Title

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Journal

Chemosphere, 38(9)

ISSN

0045-6535

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Publication Date

1999-04-01

DOI

10.1016/s0045-6535(98)00425-1

Pergamon

Chemosphere, Vol. 38, No. 9, pp. 2163-2187, 1999

0045-6535/99/ $ - see front matter

PII: S0045-6535(98)00425-1

BIOGENIC VOLATILE ORGANIC COMPOUND EMISSIONS (BVOCs)

I. IDENTIFICATIONS FROM THREE CONTINENTAL SITES IN THE U.S.

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(Received in USA 31 March 1997; accepted 19 June 1998)

ABSTRACT

Vegetation composition and biomass were surveyed for three specific sites in Atlanta, GA; near Rhinelander, WI; and near Hayden, CO. At each research site emissions of biogenic volatile organic compounds (BVOCs) from the dominant vegetation species were sampled by enclosing branches in bag enclosure systems and sampling the equilibrium head space onto multi-stage solid adsorbent cartridges. Analysis was performed using a thermal desorption technique with gas chromatography (GC) separation and mass spectrometry (MS) detection. Identification of BVOCs covering the GC retention index range (stationary phase DB-1) from approximately 400 to 1400 was achieved (volatilities C_4 - C_{14}). © 1999 Elsevier Science Ltd. All rights reserved

Overall, 63 vegetation species were sampled, and a total of 114 BVOCs were detected and characterized. Structural chemical identification was achieved on approximately 60 % of all compounds, tentative identification on 26 %, and 14 % remained unidentified. Identified compounds include isoprene and BVOCs of the classes of monoterpenes, sesquiterpenes, carbonyl compounds, alcohols, and esters. The MS data was further used to derive emission rate estimates of the identified BVOCs. Even though these data have substantial margins of error, it allows to group BVOCs into the major and minor emissions and derive conclusion on the relative contribution of individual

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compounds to the overall BVOC flux. Results obtained by this method show that besides terpenoid compounds (isoprene, monoterpenes and sesquiterpenes), oxygenated compounds may contribute a rather significant fraction of the total BVOC flux. Compounds of particular importance are *cis*-3-hexene-ol and its derivatives. Limitations of the branch enclosure technique and the analytical approach with their sources of error are critically discussed and evaluated.

1. INTRODUCTION

Many urban areas experience ambient ozone concentrations in excess of the ozone National Ambient Air Quality Standard (NAAQS) and the effects of increased ozone concentrations are of concern for human health (Lippmann, 1991). Ozone is formed through photochemical processes involving emissions of volatile organic compounds (VOC) and nitrogen oxides (NOx). Non-compliance with the ozone NAAQS continues to be a detrimental air pollution problem despite increased efforts to reduce VOC and NOx emissions by implementing stricter emission standards, in particular for motor vehicles, which are a prime contributor to VOC and NOx emissions in urban areas (Johnson, 1995).

It has been shown that biogenic VOCs (BVOCs) emitted from vegetation are of importance for atmospheric chemistry processes and have a significant impact on photochemical processes that form ozone within the planetary boundary layer (Fehsenfeld et al., 1992). In the course of the atmospheric oxidation of BVOCs, short-lived intermediate reaction products such as radicals, peroxides and aldehydes are formed. As a result of the atmospheric reactions of these products, nitrogen oxide (NO) is converted to nitrogen dioxide (NO_2); this conversion is an important precursor reaction to ozone formation. Much research has been undertaken in an effort to better understand and quantify this effect (Lloyd et al., 1983; Chameides et al., 1988,1992; Lopez et al., 1989; Atherton and Penner, 1990; MacKenzie et al., 1991; McKeen et al., 1991; Lin et al., 1992). In addition to efforts to accurately determine anthropogenic emissions of NOx ($NOx = NO + NO_2$) and VOCs, accurate estimates of BVOC fluxes are needed to fully understand the factors contributing to tropospheric ozone formation in both urban and remote areas (Roselle et al., 1991; Roselle 1994). Besides urban ozone air pollution the concurrently observed steady increase of background and rural tropospheric ozone concentrations (Altshuller and Lefohn, 1996) has also been reported to impact forest health and reduce agricultural crop yields (Manning and Krupa, 1992; Runeckles and Chevone, 1992; Chappelka and Chevone, 1992; Herstein et al., 1995). BVOC flux estimates are of fundamental importance for the successful implementation of ozone control strategies, e.g. for anthropogenic VOC and NOx emission management decisions which are required to be implemented in many metropolitan areas in order to comply with the NAAQS.

The major focus of research on BVOC fluxes thus far has been on isoprene (methylbutadiene) (Greenberg and Zimmerman, 1984; Lamb et al., 1985; Adronache et al., 1994; Guenther et al., 1996a). Isoprene has been

identified as the predominant component of the total BVOC emissions. Isoprene has been shown to be emitted in large quantities from deciduous vegetation and, in some cases, from coniferous trees such as spruce (Kempf et al., 1996). However, it has also been noted that plants emit a large number of heavier molecular compounds besides isoprene (Graedel 1979). Quantitative measurements of these "other" BVOC emissions have been far fewer than isoprene measurements because it is significantly more difficult to reliably identify and quantify them. The knowledge of the total amount and the variations of the non-isoprene part of the BVOC flux is of equal importance to include in regional (Geron et al., 1994) and global (Graedel, 1994; Guenther et al., 1995) BVOC emission inventories and in atmospheric chemistry models. An attempt to use a taxonomic methodology for assigning isoprene and monoterpene emission rates to plants occurring in urban forests was recently presented by Benjamin et al. (1996). Here, we describe a simple screening experiment and the results to access the relative importance of individual BVOCs. Emissions from vegetation in the volatility range of approximately propane (C_3) to pentadecane (C_{15}) were measured at three sites in the USA. A companion paper (Helmig et al., 1998a) utilizes this data to extrapolate the results from the branch enclosure level to the landscape scale.

2. EXPERIMENTAL

In the summer of 1993, BVOC fluxes were measured in three ecosystems: (1) Fernbank Forest, an urban forest preserve in Atlanta, GA, (2) Willow Springs, a site within a mixed deciduous and coniferous forest in the Chequamegon National Forest in northern Wisconsin and (3) Temple Ridge, a mixed shrub oak woodland site in western Colorado. Detailed descriptions of these research sites and the methods and results of the ecological characterization have been reported elsewhere (Guenther et al., 1996b; Helmig et al., 1998b; Isebrands et al., 1998).

Branch Enclosure Technique

The branch enclosure system consisted of cylindrical steel wire frames which were 100 cm long, about 50 cm in diameter and covered with photosynthetically active radiation (PAR) transparent 5 mil thick teflon bags (Cadillac Plastics, Denver, CO). One end of the bag was tied around the branch stem and teflon tubing inlet and outlet air flow lines. The volume of the enclosure was about 50 L. Branches with healthy foliage were selected from sunlight portions of trees. Cut ends were immediately placed in water and cut off again for about another 2 cm under water to prevent embolism. The use of cut branches allowed for more stable and controlled sampling procedures, thus minimizing disturbance of foliage. This has an advantage over the use of intact branches which frequently are more difficult or not at all accessible with the chamber system and cannot be sampled without significant disturbance to the branch or the whole tree, respectively. Hydrocarbon-free air with 350 ppm CO_2 (Scott Specialty Gases, Longmont, CO) flowed into the branch chamber at a rate of 10 l min^{-1}, which minimized infiltration of outside air and purged the existing headspace of residual compounds. PAR (LI-1000, LICOR, Lincoln, NE) and enclosure and ambient

temperatures were recorded during all sampling periods. Samples were collected after 10 min enclosure time.

Chemical Analysis

Two independent methods were used to analyze VOCs in the branch enclosure samples. Samples were collected in electropolished stainless steel canisters with a metal bellows pump to about 3 atmospheres pressure. The canister samples were analyzed for their isoprene concentration in the laboratory by gas chromatography (GC) and flame ionization detection (FID). Sample aliquots were cryogenically preconcentrated, injected onto a DB-1 column and separated by temperature-programmed GC (Hewlett Packard 5890, Palo Alto, CA). Details on the method and results of these measurements are reported elsewhere (Guenther et al., 1996b).

A second sample was collected by drawing 0.8 l (2 min sampling time at 0.4 l min^{-1}) of the enclosure air through a multistage solid adsorbent cartridge containing 300 mg Carbotrap C, 200 mg Carbotrap and 200 mg Carbosieve S-III (all adsorbents from Supelco, Bellefonte, PA). This adsorbent combination allowed the analysis of VOCs in the volatility range of approximately C_3 to C_{15}. A detailed description of the preparation, storage and characteristics of these sampling cartridges has been given (Helmig, 1996a). Numerous breakthrough experiments with two of these cartridges collected in series proved that sampling on the front cartridge was quantitative under these conditions. After sample collection the adsorbent cartridges were stored in an ice chest and transported to the NCAR laboratory in Boulder, CO for analysis. In the laboratory, samples were stored in a freezer at -30°C to minimize pre-analysis elution and breakdown of the sample compounds. A number of studies have shown that reasonable stability of VOCs adsorbed onto solid adsorbents can be achieved under proper storage conditions (Vandendriessche and Griepink, 1989; Linquist and Balkeren, 1990; Janson and Kristensson, 1991; Ciccioli et al., 1993; Boehler et al., 1995). Analysis was performed within 1 - 21 days after sample collection using the gas chromatography/mass spectrometry (GC/MS) system illustrated in Figure 1. The trapped VOCs were released from the adsorbent cartridge by temperature controlled thermal desorption at 250°C under a backflush flow of 25 ml min^{-1} of He and purged into a freezeout trap made of open tubular, uncoated, and deactivated fused silica column (ID 0.53 mm) and kept at -175°C. At the end of the thermal desorption cycle the freezeout trap was flash-heated to 75°C by flowing hot water over the silica tubing and the volatilized VOCs were backflushed and injected onto a DB-1 GC column (0.32 mm x 60 m, 1 mm film thickness, J & W Scientific, Folsom, CA)(Helmig, 1996b). The enrichment system was fully automated and computer controlled as described by Helmig and Greenberg (1994). Compound separation was achieved by temperature programmed GC (Model 5890, Hewlett Packard, Wilmington, DE. GC injection was performed at -50°C oven temperature, this temperature was held for 2 min and then a program rate of 6°C min^{-1} was applied to a final oven temperature of 175°C. After the run the column was baked at 250°C for 5 min.). Individual VOCs were identified by MS with electron impact ionization (70eV) in the scan mode (scan range m/z = 33 to 300 [m/z = mass/charge], Hewlett Packard MSD 5970). Semi-quantitative results were derived from the integrated total ion current signals and scaled to an internal standard (IS) of deuterated benzene (44 ng), which was

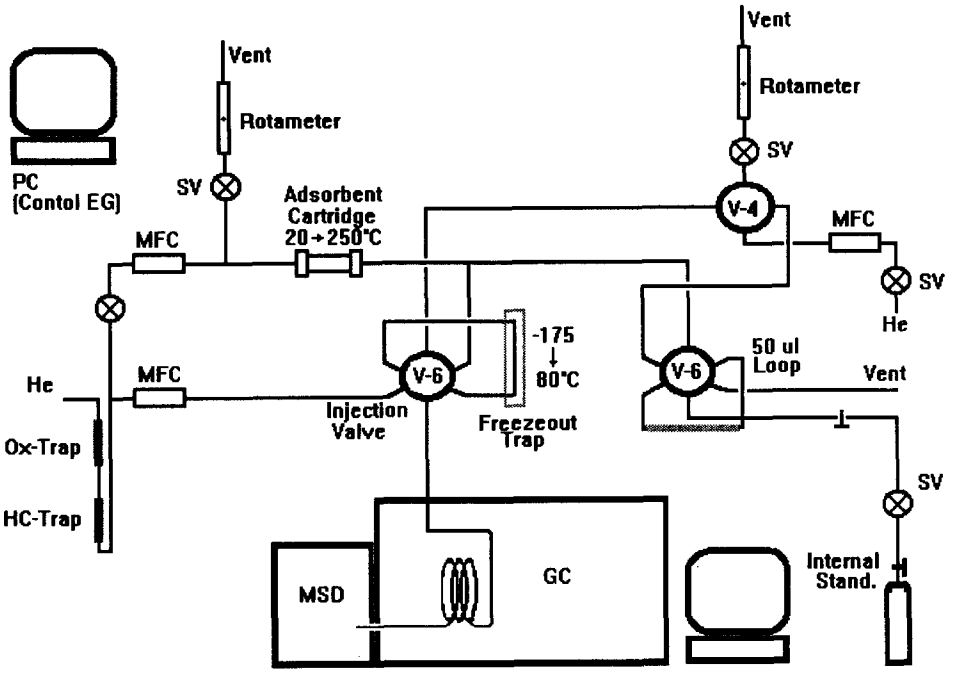

Figure 1:
Analytical GC/MS system with special inlet device for thermal desorption of adsorption cartridges. This figure illustrates an advanced version of the inlet system which allows dry purge of adsorbent cartridges in the foreflush mode. Used abbreviations are: He: helium carrier gas; MFC: mass flow controller; Ox-Trap: oxygen trap; HC-Trap: hydrocarbon trap; GC: gas chromatograph; MSD: mass selective detector; SV: shutoff valve, V-4, V-6: air actuated 4- and 6- port switching valves (Valco, Houston, TX).

added to each sample by purging the contents of a gas standard loop onto the freezeout trap prior to the thermal desorption of the sample. This analytical method is suitable for the analysis of a wide range of VOCs, including isoprene, monoterpenes, sesquiterpenes and more polar compounds such as alcohols, acids and esters. Identification of VOCs was achieved by the interpretation of the compound mass spectra, comparison with MS literature data and also by the determination of the compound linear programmed retention index (RI). For the computation of RIs, a standard sample containing a mixture of C_3 to C_{12} n-alkanes was periodically analyzed under the same conditions as the samples. Compound RIs were calculated using the compound retention time, the respective bracketing n-alkane retention times and the algorithm given by Van den Dool and Kratz (1963). Because n-alkane standard runs and sample runs in some cases were several days apart, the accuracy of the RI determination is limited and estimated to approximately ± 5 RI units.

The sampling and GC/MS analysis technique was verified by collecting a 55 component hydrocarbon standard (which is a test mixture used in the International Hydrocarbon Intercomparison Experiment [Apel and Calvert, 1994]) directly from a compressed air cylinder and after dilution with a) dry and b) humidified zero air. Results from the adsorbent sampling and analysis were compared with reference measurements on a cryogenic

enrichment system with GC/FID analysis and agreed within the deviations expected from the different detector responses. Further tests on biogenic compounds were performed by collecting BVOC standards from a capillary diffusion calibration system (Arnts et al., 1995). This system was used to load cartridges with standard atmospheres of biogenic compound mixtures. Components in this mixture were monoterpenes, oxygenated monoterpenes, sesquiterpenes, alcohols and esters. Samples were collected at varying concentrations, sampling volumes and relative humidities, and results were compared with the on-line analysis on a GC/FID system. Agreement was generally within 80 % for these biogenic compounds with the exception of results for 2-methyl-3-butene-2-ol and β-pinene (see below).

For quantitative data analysis, the total ion current chromatograms were integrated and compound peak areas were divided by the selected ion peak area of the internal standard at m/z = 84, by the biomass in the bag enclosure in gram dry weight (gdw) and by temperature and light correction factors. Temperature and light corrections are important because BVOC emissions strongly depend on these parameters. Conditions during the individual branch enclosure experiments varied; the individual measurements were scaled to normalized conditions of 30°C and 1000 μmol $m^{-2}s^{-1}$ PAR. Temperature and light dependency were considered for isoprene emissions and temperature correction factors ($C_{T,Iso}$) and light correction factors ($C_{L,Iso}$) were calculated using the algorithms developed by Guenther et al., (1991, 1993):

$$C_{T,Iso} = \frac{\exp(95000(T-303)/(8.314 \cdot 303 \cdot T))}{1+\exp(230000(T-314)/(8.314 \cdot 303 \cdot T))} \quad (1)$$

where T is the temperature in K during sampling inside the bag and

$$C_{L,Iso} = \frac{2.878 \cdot 10^{-3} \cdot PAR}{(1 + 0.0027^2 \cdot PAR^2)^{0.5}} \quad (2)$$

where PAR is the PAR during sampling as measured inside the bag.

Monoterpenes and other BVOCs were considered differently. Emissions of monoterpenes have been shown to increase with temperature (Tingey et al., 1991; Guenther et al., 1991, 1993). Some other studies have shown that for some vegetation species monoterpene emissions can also be affected by light (Yokouchi and Ambe, 1984; Steinbrecher 1989; Kesselmeier et al., 1996). Since no measurements were available for the plant species tested, it was assumed that monoterpene emissions depended on temperature only. Furthermore, during most of the enclosure experiments light conditions were within the range where saturation of light dependence of the emissions of these compounds is expected to be achieved. Other BVOCs emitted from vegetation were treated like monoterpenes. Measured fluxes of monoterpenes and other BVOCs were therefore normalized to 30°C using the monoterpene

temperature response relationship developed by Guenther et al., (1991, 1993):

$$C_{T,\,MT+Others} = \exp(0.09 \bullet (T-303)) \quad (3)$$

where T is the bag temperature in K during sampling. This correction algorithm relies on the increase of the BVOC emission rates as a function of the logarithmic increase of the compound vapor pressure with temperature. Currently this is the best universal approach for the correction of emission rates of VOCs that are stored in reservoirs rather than being emitted instantaneously, such as isoprene.

The emission rates (ER) of non-isoprene BVOCs were determined by scaling to absolute values by using measured quantitative isoprene emission rates as reference in each data set according to

$$ER_{BVOCi} = \frac{PAC^{\#}_{BVOCi}}{PAC^{\#}_{isoprene,\,Ref.}} * ER_{isoprene,Ref.} \quad (4)$$

with $PAC^{\#}$ being the peak area count corrected by C_T, C_L, the internal standard peak area count and the gram dry weight (gdw) from the enclosure experiment. The isoprene emission rates of the reference species ($ER_{isoprene,Ref.}$) were measured by sampling headspace from the same bag enclosure into stainless steel canisters and using quantitative GC/FID analysis (see above). Isoprene emission rates at 30°C and 1000 μmol m^{-2} s^{-1} (in μgC gdw^{-1} hr^{-1}) and reference species chosen were 60.7 for Fernbank Forest (average for post oak (79.2), white oak (76.2) and Southern red oak (26.8)), 70.4 μgC gdw^{-1} hr^{-1} (Northern red oak) for Willow Springs and 59.5 μgC gdw^{-1} hr^{-1} (Gambel oak) for Temple Ridge. Quantitative emission rates determined by this branch enclosure technique have been found to be approximately 75 % lower than emission rates measured by cuvette enclosures of individual leaves only (Guenther et al., 1996a,c). Because of their better environmental control, leaf cuvette measurements are thought to give more accurate absolute emission rates than branch enclosure measurements and are therefore very useful for measuring temperature and light response dependencies (Harley et al., 1998). The higher emission rates found in cuvette enclosures are thought to derive from the lack of self shading in the cuvette, a phenomenon that does occur in the branch enclosures.

3. RESULTS

Chromatograms depicting the analysis of branch enclosure samples are shown in Figures 2 to 4. Sample chromatograms chosen are from two deciduous tree species (Northern red oak and yellow birch) and a coniferous tree species (white spruce). The red oak chromatogram (Figure 2) shows a typical emission pattern for an oak species with isoprene being the dominant BVOC emission. The only other two major compounds observed are *cis*-3-hexene-

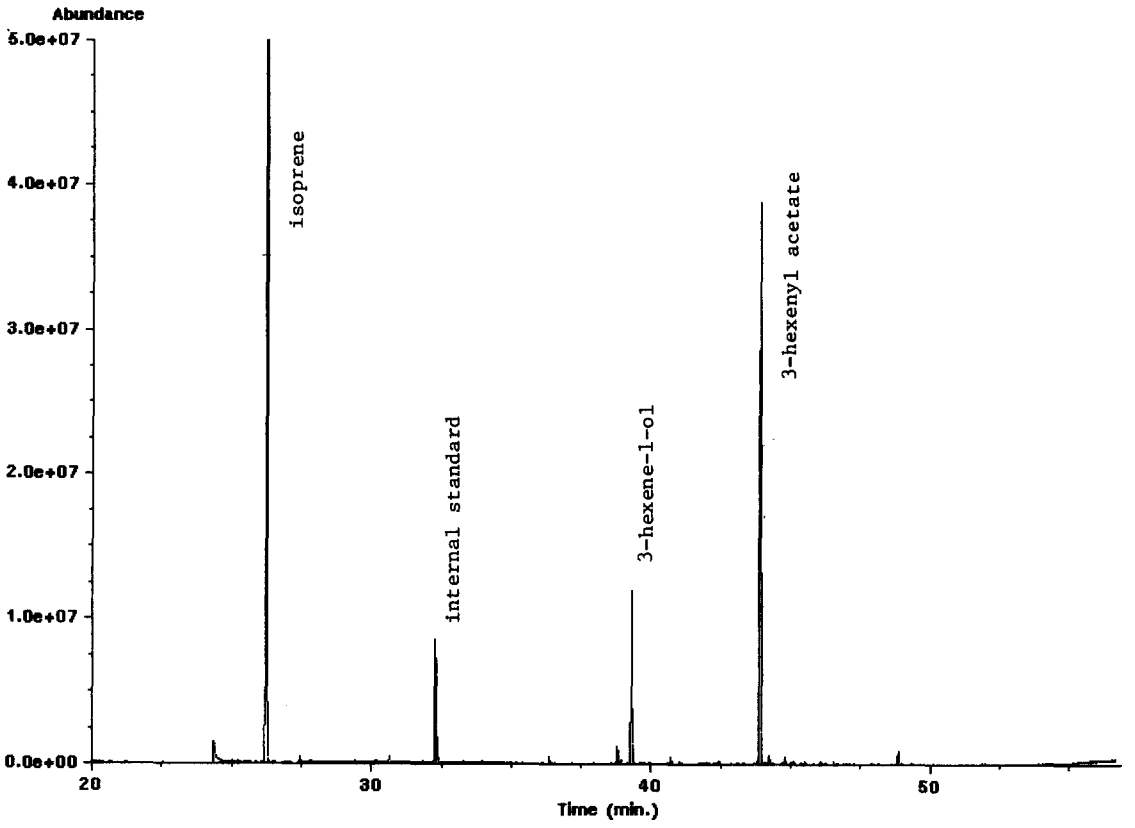

Figure 2:
Sample chromatogram showing the analysis of a 1 L branch enclosure sample of Northern red oak (*Quercus rubra*) with compound identification. This sample was collected at the Willow Springs site near Rhinelander, WI in July 1993.

1-ol and *cis*-3-hexenyl acetate. In contrast, yellow birch (Figure 3), emits only small amounts of isoprene. Additionally, four hexene-ol derivatives and a number of monoterpenes were identified in this emission sample. Spruce trees (Figure 4) show an unusual emission pattern for coniferous trees. Besides emitting monoterpenes they also exhibit substantial emissions of isoprene. For blank measurements samples were collected regularly from empty bags without any enclosed vegetation. Their chromatograms indicated that contaminants introduced from the materials and the analytical procedure used were negligible compared to the signals from BVOC emissions of enclosed vegetation. Minor signals observed in blank runs were common anthropogenic VOCs from ambient air mixing into the branch enclosures (such as halogenated and aromatic compounds) and could easily be distinguished from biogenic emissions.

Table 1 summarizes all VOCs identified in emission samples from a total of 63 plant species sampled at the

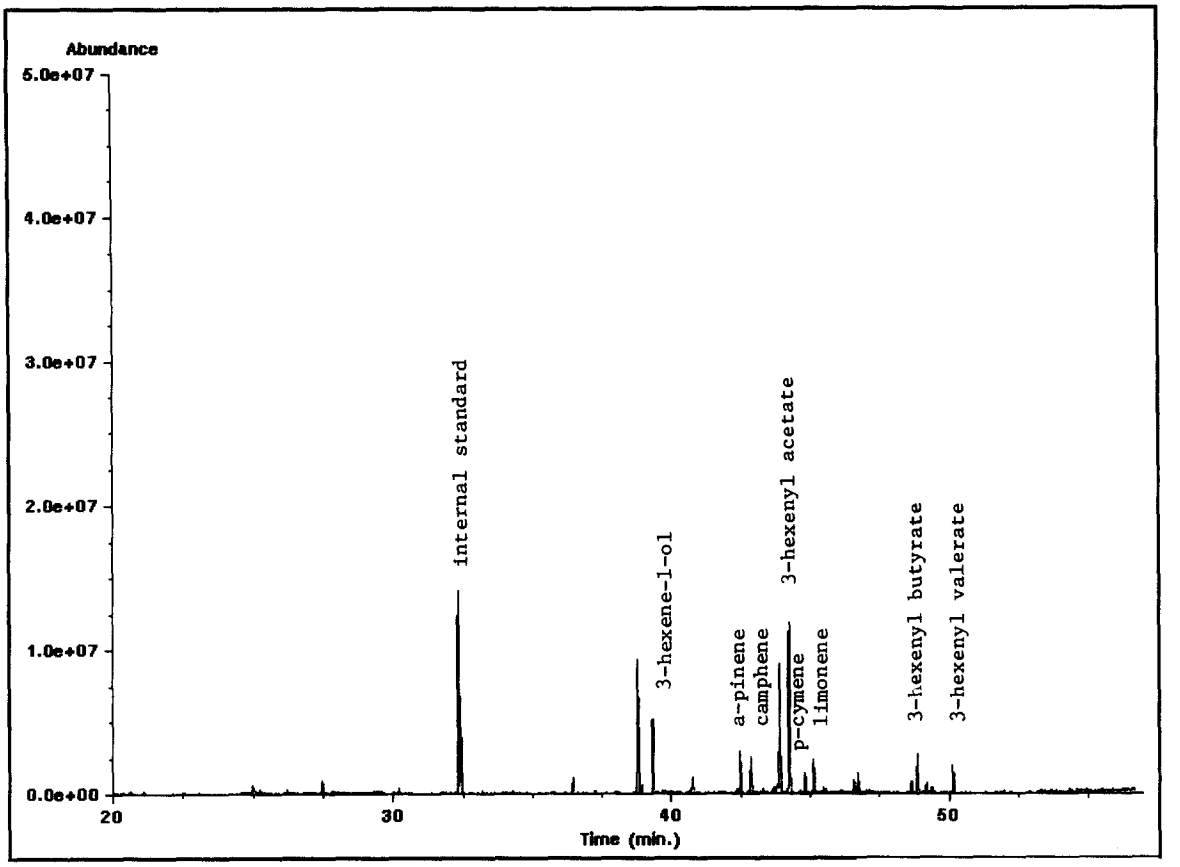

Figure 3:
Sample chromatogram showing the analysis of a 1 L branch enclosure sample of yellow birch (*Betula allagheniensis*) with compound identification. This sample was collected at the Willow Springs site near Rhinelander, WI in July 1993.

three sites in order of their RI on the DB-1 column. Table 1 includes the compound RI, mass spectral data and RI reference data. The listed mass spectral data were obtained by averaging about 6 scans around the peak maxima, performing a background subtraction and normalizing the highest signal (base peak) to 100 %. Some compounds detected in the branch enclosures are likely to be atmospheric degradation products of BVOC emissions rather than primary emissions. For example, methacrolein, methylvinylketone and 3-methylfuran were detected at very low levels and are suspected to be oxidation products of isoprene. It is not clear if these compounds derive from ambient air which infiltrated into the bag or from reactions occurring inside the bag between isoprene emissions and atmospheric reactants such as ozone and the hydroxyl radical, which may be present during the initial stages of enclosure sampling from residual ambient air inside the bag.

A total of 114 compounds were detected and structural identification was achieved on 69 VOCs. In cases

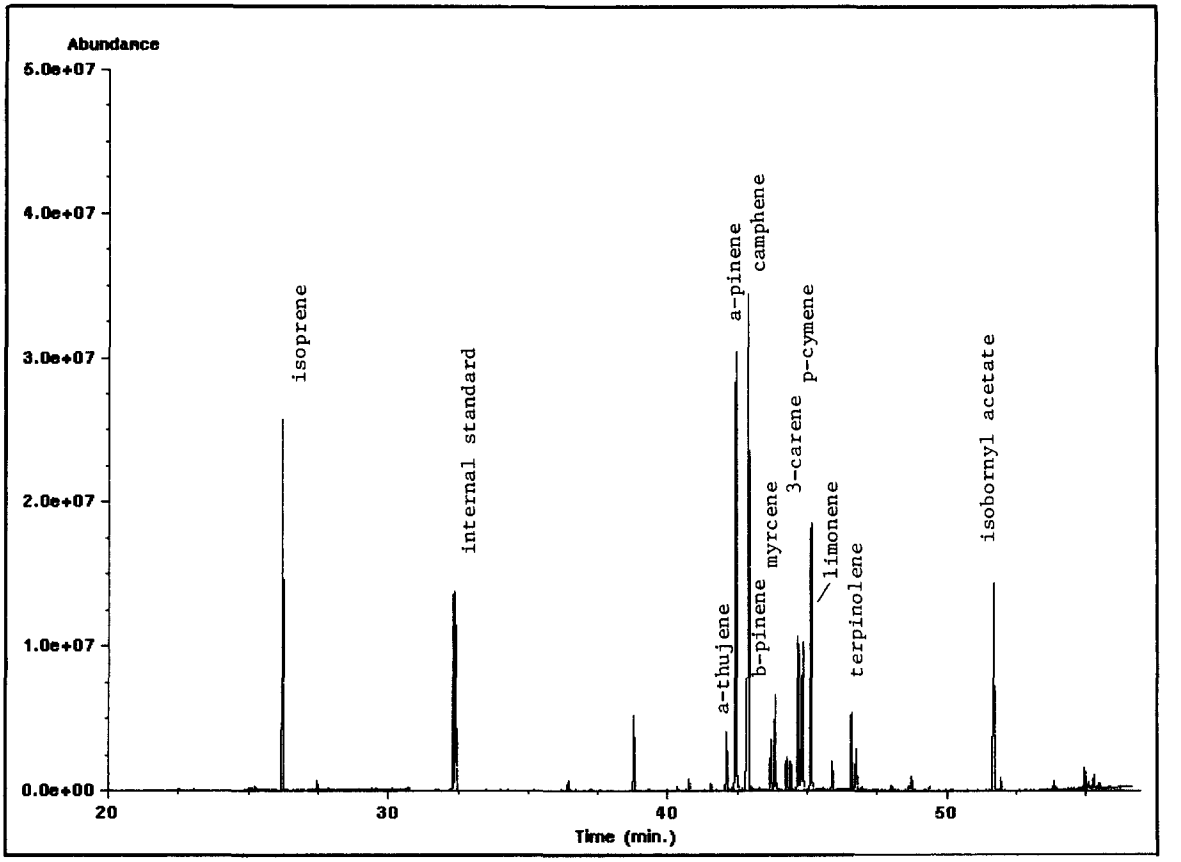

Figure 4:
Sample chromatogram showing the analysis of a 1 L branch enclosure sample of white spruce (*Picea glauca*) with compound identification. This sample was collected at the Willow Springs site near Rhinelander, WI in July 1993.

where insufficient reference data for a reliable identification is available, suggested identifications are given and thus 30 compounds are considered to be identified tentatively. This group includes a number of monoterpenes, for which typical characteristics of a monoterpene mass spectrum (such as signals at m/z = 136, 121, 93, 91) were detected but no isomeric identification was achieved. In addition to the compounds listed, approximately 25 different sesquiterpenes were detected. Sesquiterpenes could not be individually identified because of several reasons. First, the GC elution times were outside of the linear programmed temperature range and no n-alkane reference compounds in this range were available, precluding the determination of RI. Second, only very little MS reference data of sesquiterpenes is available. The tentative identification of sesquiterpenes, however, is unequivocal because of the occurrence of molecular ions at m/z = 204 and other MS ions typical in the fragmentation of BVOCs. Therefore, sesquiterpenes were treated as one general compound class.

Table 2 lists the plant species that were analyzed at the Fernbank Forest site with the BVOCs identified, their

Table 1
Volatile organic compounds identified in branch enclosure experiments from a total of 66 vegetation species sampled at three US sites in Fernbank Forest, Atlanta, GA, Willow Springs, Rhinelander, WI and at Temple Ridge, Hayden, CO with chemical data for identification (linear programmed retention index on DB-1, mass spectrum fragment abundance). Identified sesquiterpenes are not included. Used abbreviations are explained in the footnote.

Compound	Retention Index		Mass Spectrum Fragments (% Relative Abundance)
	Meas.	Reference	
Ethanol	465.0		45(100),46(23),43(20),42(12)
Acetone	488.6	481.2 Po	43(100),58(30),42(10),42(7),40(6),39(5)
Pentane	496.7	500.0 Std	43(100),42(73),41(72),39(33),57(16),72(6)
Isoprene	502.2	503.6 Gr	67(100),53(68),68(66),39(61),40(26),41(25)
Methacrolein	552.7		39(100),41(73),70(57),38(20),42(17),40(16)
Methylvinylketone	568.2		55(100),43(75),70(32),44(24),42(22),39(16)
3-Methylfuran	602.2		82(100,81(61),53(57),39(34),50(24),51(19)
2-Methyl-3-buten-2-ol	603.2		43(100),71(90),41(37),39(31),59(28),53(18)
Acetic Acid	660.4		45(100),43(88),60(48),42(18),44(16),41(7)
2-Ethylfuran	689.8	694 JS	81(100),53(36),39(30),96(25),41(21),44(16)
n.i.	710.5		44(100),94(62),65(50),39(47),66(33),45(23)
3-Methyl-2-butenal isomer (t)	719.2		55(100),83(68),39(66),41(45),84(37),53(23)
3-Methyl-2-butenal isomer (t)	728.7		55(100),39(65),83(62),41(47),84(40),53(22)
n.i.	732.7		39(100),95(85),79(84),81(77),67(71),53(66)
2-Penten-1-ol (t)	757.4		57(100),39(34),41(29),68(23),44(22),67(21)
n.i.	757.5		79(100),77(61),94(37),91(37),39(24),51(13)
2-Methyl-butanoic acid methyl ester (t)	760.0		88(100),57(89),41(71),44(52),39(43),59(26)
n.i.	768.8		73(100),41(100),87(67),56(67),55(61),54(59)
2-Methyl-4-pentenal (t)	776.3		41(100),39(45),69(35),55(30),42(19),83(13)
Hexanal	779.4	776.9 Gr	41(100),44(93),56(74),57(57),39(50),45(29)
1-Octene	788.4	785.6 Sa	41(100),55(87),43(66),39(65),56(63),56(63)
C7H10O isomer (t)	815.0		54(100),67(72),41(62),39(52),110(27),81(27)
C7H10O isomer (t)	818.0		54(100),67(78),41(67),39(55),81(36),68(34)
2-Hexyn-1-ol (t)	820.5		55(100),83(98),39(96),41(94),69(71),42(39)
2-Hexenal	828.7	823.9 Sa, 844.2 Ad	41(100),39(98),55(71),69(53),83(49),42(46)
n.i.	835.0		81(100),91(69),79(57),68(54),67(50),41(43)
cis-3-Hexene-1-ol	840.3	846.3 Ad, 847 JS	41(100),67(99),39(54),55(41),82(36),42(24)
trans-3-Hexene-1-ol (t)	842.3		41(100),67(88),39(49),55(45),82(34),42(22)
2-Hexene-1-ol	849.9	854 JS (trans-isomer)	57(100),41(43),39(31),67(29),82(22),44(17)
1-Hexanol	852.7	851.7 Sa, 860.0 Ad	56(100),43(66),41(66),55(63),42(47),39(36)
C10H16	880.0		41(100),44(90),55(74),70(73),43(72),93(59)
2,4-Hexadienal (t)	881.1		81(100),39(53),53(32),41(32),67(29),96(18)
MT	892.8		93(100),91(41),92(31),79(30),77(30),41(23)
t-Nonene	895.9	887.9 Ad	41(100),56(83),55(79),43(79),39(58),69(45)
Methoxybenzene (Anisole)	900.3	893.9 Sa, 912.1 Ad	108(100),65(68),78(62),39(39),77(19),51(17)
cis-3-Hexenyl formate	902.4	902 JS	67(100),41(40),82(33),39(28),55(13),44(13)
Santolina Triene	905.3	906.4 Ad	93(100),79(74),39(71),91(64),77(61),41(59)
MT	907.3		93(100),80(79),79(71),77(52),91(42),121(40)
Dimethyl-3(5H)-furanone isomer (t)	912.7		97(100),69(87),43(79),39(25),41(19),54(16)
trans-3-Hexenyl formate	913.9		67(100),41(38),82(32),39(23),55(13),54(11)
Dimethyl-3(5H)-furanone isomer (t)	916.6		97(100),69(90),43(85),39(25),41(18),54(17)
5-Ethyl-2(5H)-furanone (t)	917.4		83(100),55(82),57(15),84(14),56(10),54(10)
Tricyclene	920.4	921.7 Ad	93(100),91(35),77(29),92(27),79(27),39(24)
a-Thujene	927.3	925.5 Ad	93(100),91(76),77(54),92(46),119(17),41(16)
MT	931.0		93(100),108(70),91(60),77(34),41(24),79(19)
Benzaldehyde	931.3	927.9 Gr, 927.3 Sa	77(100),106(73),105(69),51(57),50(28),78(18)
a-Pinene	937.8	933.1 Sa	93(100),91(56),92(49),77(46),79(35),39(33)
MT	940.6		79(100),80(58),93(51),77(42),41(38),121(26)
MT	942.3		93(100),91(59),92(48), 39(38), 77(36), 41(31)
1-Heptanol	952.2	953.8 Sa, 963.1 Ad	55(100),70(78),57(71),41(41),39(32),43(18)
a-Fenchene	953.9	944.6 Ad	93(100),79(69),77(58),91(51),121(38),41(38)
Camphene	954.8	946.5 Ad	93(100),121(55),79(42),91(42),77(36),39(35)
Phenol	955.0	958.5 Sa	94(100),66(43),65(29),39(28),40(14),38(12)
6-Methyl-5-heptene-2-one	965.5	968 JS	43(100),41(66),55(46),39(36),69(32),108(27)
MT	967.1		93(100),91(79),121(53),42(18),44(16),41(7)
Artemiseole	967.8	972.0 Ad	43(100),79(80),95(77),67(61),39(57),81(46)
5-Methyl-3-heptanone (t)	969.7		43(100),57(89),72(47),71(36),41(36),99(33)

Compound Name	Retention Index		Mass Spectrum Fragments (% Relative Abundance)
	Meas.	Reference	
Sabinene	972.0	971.3 Ad	93(100),91(61),77(47),79(32),41(23),39(22)
n.i.	973.5		57(100),41(42),56(41),43(30),71(25),85(12)
6-Methyl-5-heptene-2-ol (t)	976.4		41(100),95(91),43(49),69(46),45(46),39(45)
b-Pinene	979.4	970.3 Sa, 975.8 Ad	93(100),41(58),39(36),77(33),91(31),79(29)
1-Methylethenylbenzene	980.0		118(100),,117(79),103(56),115(32),77(31),78(30)
MT	983.1		93(100),41(44),91(44),77(34),79(29),69(21)
Octanal	988.1	980.5 Sa, 1001.0 Ad	41(100),43(67),44(55),57(53),56(51),55(48)
b-Myrcene	988.8	989.8 Ad	41l(100),93(61),69(47),39(45),43(35),55(26)
cis-3-Hexenyl acetate	990.2	987 Std, 987 JS	43(100),67(83),8234),41(21),39(18),54(8)
trans-3-Hexenyl acetate	996.4		43(100),67(38),41(28),39(22),55(15),82(13)
a-Phellandrene	1003.2	1005.2 Ad	93(100),91(73),77(48),92(32),136(16),39(13)
3-Carene	1012.0	1009.4 Ad	93(100),91(57),77(49),79(41),92(30),39(29)
n.i.	1012.7		67(100),81(99),41(93),55(76),39(54),43(39)
a-Terpinene	1020.0	1015.6 Ad	121(100),93(94),91(72),136(60),77(50),79(35)
p-Cymene	1021.0	1022.2 Ad	119(100),91(32),134(23),117(15),39(12),77(11)
1,8-Cineole	1028.3	1028.8 Ad	43(100),41(41),81(35),71(34),57(34),55(33)
n.i.	1031.0		43(100),55(77),111(45),41(37),93(35),39(27)
n.i.	1031.1		57(100),56(41),41(33),43(27),55(17),71(16)
d-Limonene	1033.2	1026.9 Ad, 1026.8 Std	68(100),67(90),93(76),39(44),79(43),53(31)
c-Ocimene	1033.4	1034.9 Ad	93(100),91(53),79(45),77(43),92(41),39(34)
Acetophenone	1043.9	1033.4 Sa	105(100),77(78),51(21),120(18),43(14),50(13)
t-Ocimene	1045.6	1044.8 Ad	93(100),91(63),79(58),77(52),39(44),41(42),
g-Terpinene	1056.6	1057.1 Ad	93(100),91(69),77(47),121(30),136(29),92(29)
1-Octanol	1060.0	1054.4 Sa	41(100),55(95),56(80),43(65),69(53),70(49)
MT	1067.0		79(100),93(49),77(37),107(35),39(33),91(32)
Artemisia Alcohol	1071.8	1080.2 Ad	85(100),41(43),39(26),43(21),55(17),93(13)
Fenchone	1080.4	1085.4 Ad	81(100),69(47),41(39),39(25),117(19),132(16)
p-Cymenene	1083.4	1087.3 Ad	117(100),132(86),115(64),91(55),92(25),65(23)
MT	1083.7		93(100),121(83),91(79),79(57),136(34),43(34)
Terpinolene	1085.3	1086.8 Ad	93(93),121(72),91(62),136(55),77(51),79(46)
MT	1087.2		93(100),121(86),91(75),136(69),77(53),79(46)
Nonanal	1089.9	1082.8 Sa, 1102.8 Ad	41(100),57(78),43(59),39(52),56(43),55(40)
n.i.	1091.1		137(100),45(32),138(13),51(12),77(9),75(8)
a-Thujone	1097.4	1102.4 Ad	81(100),41(94),67(80),68(67),39(63),69(56)
b-Thujone	1108.3	1112.6 Ad	81(100),41(95),67(81),95(66),110(63),68(58)
b-Fenchol	1109.8	1115.0 Ad	81(100),80(62),41(62),43(47),69(37),39(35)
n.i.	1110.0		74(100),87(38),43(27),41(27),55(24),59(16)
n.i.	1113.3		69(100),41(75),39(28),79(18),81(17),53(17)
n.i.	1116.2		91(100),119(82),77(48),39(42),134(37),41(30)
C10H14	1119.3		121(100),91(77),105(60),79(59),77(53),39(41)
C10H14	1122.7		91(100),119(66),77(42),39(38),134(31),41(25)
Camphor	1136.6	1139.8 Ad	95(100),41(79),81(76),39(49),55(45),67(36)
trans-Verbenol	1139.5	1140.2 Ad	91(100),41(81),92(66),55(52),39(43),77(41)
n.i.	1154.0		85(100),43(45),41(28),39(18),93(17),91(14)
Borneol	1162.9	1162.2 Ad	95(100),41(31),67(19),93(18),43(17),55(16)
cis-3-Hexenyl n-butyrate	1170.4	1170 JS	67(100),71(60),82(53),43(50),41(39),39(30)
4-Terpineol	1174.6	1174.8 Ad	71(100),43(73),93(62),41(54),55(42),111(40)
Methyl salicylate	1177.4	1189.4 Ad	120(100),92(66),152(45),121(30),65(18),63(16)
Decanal	1192.1	1184.5 Sa, 1204.3 Ad	41(100),44(88),43(86),57(62),55(52),39(50)
cis-3-Hexenyl iso-valerate	1218.1	1223 JS	67(100),57(83),82(71),41(53),39(26),55(25)
n.i.	1238.2		82(100),110(66),39(65),41(50),109(24),54(23)
n.i.	1240.7		41(100),69(47),55(35),39(32),95(28),67(25)
Thymol	1279.7	1289.5 Ad	135(100),91(35),150(28),43(27),77(23),41(22)
Isobornyl acetate	1282.7	1284.5 Ad	43(100),95(96),93(57),41(45),121(35),55(22)
Dodeceneol isomer (t)	>1300		81(100),67(85),41(83),55(55),43(53),82(43)
Hexene-ol-hexanoate isomer	>1300		67(100),82(74),41(60),55(42),43(41),39(28)
n.i.	>1300		41(100),57(75),43(74),55(66),44(46),39(44)

Footnotes:
used abbreviations: (t): tentative identification, no confirmation by retention index; n.i.: not identified; MT: monoterpene
retention index references: Po: W. Pollock, NCAR, Boulder, CO, unpublished results; Gr: J. Greenberg, NCAR, Boulder, CO, unpublished results; Ad: Adams (1989), JS: Jennings and Shibamoto (1980), Sa: Saddler (1985), Std: from standard measurement.

Table 2
Compound emission rates of VOCs (in ugC hr-1 gdw-1) measured from 19 vegetation species at Fernbank Forest, Atlanta, GA. Tentative identifications and non-identified compounds are given with the retention index for reference with Table 1. All measurements are single determinations.

Compound	Northern Red Oak	Dawn Redwood	Basswood	White Mulberry	Eastern Hemlock	Ironwood	American Beech	Post Oak	Slippery Elm	Tulip Poplar	Ginkgo	Sweet Gum	Loblolly Pine	Red Mulberry	Black Oak	White Oak	Sth. Red Oak	Black Gum
Ethanol										0.5						0.2		
Acetone		0.4								0.2	0.0		0.6			0.1		
Pentane					1.7								0.2			0.2		
Isoprene	140	3.1	0.1	2.9	0.9	1.4	2.9	77	1.4	0.1	0.0	9.3*	0.8	0.5	67	77	29	4.3*
Methacrolein																	1.0	
Methylvinyl ketone																	0.2	
2-Methylfuran																	0.3	
Acetic Acid	0.3	0.1			0.5	0.3	0.3									0.2		
2-Ethylfuran	0.6									0.3								
n.i. (710.5)	0.4									0.0								
Butanoic acid methyl ester										0.2								
Hexanal	0.5	0.9	0.8							0.3								
C7H10 (t) (818.0)		0.3																
C7H10 (t) (815.0)		0.3																
2-Hexenal			1.6				0.3			1.3					0.8			
n.i. (835.0)		0.2																
cis-3-Hexene-1-ol	3.7	0.2	2.0	0.0		0.4	2.5	0.6		0.3						0.1		
trans-2-Hexene-1-ol	0.7		1.0															
1-Hexanol		0.1																
MT (880.0)		0.7																
Methoxybenzene																	0.7	
a-Thujene							0.4					0.2						
MT (931.3)		0.2											0.6					
Benzaldehyde		0.6				0.5		0.3					0.2					
a-Pinene		5.7			0.2	0.3	9.9**	0.3				2.1	1.6				0.2	
1-Heptanol		0.1																
a-Fenchene							0.7						0.9					
Phenol		0.1																
Camphene		2.1			0.2	0.2	5.3**					1.4	0.9				0.2	
MT (967.1)							0.4					0.4						
n.i. (973.5)		1.5																
Sabinene							0.3					0.4						
b-Pinene		0.1				0.2	1.6**					0.2	0.4					
1-Methylethenylbnezene														0.1				
b-Myrcene		0.9					2.3			0.3		0.3						
Octanal	0.8	0.2	1.2		0.2	0.2			0.4				0.2					0.6
cis-3-Hexenyl acetate	2.6		2.3	0.0		1.2	13.3	0.7	2.4						0.3	1.5	0.2	
trans-3-Hexenyl acetate						0.1			0.2									
a-Phellandrene		0.1					3.7					1.8	0.5					
3-Carene		0.6																
n.i. (1012.7)			0.5															
a-Terpinene		0.1					12**					8.3	0.3					
p-Cymene	1.3	0.9			0.2	0.2	17**					10	0.7				0.3	
n.i. (1031.1)			0.2															
d-Limonene		1.4			0.1	0.2	23**	0.2				2.9	0.7				0.2	
c-Ocimene										2.2**								
Acetophenone														0.1				
t-Ocimene										3.3**								
1-Octanol		0.1																
g-Terpinene		0.2					9.2					5.8	0.5					
MT (1067.0)							0.2					0.2						
p-Cymenene		0.5					6.5					0.9	0.2				0.8	
MT (1083.7)		0.1													0.1			
Terpinolene		0.2										1.3						
MT (187.2)							5.0					1.5						
Nonanal	1.8	0.3	1.3		0.3	0.3		0.7	0.9				0.2	0.2			0.1	0.8
n.i. (1110.0)		0.2																
cis-3-Hexenyl n-butyrate							5.2											
Methyl salicylate							0.5								0.3			
Decanal			0.3		0.2		0.3		0.5									
Dodecene-1-ol			0.6															
n.i. (>1300)	0.7	0.1												0.1				
total Sesquiterpenes						0.8		78							8.5	2.6		
total VOC emission rate	150	20	12	2.9	4.4	5.4	120	160	5.9	8.6	0.0	46	5.9	1.1	76	82	30	5.6

* Emission rate is signifcantly lower than reported in previous studies.
** Emission rate is significantly higher than reported in previous studies.

calculated emission rates and the total BVOC emission rate from the sum of all individual BVOCs combined. The respective results for the Willow Springs and Temple Ridge sites are given in Tables 3 and 4, respectively. For the latter two sites a number of plants were measured in replicates. The number of replicates is given and the tabulated data are the average from all measurements in those cases. For Willow Springs a branch enclosure sample collected from willow (*Salix sp.*) was excluded from the data analysis because it was suspected to be contaminated. Also, the branch enclosure experiment on quaking aspen resulted in saturated water vapor levels inside the bag from the high plant transpiration rate. Hence, the chromatogram obtained for this sample showed interferences from water co-elution in the earlier part of the chromatogram which prohibited the quantification of isoprene. Instead, reported literature data on the isoprene emission rate (70 $\mu gC\ hr^{-1}\ gdw^{-1}$) for *Populus* (it al.) species (Guenther et al., 1994; Martin and Guenther, 1995) was used for data analysis.

4. DISCUSSION

The high variability in isoprene and monoterpene emissions from different plant species was the focus of a study recently published by Benjamin et al. (1996). Plants were grouped according to their total emission rates into "High-Emitters" (> 10 $\mu gC\ hr^{-1}\ gdw^{-1}$), "Moderate-Emitters" (1 - 10 $\mu gC\ hr^{-1}\ gdw^{-1}$) and "Low-Emitters" (< 1 $\mu gC\ hr^{-1}\ gdw^{-1}$). The sample chromatograms and the data given in Tables 2 to 4 clearly confirm this high variability in emission patterns and total BVOC emissions. Several plants, such as mulberry, ginkgo, service berry, black cottonwood and white pine were found with low total emission rates (< 3 $\mu gC\ hr^{-1}\ gdw^{-1}$) whereas other species, such as Northern red oak, American beech, post oak, quaking aspen, red raspberry, spruce and rabbit brush were found with emission rates at levels about two orders of magnitude higher (> 100 $\mu gC\ hr^{-1}\ gdw^{-1}$). Similar observations were made by Corchnoy et al. (1992) in a study of 12 urban shade trees. In their study Corchnoy et al. (1992) focused on isoprene and monoterpene emissions. No light correction and normalization for isoprene emissions was made. Total BVOC emission rates found ranged from < 0.03 to 49 $\mu g\ g^{-1}\ h^{-1}$. Total BVOC emission rates for ginkgo (3.0 $\mu gC\ h^{-1}\ gdw^{-1}$) and sweet gum (37 $\mu gC\ h^{-1}\ gdw^{-1}$) are in reasonable agreement with emission rates found here (<0.1 and 46 $\mu gC\ hr^{-1}\ gdw^{-1}$, respectively). A detailed study on light, temperature and seasonal effects of isoprene and monoterpene emissions of a series of spruce species was recently published by Kempf et al. (1996). Emission rates reported by Kempf et al. (1996) were derived after a regression of their data over a series of light and temperature conditions. In contrast, the data obtained in this study is mostly from measurements at one light and temperature condition. The normalized isoprene emission rates from both studies compare reasonably well. Standardized isoprene emission rate results were (this study/Kempf et al., (1996) [in $\mu gC\ hr^{-1}\ gdw^{-1}$]) (2.8/14) for Engelmann spruce, (16/15) for black spruce and (9.5/7.3-12) for white spruce. Total monoterpene emission rates found in this study are generally larger than reported by Kempf et al. (1996) which possibly can be explained by the different analytical techniques, e.g. higher recovery rates from the adsorbent cartridges than from the stainless steel canisters sampling used by Kempf et al. (1996) or from enclosure disturbances (see below). Emission rates found in this study that deviate significantly (more than a factor of 3) from previous studies are indicated in the data tables by

Table 3
Compound emission rates of VOCs (in ugC hr-1 gdw-1) measured from 33 vegetation species at Willow Springs, WI. Tentative identifications and non-identified compounds are given with the retention index for reference with Table 1.
All measurements are single measurements except in cases where the number of replicates is given in parantheses behind the plant species name.

Compound	Speckled Alder (3)	Black Spruce (2)	Beaked Hazelnut (2)	Hop Hornbean (3)	Sugar Maple (2)	Northern Red Oak (2)	Quaking Aspen	Bass-wood	Service Berry	Black Cherry	Cotton Grass	Red Raspberry	White Spruce	Big Toothed Aspen	Paper Birch	Chinese Spruce
Acetone										1.2	0.4	0.5				
Isoprene	0.1	16		0.2		70	70***	0.4			13		9.5	39*		27
2-Methylfuran						0.2					0.5					
2-Ethylfuran	0.2						0.4								0.2	
2-Methyl-4-pentenal (t) (776.3)							0.2									
Hexanal							0.3									
2-Hexenal	1.3		0.6	0.5		0.1	4.7	0.7							0.7	
cis-3-Hexene-1-ol	2.5		1.5	1.3	0.3	3.9	28	2.4			0.3	7.7		1.5	3.3	0.2
trans-2-Hexene-1-ol	0.4						0.4								0.1	
MT (892.8)																0.3
cis-3-Hexene-1-ol-formate							0.4									2.3
MT (97.3)													0.2			
5-Ethyl-3(5H)-furanone (t) (917.4)							0.4									
a-Thujene	0.1												1.6			3.2
MT (931.)																0.2
Tricyclene																
Benzaldehyde			0.2	0.1	0.1	0.1		0.3		0.7		1.0				
a-Pinene	0.6	0.6		0.1		0.2				17**	0.8	80**	13**	1.5	0.4	43
MT (94.6)	0.5												0.2			2.0
a-Fenchene												0.2	0.7			6.2
Camphene		0.4		0.2		0.1				0.9	0.2	1.5	15	0.5	0.3	39
6-Methyl-5-hepten-2-one											11					
5-Methyl-3-heptanone (t) (969.7)																
n.i. (973.5)																
6-Methyl-5-hepten-2-ol (t) (976.4)											0.6					
b-Pinene	2.1									7.4**		9.5**	1.4			23
MT (983.1)	0.1															
Octanal					0.1						0.3					
b-Myrcene										0.6		1.5	2.6			0.9
cis-3-Hexenyl acetate	5.7		3.9	4.9	4.0	22		6.0	0.4	1.6	0.2	25		8.7	6.0	
trans-3-Hexenyl acetate	0.1														0.3	
a-Phellandrene												0.8	1.0			1.9
3-Carene		1.2											4.4			0.7
n.i. (112.7)								1.2								
a-Terpinene													1.0			2.5
p-Cymene	0.1	0.2		0.1		0.4				0.4		1.2	3.9	0.2	0.3	2.4
d-Limonene	1.0	0.7		0.1		0.1				1.7	0.3	3.8	7.9	0.5	0.4	14
t-Ocimene	0.9															
g-Terpinene													0.8			1.6
Fenchone																
p-Cymenene												0.3	2.1			0.6
Terpinolene												1.0	1.6			3.1
Nonanal	0.3	0.1	0.5	0.3	0.8	0.3									0.3	
a-Thujone																
b-Thujone																
b-Fenchol																0.6
Camphor													0.2			
trans-Verbenol																0.4
Borneol																
cis-3-Hexenyl n-butyrate						0.5										
Methyl salicylate																
cis-3-Hexenyl iso-valerate																
Thymol																
Isobornyl acetate	0.7												5.9			
Dodeceneol isomer (t) (>13)																
total Sesquiterpenes	0.3									3.8		73	1.5			
total VOC emission rate:	17	19	6.7	7.8	5.3	98	110	11	0.4	11	27	120	61	13	12	170

*Emission rate is significantly lower than reported in previous studies.
**Emission rate is significantly higher than reported in previous studies.
***Literature value

Table 3 (continued)

Compound	Red Pine	alt.lvd Dogwood	North.White Cedar	Poplar	Eastern Hemlock	Yellow Birch	Black Cottonwood	Sphagnum	Labrador Tea	White Pine	Red Maple	Bog Heather	Black Ash	Balsam Fir	White Ash
Acetone						0.4									
Isoprene			0.3	36*	0.3	1.0	1.9*	4.1	0.9		0.8		0.7		
2-Methylfuran															
2-Ethylfuran															
2-Methyl-4-pentenal (t) (776.3)															
Hexanal															
2-Hexenal						0.2							1.1		0.2
cis-3-Hexene-1-ol		0.3				2.0					2.8	0.4	6.4		1.3
trans-2-Hexene-1-ol													1.2		
MT (892.8)															
MT (907.3)			0.0		0.1									0.3	
trans-3-Hexenyl formate															
5-Ethyl-3(5H)-furanone (t) (917.4)															
a-Thujene			0.1		0.3				0.6	0.3		1.0			
MT (931.0)															
Tricyclene														1.1	
Benzaldehyde					0.0							11			
a-Pinene	0.1	1.8	2.9		2.8	1.2					0.1	7.3	10**	4.6	
MT (940.6)	0.1		0.0		0.0									0.3	
a-Fenchene	0.1		0.2		0.2	0.1			0.8					1.0	
Camphene	1.7	1.0	1.2		1.8	1.1		0.4	13	0.6	0.2		0.3	12	
6-Methyl-5-hepten-2-one															
5-Methyl-3-heptanone (t) (969.7)								1.0							
n.i. (973.5)						0.1									
6-Methyl-5-hepten-2-ol (t) (976.4)															
b-Pinene			0.3		1.3	0.2			4.2			24	4.1	3.0	
MT (983.1)															
Octanal						0.2									
b-Myrcene	0.6		0.1		0.3	0.2			0.5			0.8		1.0	
cis-3-Hexenyl acetate	0.1	8.5				3.4					2.2	1.0	13		1.8
trans-3-Hexenyl acetate															
a-Phellandrene	0.2		0.1		0.1				0.8			0.4		2.0	
3-Carene	0.2		0.1		0.2							1.3	1.3		
n.i. (1012.7)															
a-Terpinene	0.4		0.0		0.1				0.5			0.5		2.8	
p-Cymene	1.9	0.6	0.7		0.6	0.6			4.0			0.7		4.9	
d-Limonene	3.0	0.9	1.0		1.4	1.0			9.1			11	0.4	12	
t-Ocimene									0.4						
g-Terpinene	0.2		0.1		0.2				0.5					1.0	
Fenchone			1.3												
p-Cymenene	1.3	0.2			0.3	0.3			1.7					2.3	
Terpinolene	0.4		0.1		0.3				1.2					1.6	
Nonanal		0.4				0.6							0.4		
a-Thujone			0.9												
b-Thujone															
b-Fenchol			0.2											0.2	
Camphor			0.2		0.0										
trans-Verbenol															
Borneol														0.2	
cis-3-Hexenyl n-butyrate						1.0									
Methyl salicylate						0.3							0.1		
cis-3-Hexenyl iso-valerate						0.8									
Thymol			0.1												
Isobornyl acetate	0.7		0.1		0.3				14			4.0		5.0	
Dodeceneol isomer (t) (>1300)															
total Sesquiterpenes					0.1				14						
total VOC emission rate	11	14	9.8	0.0	11	14	0.0	5.5	65	1.0	6.0	64	28	55	3.3

*Emission rate is significantly lower than reported in previous studies

**Emission rate is significantly higher than reported in previous studies

Table 4
Emission rates of selected BVOCs (in ugC hr-1 gdw-1) measured from 14 vegetation species sampled at Temple Ridge, Hayden, CO. Tentative identifications and non-identified compounds are given with the retention index for reference with Table 1. All measurements are single measurements except in cases where the number of replicates is given in paranthesis behind the plant species name.

Compound	Apple	Subalpine Fir	Aspen	Big Sagebrush	Willow	Englemann Spruce (2)	Lodgepole Pine	Gambel Oak (4)	Rabbit Brush	Choke Cherry	Service Berry	Snow Berry	Salt Bush	Mountain Mahogany
Ethanol								0.4						
Acetone				0.4			0.1	0.2	0.5				1.6	
Isoprene			20*	0.2	56	2.8*	2.7	60	0.2				0.1	
Methacrolein				0.7										
2-Methyl-3-buten-2-ol						0.2	0.5**							
Acetic Acid				0.2										
n.i. (732.7)				0.6										
n.i. (757.5)									0.7					
n.i. (768.8)									0.8					
Hexanal									1.5					
1-Octene				0.1										
2-Hexenal				0.1					0.9		0.1			
cis-3-Hexene-1-ol				0.9				1.9	0.6	11	6.7		0.6	
1-Hexanol									0.6					
1-Nonene				0.4										
Santolina Triene				0.3										
MT (907.3)							0.2							
Dimethylfuranone isomer (t) (912.7)				0.9									1.5	
Dimethylfuranone isomer (t) (916.6)				2.5										
5-Ethyl-2(5H)-furanone (t) (917.4)											1.0			
Tricyclene				5.0			0.3							
a-Thujene		0.2						0.1	0.4				0.1	
Benzaldehyde									0.9					
a-Pinene		0.4	0.4	0.2	0.5	0.4	2.5	0.1	15				15	
MT (940.6)		<0.1					0.2							
a-Fenchene			0.1				0.6		0.3				0.1	
Camphene		2.0	1.0	0.5		0.2	4.1	0.2	2.3				0.7	
Phenol									0.6					
Artemiseole				0.7										
Sabinene		0.1					0.4						0.1	
b-Pinene		0.1					1.6		1.7				1.3	
MT (983.1)			0.2	0.1		<0.1								
Octanal	0.3			0.1	0.3			0.1			0.1	0.3	0.2	
b-Myrcene		0.3	0.3			<0.1	1.0		1.6				0.2	
cis-3-Hexenyl acetate	0.7			7.3				2.4	0.3	4.5	19	1.5	2.0	
a-Phellandrene		1.0	0.6			<0.1	4.1**		7.6				0.5	
3-Carene		0.2	0.1			<0.1	1.0							
a-Terpinene		2.5	0.1			<0.1	8.7**		5.0				0.6	
p-Cymene		1.7	1.0	0.1	1.1	0.2	3.6		6.7				3.4	
1,8-Cineole				0.7										
d-Limonene		2.7	2.1		1.2	0.2	6.7**	0.2	39				2.2	
t-Ocimene								0.8	1.3					
g-Terpinene		0.6	0.1				2.2		2.9				0.7	
MT (1067.0)		0.1					0.3							
Artemisia Alcohol				1.3						<0.1				
p-Cymenene		0.5	0.3			<0.1	1.4		1.4				0.3	
Terpinolene		0.4	0.4				1.5		2.2				0.9	
MT (1087.2)		0.6					2.4							
Nonanal	0.6				0.6	<0.1		0.4		0.2	0.1	0.3		
n.i. (1091.1)									0.4					
a-Thujone							0.2							
n.i. (1113.3)								0.3	1.1					
n.i. (1116.2)									0.5					
C10H14 (1119.3)									4.3					
n.i. (1122.7)									1.9					
Camphor		0.1		1.0		0.2	<0.1							
n.i. (1154.0)				4.0										
Borneol		0.1		0.1										
cis-3-Hexenyl n-butyrate				0.8						0.2				
4-Terpineol				0.1									1.1	
Decanal									0.5					
cis-3-Hexenyl iso-valerate				0.3										
n.i. (1238.2)		0.1												
n.i. (1240.7)		0.1												
Isobornyl acetate		1.8	0.2											
Hexenyl hexanoate isomer (>1300)				0.2										
total Sesquiterpenes		0.8	0.3	1.3		<0.1	0.3	1.5	3.2				15	
total VOC emission rate	1.6	16	28	31	60	4.2	47	68	110	16	27	2.1	48	<0.1

*Emission rate is significantly lower than reported in previous studies.
**Emission rate is significantly higher than reported in previous studies

asterisks.

The three highest total BVOC emission rates for plant species sampled at the three sites (Tables 2 to 4) were found for post oak (160 μgC hr^{-1} gdw^{-1}), Northern red oak (150 μgC hr^{-1} gdw^{-1}), and American beech (120 μgC hr^{-1} gdw^{-1}) at Fernbank Forest; red raspberry (210 μgC hr^{-1} gdw^{-1}), quaking aspen (110 μgC hr^{-1} gdw^{-1}) and Northern red oak (98 μgC hr^{-1} gdw^{-1}) for Willow Springs; and rabbit brush (110 μgC hr^{-1} gdw^{-1}), Gambel oak (69 μgC hr^{-1} gdw^{-1}), and willow (60 μgC hr^{-1} gdw^{-1}) at Temple Ridge. Oak trees measured at all sites were always among the highest overall emitters, mainly because of their high isoprene emission rates. However, considering the decline of these emissions at night, other plant species with high levels of non-isoprene emissions increase in significance when the daily total time-averaged emissions are considered.

While isoprene and monoterpenes have been investigated in numerous studies, many of the other identified BVOCs have not been quantified previously. Because of improvements in the techniques used here a number of more polar compounds, such as alcohols and their esters could be identified. Most of these compounds are derivatives of C_6 alcohols. Some previous studies have reported the identification of some of these compounds, mainly of *cis*-3-hexene-1-ol and *cis*-3-hexenyl acetate in BVOC emissions (Bicchi et al., 1989; Arey et al., 1991; Winer et al., 1992; König et al., 1995). Arey et al. (1991) measured emission rates of 18 agricultural crops and 2 natural plants and found rates up to 1.3 μg $hr^{-1}gdw^{-1}$ for *cis*-3-hexene-1-ol and 3.4 μg $hr^{-1}gdw^{-1}$ for *cis*-3-hexenyl acetate. In our study, we identified several additional C_6 alcohols and esters such as 2-hexene-1-ol, *trans*-3-hexene-1-ol, 1-hexanol, *cis*-3-hexenyl formate, *trans*-3-hexenyl formate, *trans*-3-hexenyl acetate, *cis*-3-hexenyl *n*-butyrate, *cis*-3-hexenyl *iso*-valerate and one hexenyl hexanoate isomer (some of the isomer identifications are tentative because of the lack of standard data [Table 1]). These results indicate that C_6 alcohols/esters constitute a major compound class emitted from vegetation. The highest emissions were observed from deciduous vegetation and often from concurrent isoprene emitters. The most frequently identified C_6 alcohol/ester is *cis*-3-hexenyl acetate. *Cis*-3-hexenyl acetate was emitted to at least some degree from 28 of the plants sampled. The highest emission rates observed were in the 20 to 25 μg C $hr^{-1}gdw^{-1}$ range (Northern red oak, red raspberry, service berry). The atmospheric chemistry of C_6 alcohol/esters has been studied and the tropospheric lifetimes of these oxygenated compounds were calculated to be within a few hours (Arey et al., 1991; Grosjean et al., 1993; Atkinson et al., 1995). Thus, biogenic emissions of these compounds may be of significance to photochemical processes in the planetary boundary layer. *Cis*-3-hexenyl acetate has recently been identified in ambient air within a forest stand at Oak Ridge/TN and was monitored over a one week period. Ambient levels increased after a thunderstorm which may indicate an increased release induced by ambient physical stress factors (Helmig et al., 1998b).

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 event that may trigger the release of these compounds, besides physical damage or mechanical agents, include herbivory (Monson et al.,

1995). Since flux measurements by branch enclosure have a potential of imposing stress on the investigated plant an artificial increase of emissions of these compounds is possible. During this experiment we attempted to insert the branches into the bags as carefully as possible without causing injury to the plant parts enclosed. In addition, branches were kept in their original orientation as much as possible and contact with the chamber walls was minimized. However, despite these precautions, stress-induced emissions of hexenol compounds can not be excluded.

5. METHOD UNCERTAINTIES AND IMPROVEMENTS

A number of procedural weaknesses of the described method were identified during the course of this study and approaches for improvements are discussed in the following:

Branch Enclosure/Temperature and Light Control. It was attempted to keep temperature and light conditions during the enclosure times as close to ambient and as uniform as possible. Median temperature and light conditions for all experiments were 40°C/1700 μmol $s^{-1}m^{-2}$. However, on a few occasions the bag temperature exceeded 45°C due to intense solar radiation. The temperature was taken in the upper and non-shaded area of the bag and should represent a maximum value because a significant fraction of the enclosed branches will be at somewhat lower temperatures from self-shading. The temperature correction algorithms are not expected to adequately correct emission rates under the more extreme conditions. Better temperature and light control could be obtained by shielding the enclosure from excessive solar radiation with, for instance, screens and infrared filters. In this study, isoprene emissions were corrected for light and temperature and other BVOCs were corrected for temperature only. However, as mentioned above, some studies have shown that for some vegetation species, monoterpene emissions can also be affected by light. These effects require more attention and possible light correction algorithms for non-isoprene emissions need to be considered. Furthermore, all BVOC fluxes except for isoprene were calculated using temperature algorithms developed mainly from the response curves of some selected monoterpenes (Guenther et al., 1991; 1993). It is not certain that these algorithms describe the temperature dependence of other BVOCs adequately. In particular, it is uncertain if the significant emission rates found for hexenol derivatives or sesquiterpene compounds in some of the experiments may have been induced by these extreme conditions and if the temperature response algorithms used consider these conditions correctly. Overall, we estimate that the error introduced form the adverse enclosure conditions may well be on the order of a factor of 2-3. However, since all measurements were conducted in similar conditions and then normalized to reference flux measurements the ultimate error is expected to be significantly lower. The error associated with using cut versus intact branches for hydrocarbon emissions has not yet been fully quantified. It has previously been shown that by using careful cutting practices to prevent embolism, isoprene emissions from cut versus intact branches are minimally affected (P. Harley, NCAR, Boulder, Co, unpublished data). Likewise, we estimate the effect for non-isoprene BVOC emissions to be well within the total experimental error.

Sample Collection. Solid adsorbent sampling and analysis methods have become widely accepted for atmospheric analysis during the past 10 years, and have become a routine analytical method in VOC analysis (EPA 1997). Even though a wide range of VOCs can be reliably analyzed by this analytical technique, problems in the analysis of certain BVOCs have been identified. Of critical importance for the reliable analysis of biogenic hydrocarbons is the adsorbent choice. A three layer multibed adsorbent system (Carbotrap C, Carbotrap, Carbosieve S-III) was used in this study. This multi-bed trap has been proven to cover a wide range of VOC volatilities. This method has been extensively tested and reported (Helmig and Greenberg, 1994; Helmig 1996a; Helmig et al., 1996). From our measurements of quantitative hydrocarbon standards we found the reproducibility to be well over the 80 % range. Recent studies have shown that a few individual BVOCs may undergo rearrangement reactions during adsorption/thermal desorption. The major problems identified are the isomerization of β-pinene (Cao and Hewitt, 1993, Arnts et al., 1995) and isoprene formation during the thermal desorption of 2-methyl-3-butene-2-ol (R. Arnts, US-EPA, Research Triangle Park, NC, 1995, personal communication; J. Greenberg, NCAR, Boulder, CO, 1995, personal communication). The emission rates reported here for these compounds should therefore be regarded as lower limits. Recent, unpublished results (R. Arnts, US-EPA, Research Triangle Park, NC, 1995, personal communication; J. Greenberg, NCAR, Boulder, CO, 1995, personal communication) have shown that substitution of the Carbotrap C layer by Porasil or glass beads (Restek, Bellefonte, PA) seems to reduce the β-pinene and methyl-butenol rearrangement reactions. In addition, certain VOCs, such as highly polar compounds or thermally labile species, may not be detected or recovered quantitatively by this method because of their depletion or loss during the analytical sampling and analysis. Because of the lack of analytical standards we have not yet been able to properly investigate recoveries for sesquiterpenes. Hence, reported emission rates for sesquiterpenes should also be considered as lower limits.

Water Management. Vegetation with high transpiration rates can cause moisture levels to build up inside the bag during the enclosure time. A significant fraction of the water vapor is retained on the adsorbent cartridge during sampling and can pose analytical interferences during sample preconcentration and GC analysis and cause a deterioration of the analytical precision. The water trapping capacities of individual adsorbents have recently been determined (Helmig and Vierling, 1995) and strategies for water management (for instance by including a cartridge dry purge step) have been developed (McClenney et al., 1995; Helmig and Vierling, 1995). The GC/MS inlet system (Figure 1) has been modified to include a dry purge step of the adsorbent cartridge prior to the thermal desorption. Also, the IS is now added onto the adsorbent trap at the beginning of the desorption sequence rather than being added onto the freezeout trap to correct for possible reductions in compound recovery from moisture effects, the dry purge step or during thermal desorption.

Chromatography Analysis. Chromatographic peaks were integrated in the total ion current mode (TIC). The response of the mass spectrometer is not strictly proportional to the number of carbons in the molecule, but depends

on a number of parameters such as molecule size, ionization yield and fragmentation pattern. Also, light compounds (such as methanol, formaldehyde, C_3-hydrocarbons) have low molecular mass parent and fragment ions which are precluded from the detection because of the chosen scan window of m/z = 33 to 300. For instance, methanol, which previously has been noted to be a major emission of a variety of plants (MacDonald and Fall, 1993), is not detected by the MS detector because of the lack of mass fragments with m/z > 33. From the analysis of certified VOC calibration standards we found that the TIC quantification has an accuracy error of about 30 % within a compound class. Overall, the uncertainty of the quantitative analysis is estimated to be approximately ± 50 %. Because of the reasons discussed above, the errors for β-pinene and methyl butenol may be higher.

Precision and Accuracy of Quantification. For future studies the GC/MS instrument will be equipped with an additional flame ionization detector (FID). The column flow is split in a manner where 80 % of the flow is directed into the mass spectrometer for compound identification and 20 % into the FID for compound quantification. The FID can be calibrated using certified hydrocarbon standards. With the uniform and linear FID response this method allows substantially improved precision and accuracy for quantitative analysis. These changes will be particularly important for a better quantification of lighter compounds, such as methanol, acetone and ethanol, which can not be measured sensitively in the MS scan mode because of their low m/z ions (see above).

Representativeness. Most measurements were performed on one branch for each plant species at each site. Replicate samples were taken only from a few species at the Willow Springs and Temple Ridge sites. In those repeat measurements, quantitative data of the main emissions usually agreed within ± 30 % with relative standard deviations increasing with lower emission rates. For instance, four replicate measurements on Gambel oak performed at Temple Ridge gave relative standard deviations of 18 %, 26 % and 56 % for isoprene, *cis*-3-hexenyl acetate and *cis*-3-hexene-1-ol, respectively. However, branch to branch and plant to plant variations within the same species may be significantly higher. One reason for this, in the case of isoprene, is that the emission capacity of shade leaves may be significantly lower than the emission capacity of sun leaves, hence the position of the branch on the tree is likely to have an impact on the emission rate (Harley et al., 1996).

Statistical Measures. To improve the significance of quantitative measurements, branch enclosure experiments should best be conducted on two experimental levels: Firstly, vegetation should be screened to identify the major emitters, and secondly the major emitters should be examined more thoroughly by doing replicate sampling on multiple branches of the same vegetation species with replicate analysis. These considerations are of great importance due to the possibility of increased foliar BVOC emissions resulting from improper handling during sampling (Arey et al., 1991). We are currently planning measurements on cloned poplar trees to measure statistical parameters, investigate the degree of disturbance of the branch from the enclosure, and possible differences in emissions between branches attached to the tree and branches that were cut off the tree and kept in water. For an improvement of the statistical significance of the data the major emitters at each site should be analyzed in at least 3

replicates. Furthermore, we did not have a way to standardize the canopy position of the sampled branches. This may add uncertainty to the measurements because the sampled branches may have grown in different light and temperature environments and thus adapted differently (Harley et al., 1996).

6. CONCLUSIONS

Due to the identified and above discussed procedural uncertainties and analytical margins of error, data for absolute emission rates presented in this study should be considered as semi-quantitative and preliminary in nature. However, because random errors are expected to cancel out and the scaling of the bag enclosure results to emission rates from cuvette experiments reduces some of the biases from the enclosure experiment, valuable data is achieved. The results allow to define the range of emission rates for many BVOCs that to date have not been quantified by other methods. Furthermore, it allows to identify the future research focus needed to achieve improvements in the understanding of BVOC fluxes from different ecosystems. More elaborate studies to investigate the degree of emissions of hexene-ol derivatives and the dependency of these emissions on stress factors are needed. Emissions of these compounds may be artificially enhanced from the experimental treatment. However, it appears reasonable that a number of the stress factors encountered in the experiment may also occur under ambient conditions, such as in high wind conditions, thunderstorms or from damage by insects and other plant-feeding animals. Emission estimates based on these enclosure measurements need to be validated by ambient measurements. Other important compound classes that deserve more attention are sesquiterpenes.

ACKNOWLEDGMENTS

This research was partially supported by the U. S. Environmental Protection Agency, Research Triangle Park, NC, under Interagency Agreement Grant No. DW49934973-01-0 and the Southern Oxidants Research Program - Emissions and Effects (SORP-EE) of the Southern Oxidants Study (SOS). We thank the City of Boulder Wastewater Treatment Plant for making us available the GC/MS instrument used for analysis. We thank R. Lowe for valuable help during the field experiment, J. Isebrands, USDA Forest Service, Rhinelander, WI for logistical support at the Willow Springs site and R. Arnts, US Environmental Protection Agency, Research Triangle Park, NC for collaboration on the biogenic VOC calibration system. The National Center for Atmospheric Research is sponsored by the National Science Foundation.

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