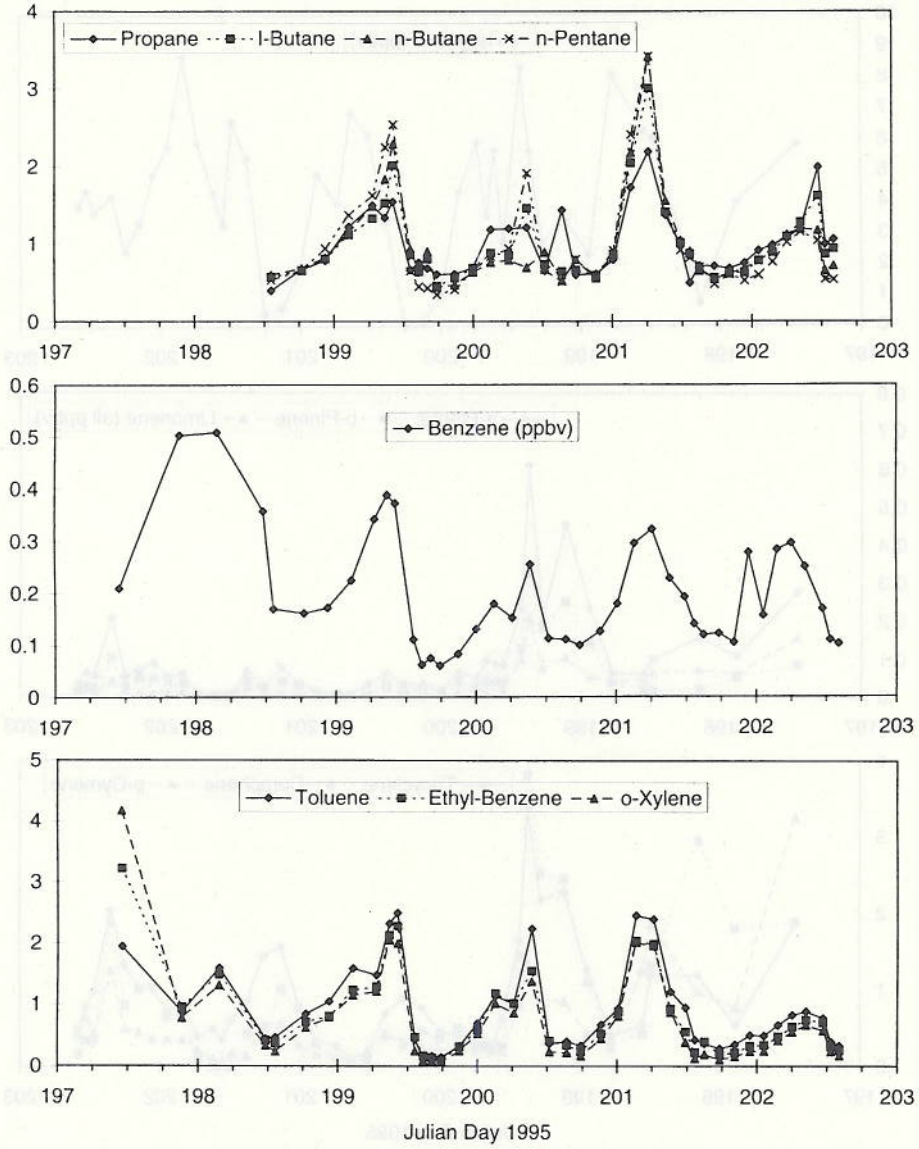

Figure 8. Relative mixing ratio time series of hydrocarbons with top light alkanes (propane, isobutane, *n*-butane, *n*-pentane) (middle) benzene (in ppb),and bottom toluene, ethylbenzene, and *o*-xylene.

temperature and light and recede during night [*Guenther et al.*, 1991, 1993]. Diurnal isoprene emission rate changes from both cuvette measurements and from model simulations considering the light and temperature dependence have been discussed by *Guenther et al.* [1996a]. The results of an extensive isoprene flux measurement study at the Oak Ridge site were recently published [*Guenther et al.*, 1996b]. The main contributors to the isoprene emissions were the tree species *Quercus*, *Liquidambar,* and *Nyssa*. Typical mean midday surface fluxes were of the order of 3-5 mg C $m^{-2} h^{-1}$.

In addition to the temperature and light controls on the diurnal isoprene emission pattern, ambient concentrations are dependent on the mixing within the mixed boundary layer and atmospheric depletion by OH, ozone, and the nitrate radical. During daytime the isoprene atmospheric lifetime is mainly determined by its reaction with OH and is estimated to be of the order of 1-2 hours during sunny summer time conditions. Estimates of the nighttime lifetime are more difficult because of larger uncertainties in the NO_3 reactions. In a recent study, *Goldan et al.* [1995] concluded that the observed isoprene depletion at night is too fast to be explained by known chemical loss processes.

Monoterpenes (Figure 9) show a much different diurnal mixing ratio cycle than isoprene. Mixing ratio maxima occur during night between midnight and sunrise. Nighttime mixing ratios are typically about 1 order of magnitude higher than during noontime. The quantitative range found for α-pinene, β-pinene, and limonene lies well within reported concentrations from other mixed deciduous forest sites [*Goldan et al.*, 1995] but is somewhat lower than reported concentrations from coniferous forests [*Riba et al.*, 1987]. The diurnal monoterpene time series seen here are in good agreement with observed data reported at other sites [*Riba et al.*, 1987; *Goldan et al.*, 1995]. Monoterpene emission rates increase exponentially with temperature. With a typical noontime (30°C)/nighttime (20°C) temperature gradient of about 10°C (Figure 4a), monoterpene emission rates are expected to be ≈ 59 % lower at night. It becomes evident that the effect of the strongly reduced vertical mixing at night has a much higher effect on ambient concentration levels than the decrease in

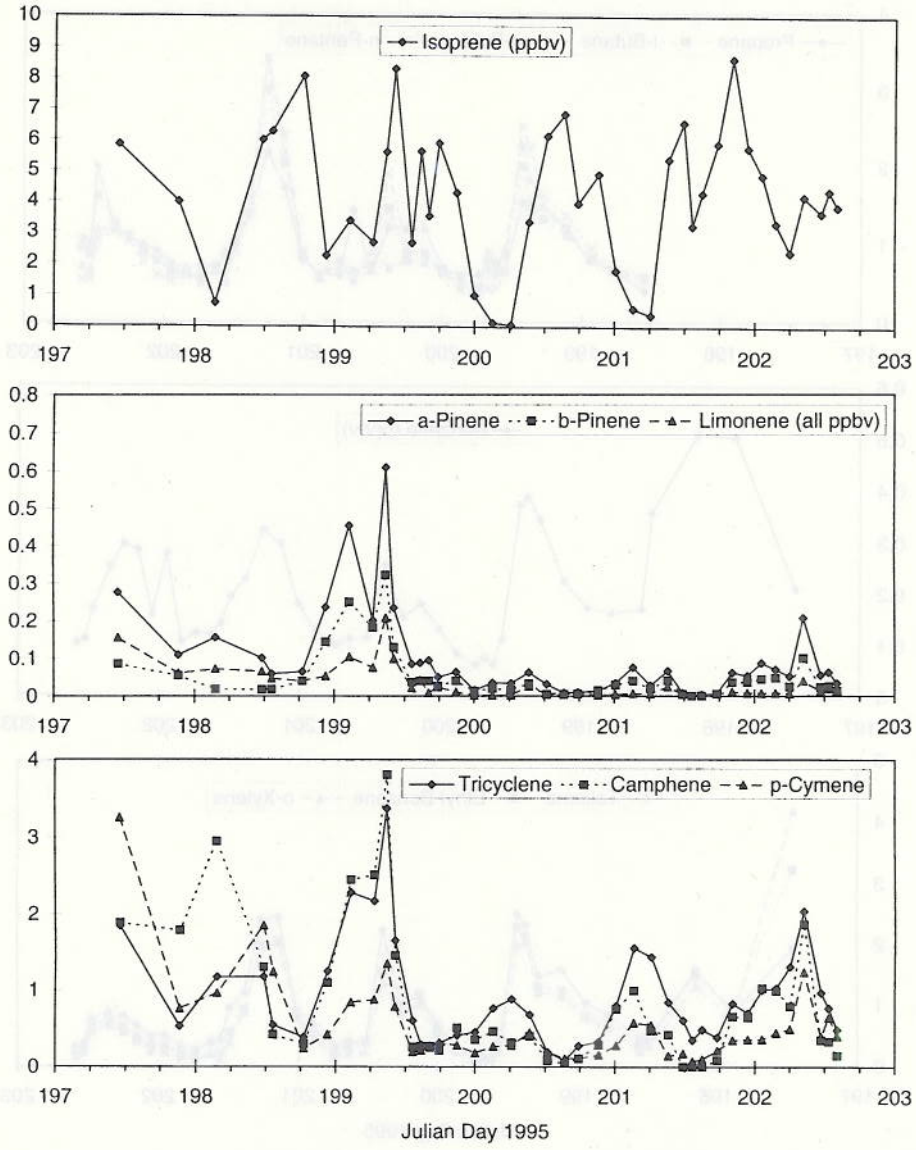

Figure 9. Mixing ratio time series of biogenic emissions with top isoprene (in ppb), (middle) α-pinene, β-pinene, limonene (in ppb), and bottom relative mixing ratio time series for tricyclene, camphene, and *p*-cymene.

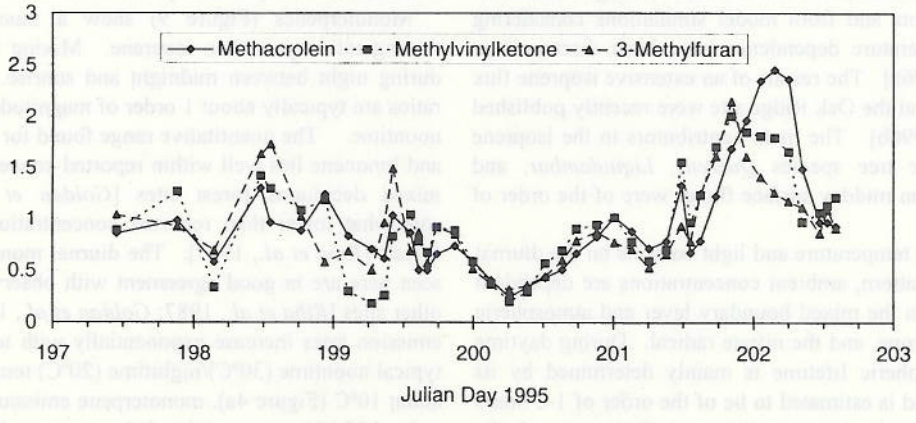

Figure 10. Relative mixing ratio time series of the isoprene oxidation products methacrolein, methylvinylketone, and 3-methylfuran.

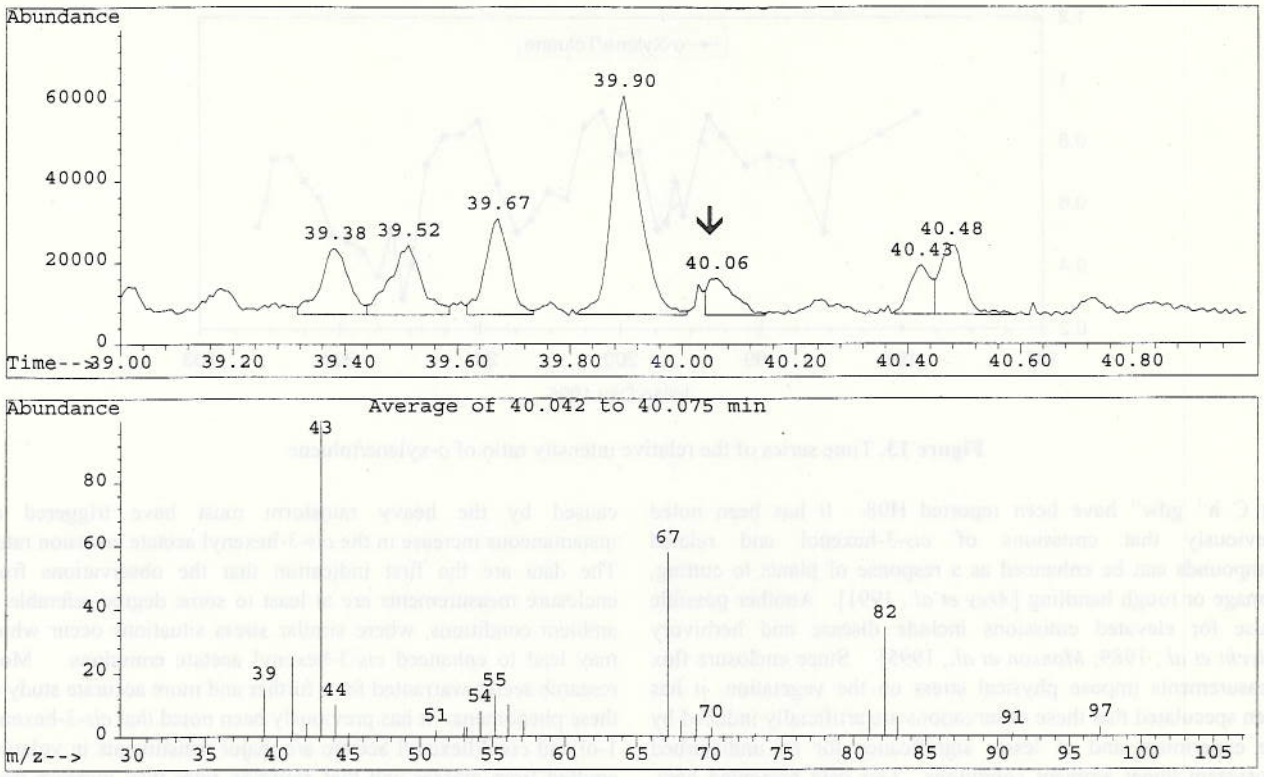

Figure 11. Chromatogram section with peak for (top) *cis*-3-hexenyl acetate and (bottom) its mass spectrometric identification.

emission rates at night and is responsible for the observed nighttime mixing rate maxima. The overall highest monoterpene levels were observed in the early morning hours of July 18 (Julian day 199). This event follows a series of heavy rainstorms in the late afternoon and evening of July 17 (Julian day 198). The meteorological data reveal no other unusual parameter during this period, which may serve as a plausible explanation for these elevated monoterpene levels. Therefore the most likely conclusion appears to be that the rainstorm may have effected an increase in the release of monoterpenes from the vegetation. This theory is backed by results from plant enclosure experiments. *Arey et al.* [1991] observed increases in emission rates of biogenic oxygenated compounds in enclosure experiments which were attributed to a response to physical stress and to the change of the environmental parameters. *Dement et al.* [1975] found a positive dependence between humidity and monoterpene volatilization. Likewise, *Lamb et al.* [1985] noted that BVOC fluxes measured in enclosure experiments from a wet branch were approximately one order of magnitude larger than from a dry branch. A heavy rainstorm appears likely to induce similar stress factors onto the vegetation and therefore may similarly cause short-term increases in emission rates as reflected by the record of mixing ratio time series and the ambient meteorological data presented here.

Another VOC identified that can be assigned to biogenic sources is *cis*-3-hexenyl acetate (Figures 11 and 12). Emissions of hexene-ol derivatives, in particular of *cis*-3-hexenyl acetate have been observed by numerous investigators in enclosure experiments [*Bicchi et al.*, 1989; *Arey et al.*, 1991; *Winer et al.*, 1992; *König et al.*, 1995; H98]. Emission rates up to the 20-25

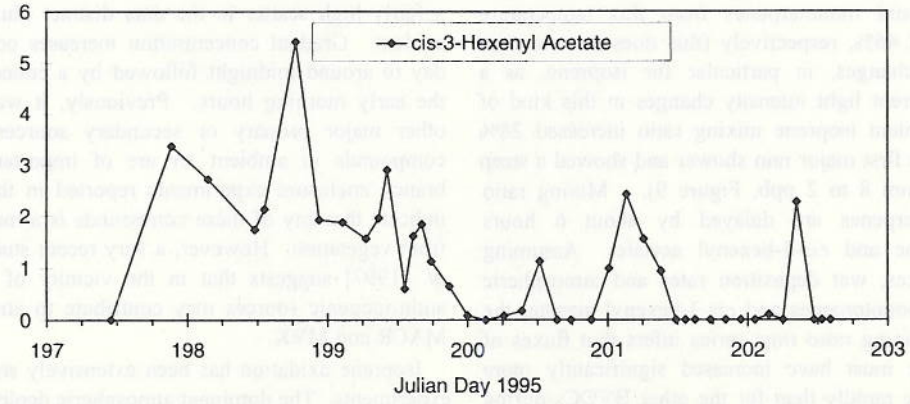

Figure 12. Relative mixing ratio time series for *cis*-3-hexenyl acetate.

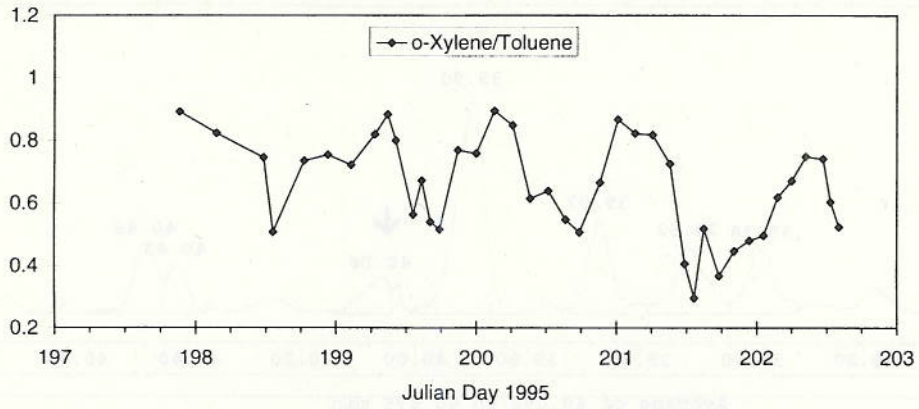

Figure 13. Time series of the relative intensity ratio of *o*-xylene/toluene.

μg C h^{-1} gdw^{-1} have been reported H98. It has been noted previously that emissions of *cis*-3-hexenol and related compounds can be enhanced as a response of plants to cutting, damage or rough handling [*Arey et al.*, 1991]. Another possible cause for elevated emissions include disease and herbivory [*Bicchi et al.*, 1989; *Monson et al.*, 1995]. Since enclosure flux measurements impose physical stress on the vegetation, it has been speculated that these observations are artificially induced by the experiment and of lesser significance for an undisturbed ecosystem under ambient conditions. Our data presented here, indeed show the presence of the major compound of this class, *cis*-3-hexenyl acetate as a consistent ambient air component in a forest atmosphere. It should be noted that to date we have not experimentally proven quantitative recovery of this compound for our analytical system because of the lack of a stable quantitative standard. The data presented may therefore underestimate the overall abundance. Interestingly, the highest ambient levels of *cis*-3-hexenyl acetate were observed in a sample collected on July 17 (Julian day 198) about 3.5 hours after a thunder shower. Ambient levels of *cis*-3-hexenyl acetate more than doubled from before to after the rain. There are two possible explanations for this observation. Firstly, after a heavy rain event a substantial decrease of the vertical mixing from the adherent surface cooling is expected. This lower vertical mixing will cause more stagnant air conditions and lead to enhanced ambient air BVOC concentrations near the surface. However, the concurrent temperature drop following the rainstorm (approximately 7°-8°C, Figure 4) will lead to a decrease of the BVOC emission rates which will counteract the mixing effect. Using the temperature response algorithms developed by *Guenther et al.* [1991, 1993], calculated decreases in the emission rates for isoprene and monoterpenes from this temperature change are 56% and 46%, respectively (this does not consider any emission rate changes, in particular for isoprene, as a response to the adherent light intensity changes in this kind of situation). The ambient isoprene mixing ratio increased 28% immediately after the first major rain shower and showed a steep decline afterward (from 8 to 2 ppb, Figure 9). Mixing ratio increases of monoterpenes are delayed by about 6 hours compared to isoprene and *cis*-3-hexenyl acetate. Assuming similar ground sources, wet deposition rates and atmospheric depletion rates for monoterpenes and *cis*-3-hexenyl acetate, the comparison of the mixing ratio time series infers that fluxes of *cis*-3-hexenyl acetate must have increased significantly more overall and also more rapidly than for the other BVOCs during this period. Therefore it appears plausible that physical stress caused by the heavy rainstorm must have triggered an instantaneous increase in the *cis*-3-hexenyl acetate emission rates. The data are the first indication that the observations from enclosure measurements are at least to some degree referable to ambient conditions, where similar stress situations occur which may lead to enhanced *cis*-3-hexenyl acetate emissions. More research seems warranted for a further and more accurate study of these phenomena. It has previously been noted that *cis*-3-hexene-1-ol and *cis*-3-hexenyl acetate are major constituents in volatiles emitted from grasses and that emission rates may increase from mowing [*Schulting et al.*, 1980; *Ohta*, 1984; *Arey et al.*, 1991]. Since our measurement site was located within a forest clearing with mostly grassy ground cover, it is also possible that our observations stem from grass emissions rather than from emissions from the surrounding forests. With our currently available information we have no way to distinguish between these potential sources. Grass mowing of the clearing area did not occur during the measurement period.

3.4. Isoprene Oxidation Products

Even though isoprene oxidation has been thoroughly studied for many years, measurements on identification and concentrations of its atmospheric oxidation products in ambient air have only been accomplished very recently [*Pierotti et al.*, 1990; *Martin et al.*, 1991; *Montzka et al.*, 1993, 1995; *Riemer et al.*, 1994; *Yokouchi*, 1994; *Goldan et al.*, 1995; *Biesenthal et al.*, 1997]. Isoprene oxidation products that previously were detected in ambient air include MACR, MVK, and 3-methylfuran. All three of these compounds were identified in this study, and their relative mixing ratio time series are plotted in Figure 10. Despite a fairly high scatter in the data distinct diurnal cycles become evident. Gradual concentration increases occur throughout the day to around midnight followed by a concentration decline to the early morning hours. Previously, it was assumed that no other major primary or secondary sources of any of these compounds in ambient air are of importance. Furthermore, branch enclosure experiments reported in the literature do not indicate that any of these compounds is a major direct emission from vegetation. However, a very recent study by *Biesenthal et al.* [1997] suggests that in the vicinity of large urban areas, anthropogenic sources may contribute to atmospheric levels of MACR and MVK.

Isoprene oxidation has been extensively studied in laboratory experiments. The dominant atmospheric depletion pathway is the daytime reaction with the OH radical. Other important reactions

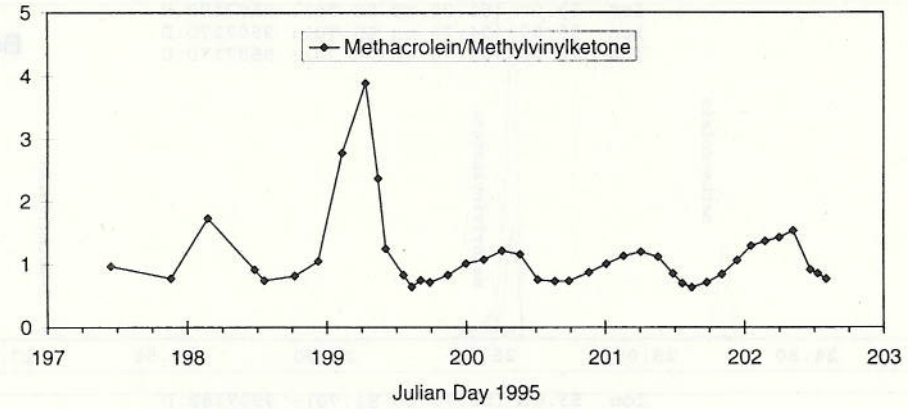

Figure 14. Time series of the relative intensity ratio of methacrolein/methylvinylketone.

are with ozone and NO_3. The reaction rate constants, estimated lifetimes and product yields from these reactions in regard to their atmospheric occurrence have been discussed extensively [*Yokouchi* 1994; *Montzka et al.*, 1993, 1995]. It has been estimated that about 95% of the daytime isoprene oxidation can be attributed to reaction with OH [*Martin et al.*, 1991]. The observed mixing ratio time series are readily explainable by the atmospheric reaction pathways involved in the formation and depletion of these compounds. A graphical plot of the ratio of MACR to MVK is shown in Figure 14. For four of the six days a regular pattern of this ratio time series is found. The amplitude of the variation is of the order of ≈ 2 with the highest MACR/MVK ratios occurring during the early morning hours and the minima in the midafternoon. Quantitative measurements of MACR and MVK done by *Martin et al.* [1991] in a central Pennsylvania deciduous forest gave a typical mixing ratio range of 0.5 to 3.0 ppb for both compounds. *Riemer et al.* [1994] report MACR and MVK levels in the 0.1 to 1.3 ppb range. Median mixing ratios found by *Yokouchi* [1994] in a pine forest were somewhat lower with 0.061, 0.091, and 0.019 ppb for MACR, MVK, and 3-methylfuran, respectively. Extensive studies of diurnal concentration cycles of isoprene and its oxidation product MACR and MVK were recently published by *Montzka et al.* [1993, 1995]. Overall, median ambient mixing ratios were 0.87 ppb and 0.98 ppb for MVK and MACR, respectively [Montzka et al., 1993]. Mean mixing ratios in the later study were ≈ 25% lower. Data from ambient measurements were compared to the results of a one-dimensional photochemical model incorporating the available knowledge on formation and depletion reactions. The observed nighttime increase of MACR/MVK ratios has two causes: (1) The yield ratio of MACR/MVK from reaction of isoprene with OH is ≈ 2:3, whereas the yield from O_3 reactions is ≈ 3:2 to 2:1 [Montzka et al., 1993; *Aschman and Atkinson*, 1994]. Reactions with OH are expected to be less significant at nighttime because of lower OH radical concentrations. It has recently been shown [*Atkinson et al.*, 1992] that OH radicals can be formed in the ozonolysis of biogenic unsaturated compounds. However, it has not yet been demonstrated that this mechanism contributes to OH radical initiated reaction products at night under ambient conditions. Consequently, during nighttime relatively more MACR is formed than during daytime. (2) The OH reaction lifetime of MVK is about a factor of 2 longer than for MACR, whereas the O_3 reaction lifetime of MVK is about a factor of 4 shorter than for MACR. This means that during nighttime the overall atmospheric lifetime of MACR compared to MVK is relatively longer. Combined, these two effects cause the diurnal cycles in the mixing ratios shown in Figure 14. The data presented here agree well with the field observations and model simulations by *Montzka et al.* [1993, 1995] who found similar diurnal patterns and amplitudes in the MACR/MVK ratio.

It is remarkable that in the early morning hours of July 18 (Julian day 199) the MACR/MVK ratio reached a maximum that is about 3 times higher than values reached on the other days. This increase is preceded by a series of heavy rain showers in the late afternoon and evening of July 17 (between 15.00-16.00 and 23.00-24.00 hrs). Figure 15 shows the chromatograms of two samples collected right before (sampling time 12.55 to 13.35 hrs) and after the last of three rain showers (sampling time 06.32 to 06.42 hrs). From this comparison a change in the relative abundance of MACR and MVC becomes clearly visible with MVK demonstrating a much higher mixing ratio decline than MACR during this time. This effect is explainable by differences in the wet deposition rates. We were not able to find literature data on the Henry's constants of either of these two compounds. However, a comparison with data on analogous compounds allows us to estimate differences in the wet deposition rates. MACR Henry's constant is expected to be at the lower end of the range of the Henry's constants for acetaldehyde, propanal, butanal, and acrolein, which are 15, 13, 9, and 7, respectively [*Sander*, 1997]. MVK is expected to have a Henry's constant similar to acetone and 2-butanone, which are 30 and 20 respectively [*Sander*, 1997]. Consequently, Henry's constants for MACR and MVK are expected to differ by about a factor of ≈ 2, with MVK being the compound with the higher Henry's constant and therefore having the higher washout ratio and wet deposition rate. This is reflected by the larger decrease in MVK ambient air mixing ratios yielding the steep increase in the MACR/MVC ratio observed on July 17/18. The data from the in-situ monitoring is in agreement with observations from tethered balloon measurements of VOCs conducted during this period (G98).

Atmospheric levels of 3-methylfuran closely follow those of MACR and MVK, suggesting the same sources and formation routes (Figure 10). On most days 3-methylfuran mixing ratios decline sooner from their maximum values in the late evenings than for MACR and MVK. Similar observations were reported by *Montzka et al.* [1995]. Their mean mixing ratio measured was ≈ 50 ppt and ≈ 3-5% of the sum of MACR and MVK. The data presented here is in reasonable qualitative agreement with this

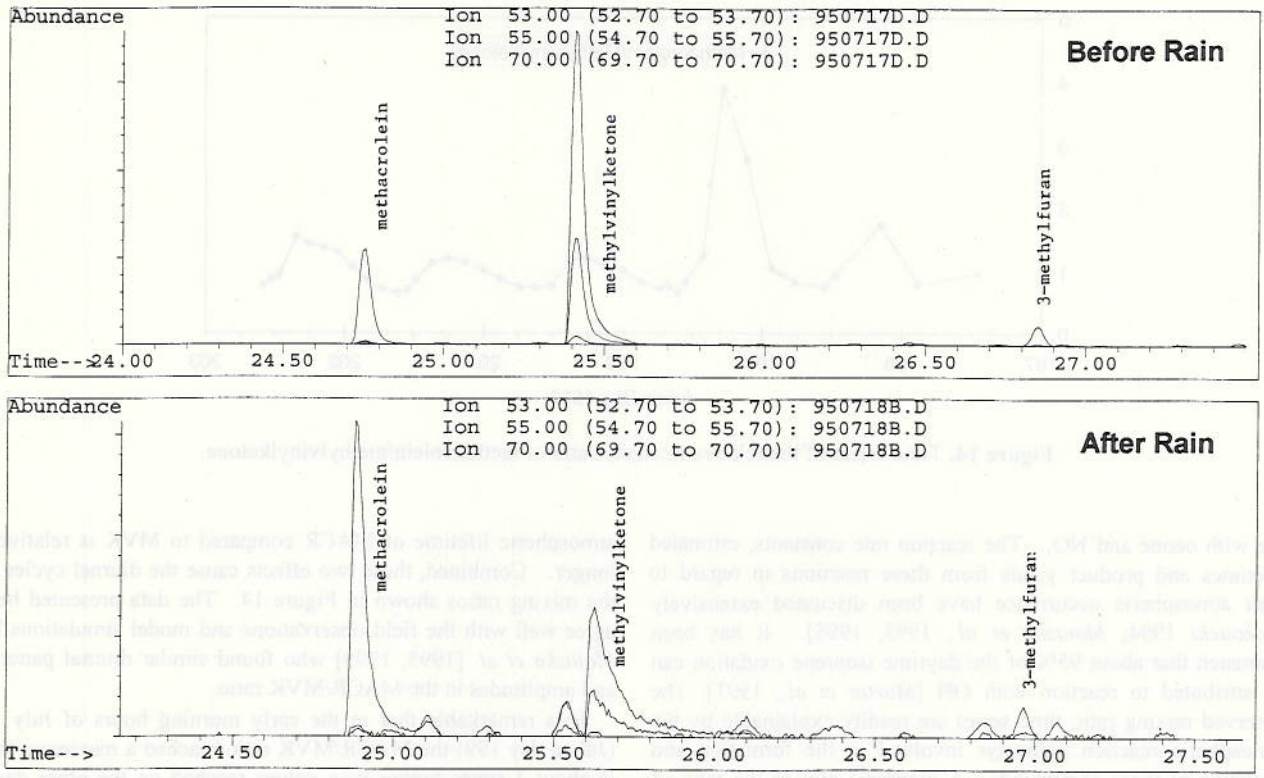

Figure 15. Selected ion current signals of isoprene oxidation products methacrolein, methylvinylketone and 3-methylfuran in two samples collected before (upper window) and after (lower window) a series of three rain thunderstorms on July 17.

reference with regard to the relative abundance and diurnal cycles.

4. Conclusion

The solid adsorbent trapping/cryogenic focusing and in situ GC/MS analysis technique applied here appears to be a viable alternative to the cryogenic sampling technique used by others for the analysis of VOCs, BVOCs, and the biogenic oxidation products MACR, MVK, and 3-methylfuran. This method has advantages such as lower use of cryogen and no need for water and carbon dioxide removal in the sample airflow. A total of 98 VOCs and BVOCs were identified at a forest site near Oak Ridge, Tennessee.

Long-lived compounds, such as CFCs show very steady mixing ratios with little diurnal variations. In contrast, the mixing ratios of the hydrocarbons, BVOCs, and their oxidation products show distinct diurnal patterns. Observed concentration time series of anthropogenic VOCs, CFCs, and BVOCs can be attributed to a number of different factors, such as diurnal emission rate changes from light and temperature dependence of the BVOC emissions, boundary layer dynamics, and to the photochemical depletion. The correlation of the meteorological parameters and mixing ratio time series of anthropogenic compounds, biogenic emissions, and their oxidation products reveals information on the atmospheric oxidation processes and atmospheric transport of these organic compounds under ambient air conditions. At nighttime anthropogenic VOCs are trapped within the shallow nocturnal boundary layer and transported distances of the order of 50-100 km to remote sites without any significant mixing with the overlaying tropospheric air.

Mixing ratio time series of the isoprene oxidation products MACR and MVK confirm previous observations and are in accordance with the current understanding of their atmospheric formation and removal kinetics. Wet deposition of MVK is faster than for MACR and in qualitative agreement with estimates of their wet deposition rates. Attention should be given to bursts of non-isoprene BVOC emissions, such as monoterpenes and *cis*-3-hexenyl acetate as a response to physical stress such as rain showers or possibly heavy winds. The data presented here suggest that emission rates may increase by several factors for a period of about half a day as a response to these events.

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