

Development of a Novel Sampling Technique for Natural VOC Emissions

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Abstract

In recent years there have been growing interests in the potential environmental effects of global climate change. Of specific interests is the role that climate change may play in altering natural volatile organic compound (NVOC) emissions from trees and the subsequent impact of this perturbation on air quality and ozone formation. A novel vegetation enclosure chamber method was designed and constructed of Tedlar in order to estimate more accurate and precise NVOC emission rates of either small whole plants or the branches of large trees. The enclosure chamber was initially tested in the laboratory and also successfully evaluated in the field. Overall precision for this enclosure was estimated as $RSD < 10\%$ ($n = 9$). The overall errors associated with the enclosure method in a laboratory system might be relatively small (say $< \pm 15\%$); however, they might be rather large (say $\pm 40\%$) in a field-based system. Two consecutive samples were collected on each sampling day from the two pine species during the test period. Slash pine studies showed that the absolute percentage differences between the first and second samples varied from 0.33 to 29%. The percent differences between consecutive emission samples for loblolly pines varied from 0.74 to 24.2%.

Key words : Monoterpene, Slash and Loblolly pines, Natural VOC, Enclosure chamber

1. INTRODUCTION

Recently, there have been growing interests in the potential environmental effects of global climatic change on the natural volatile organic compound (NVOC) emissions from trees and in their impact on air quality and ozone formation (Coeur *et al.*, 1999; Isebrands *et al.*, 1999; Pio *et al.*, 1998; Guenther *et al.*, 1995).

Early measurements of NVOC emissions in the 1960's suggested that, on a regional or global scale,

they overshadowed hydrocarbon emissions from anthropogenic sources (Singh and Zimmerman, 1991; Lamb *et al.*, 1987; Altshuller, 1983; Winer *et al.*, 1983; Dimitriadis, 1981; Rasmussen, 1972). On a global scale, annual NVOC emissions have been estimated at 1,150 Teragrams (Tg) of carbon (C), more than seven times the estimated emissions of anthropogenic hydrocarbons, 150 Tg of C per year (Guenther *et al.*, 1995). Emphasis has been placed on how to model individual key NVOCs, such as α -pinene and isoprene, in chemical mechanisms for air quality simulations (Novak and Reagan, 1986). The accuracies of estimates for both natural and anthropogenic emission inventories, however that are used in these models may be suspect

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(Kim, 2001; Roselle, 1994). This problem, in large part, stems from apparently contradictory measurements of these compounds in ambient air and the further possibility of measurement design errors biasing emissions data. There are three types of field sampling methods and one laboratory method which has been used to measure natural VOC emission rates from trees. The field methods include vegetation enclosure, micrometeorological, and atmospheric tracer techniques (Khalil and Rasmussen, 1992; Winer *et al.*, 1989; Lamb *et al.*, 1987; Lamb *et al.*, 1986; Lamb *et al.*, 1985; Lamb *et al.*, 1984; Arnts *et al.*, 1982; Seila *et al.*, 1982; Zimmerman, 1979a). The laboratory approach involves a gas exchange chamber (Tingey *et al.*, 1979). Micrometeorological and atmospheric tracer techniques have primarily been used as independent checks upon enclosure type measurements although their systems are very bulky and more applicable to the homogeneous plant species.

In order to generate reliable estimates of emissions for specific natural VOCs in a region, more detailed representative and accurate measurements of seasonal

natural VOC emissions are required. A review of the difficulties encountered by previous workers in obtaining representative and reproducible biogenic emission data suggest that the development of a novel sampling approach is needed (Kim, 2001; Kim, 1995).

2. SAMPLING METHOD

A novel dynamic flow-through vegetation enclosure chamber was designed and tested for field sampling of NVOC emissions from pine saplings (see Fig. 1). The technique evolved from the need to estimate or reduce the limitations and disadvantages (e.g., rough handling) inherent in vegetation enclosure technique (VET), such as semi-static enclosures (Lamb *et al.*, 1985; Zimmerman, 1979a) and dynamic flow-through chambers (Winer *et al.*, 1983). The modified enclosure chamber was designed for emission rate studies of either small whole plants (< 1 year old) or the branches of large trees (3~10 years old).

The modified sampling method required enclosing

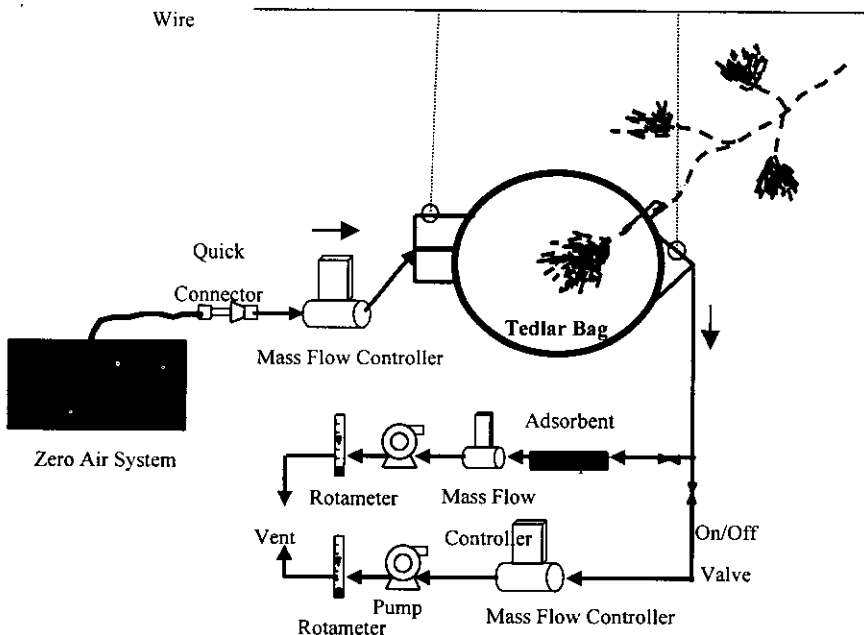


Fig. 1. Sampling train for developed emission rate determinations.

the branch in an open Tedlar bag that was externally surrounded and supported by wire mesh. The enclosure is left open at one end and at both ends of the chamber are mounted on/off valves. At the open end of the bag, two-inch wide and half-inch long lines were drawn in the middle of the outside edge of the bag. A Handy-Lok closure device (Instruments for Research and Industry, I2R, Inc., Cheltenham, PA, U.S.A.) and double-sided sticky tape were used to pinch and seal the open end of the Tedlar bag. A zero-air generator (Model #111, Thermo-Environmental Engineering, U.S.A.) supplied clean air to the inlet of the bag (A). This air flow was used to flush out ambient air that was initially trapped in the bag, in about 3 volume exchanges. The branch emissions and the air flow were then allowed to obtain steady state emission conditions at a flow of 2 liters per minute. The air inside the bag was pulled out by a vacuum pump (B-E), at a flow rate equal to the rate of inflowing zero air. After allowing zero air to flow through the Tedlar bag containing the pine branch for about 35 minutes (4 volume exchanges), a portion of the effluent air stream was redirected to a sorbent trap (B-C) and the remaining air flow (E) was vented to the atmosphere (see Fig. 1). The hydrocarbon emission rates from the branch were estimated from the product of total flow rate through the bag and the sample hydrocarbon concentrations at steady state conditions.

Traceable digital thermometers (# 15-077-8, Fisher Scientific, U.S.A.) with stainless steel thermocouples and some Fisherbrand mercury thermometers were used for enclosure bag and environmental temperature measurements. Another temperature measurement system (#100093, Climatronics, U.S.A.) with a data logger was used to get the ambient temperature data at 1m and 8m levels above ground. All the thermometers were placed away from direct sunlight. It was assumed that needle and bag temperatures are the same as environmental temperature because zero air flowed into the enclosure bag continuously. The air line tube length from the zero air generator to the enclosure system was about 40 m long on purpose, so that the

zero air temperature was adjusted to environmental temperature before it flowed into the enclosure bag. It was necessary to compare environmental temperatures with enclosure bag temperatures. This comparison was carried out using calibrated thermometers, and the bias between the two temperatures was within $\pm 1^\circ\text{C}$. However, the needle temperature was not measured in order to prevent rough handling effects of pine needles.

Flow-in and flow-out of the enclosure bag were controlled by two mass flow controllers (Model#CRP-1A, Hastings, Hampton, VA, U.S.A.) (see Fig. 1). Flow through the sample tube was maintained in the range from 0.15 to 0.25 L/min by a diaphragm pump (Model#JB2N050N, Universal Electric Motor, Owosso, MI, U.S.A.) and monitored using another mass flow controller or a calibrated rotameter (Model#6-1355, Brooks, Hatfield, PA, U.S.A.). The mass flow controllers and rotameter were calibrated every three months under field conditions and also checked with an electronic bubble meter (Gilian model D-800268, U.S.A.) in the field regularly to determine if any substantial changes in calibration had occurred.

The field site was located at the Austin Cary Forest, within a 2 hectare cleared area surrounded by commercial pine plantations. Field samples for emission studies were taken from three to four year old slash (*Pinus elliottii* Engelm.) and loblolly (*Pinus taeda* L.) pine saplings provided by the UF (University of Florida) Forestry School. The samples collected in the field were analyzed in the air pollution laboratories at UF.

3. RESULTS AND DISCUSSION

3.1 Sampling

The enclosure chamber was initially tested in the laboratory with ethanol vapor ($\geq 97\%$ purity, Fisher Scientific, Pittsburgh, PA) and subsequently it was tested with the monoterpenes of interest. Ethanol vapor was continuously injected into a constant flow of zero air through an enclosure chamber (19 L) using a vacuum pump at about 0.15 L/min in order to observe

physical mixing phenomenon and approach to equilibrium of the ethanol vapor inside the Tedlar bag. About 35 minutes was found to be necessary after injection to reach equilibrium, as shown in Fig. 2(a). Also, it was found that the same time (~35 minutes) was necessary to remove all of the ethanol vapor from the enclosure bag when the ethanol injection was terminated (Fig. 2(b)). Emission simulation tests with monoterpene and methanol mixtures were carried out following the initial emission simulation study with ethanol. A Model 355 syringe pump (Sage Instruments, Oregon Research Inc.) was used to generate gas phase terpenes (α -pinene, β -pinene, d-limonene) and p-xylene mixtures in zero-air flowing through the bag. The results of these simulated emission tests with ethanol are presented in Table 1a, and the results of emission simulation tests using methanol-terpene mixtures are shown in Table 1b. Recovery of ethanol continuously injected into the enclosure chamber was 101% ($n=4$, relative std.dev., RSD = 5%) and that for α -pinene was 109% ($n=3$, RSD = 7%). Recoveries of other monoterpenes were similar to that for α -pinene. Overall precision for this enclosure measurement (including the VOC analysis and components of the emission measurement) was estimated as RSD < 10% ($n=9$). The overall errors associated with the enclosure method in a laboratory system might be relatively small (say $< \pm 15\%$); however, they might be rather large (say $\pm 40\%$) in a field-based system, resulting from some unexpected factors, such as temperature variation, wind. In comparison, the overall errors associated with the vegetation enclosure approaches by previous workers (Winer *et al.*, 1983; Zimmerman, 1979a, b) were estimated over 50% in a field based system.

Hydrocarbon emission rates were estimated from the product of total zero air flow rate and hydrocarbon sample concentrations at steady state conditions. The emission rate estimates in appropriate units were derived as follows:

$$[\text{Emission Rate (ng (gdw)}^{-1} \text{ hr}^{-1}) : \text{on Leaf Weight}$$

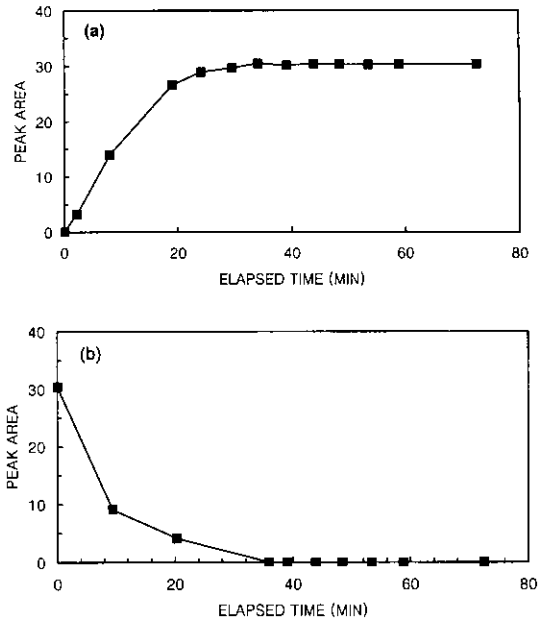


Fig. 2. Approach to equilibrium (a) and flush test (b) using ethanol injection into zero air (~0.15 L/min) and 19 L tedlar bag.

Basis]

$$= [\text{total flow rate (L hr}^{-1}) \times \text{sample concentration (ng L}^{-1}) \div \text{total dry weight of needles (gdw)}] \quad (1)$$

or

$$[\text{Emission Rate (ng m}^{-2} \text{ hr}^{-1}) : \text{on Leaf Area Basis}] \\ = [\text{total flow rate (L hr}^{-1}) \times \text{sample concentration (ng L}^{-1}) \div \text{total surface area of needles (m}^2)] \quad (2)$$

Total dry weight and total surface area of the needles were measured as described elsewhere (Johnson, 1984)

The enclosure chamber was also successfully evaluated in the field as well as in the laboratory. Two consecutive samples (i.e., not simultaneous samples) were collected on each sampling day from the two pine species during the test period. If the emission rates are constant, then the terpene concentrations in the enclosure bag should be also consistent after an exposure period of 35 minutes to allow for equilibrium. Slash pine studies showed that the absolute percentage differences between the first and second samples vari-

Table 1a. Testing of a modified enclosure technique.

Observation #	Emission Rate (ER) for Ethanol ($\mu\text{g}/\text{min}$)	Measured ER for Ethanol ($\mu\text{g}/\text{min}$)	Recovery (%)
1	387.9	382.7	98.7
2	532.9	572.1	106
3	580.2	549.0	95
4	383.9	407.2	106

Note : The flow rate of zero air was 2 liters per minute.
The recovery of ethanol was $101 \pm 6\%$.

Table 1b. Testing of a modified enclosure technique.

Observation #	Emission Rate (ER) for α -pinene ($\mu\text{g}/\text{min}$)	Measured ER for α -pinene ($\mu\text{g}/\text{min}$)	Recovery (%)
1	0.140	0.141	99.3
2	0.111	0.125	113
3	0.110	0.127	115

Note : The recoveries of the other hydrocarbons were very similar to that for α -pinene.

Table 2. Reproducibility of slash pine emission measurements.

Experimental Cases	Temperature ($^{\circ}\text{C}$)	Total ER ($\mu\text{g}/\text{m}^2\text{-hr}$)	% difference
Case 1	15.5	4.79	-16
	15.8	4.03	
Case 2	22.4	84.0	+4.4
	21.7	87.7	
Case 3	18.5	29.0	-14
	19.0	24.9	
Case 4	25.8	310.8	+29
	26.7	401.0	
Case 5	28.5	193.1	+0.3
	29.1	193.7	
Case 6	28.0	173.6	-11
	29.0	155.1	

Note: % difference based on first emission data set.

ed from 0.33% to 29%, as shown in Table 2. The percent differences between consecutive emission samples for loblolly pines varied from 0.74% to 24.2% (see Table 3). Weather conditions that existed when the maximum bias (24%) was observed between the paired samples were not normal. Approximately three hours before setting up the enclosure system, on this particular day there was a rain event.

Table 3. Reproducibility of loblolly pine emission measurements.

Experimental Cases	Temperature ($^{\circ}\text{C}$)	Total ER ($\mu\text{g}/\text{m}^2\text{-hr}$)	% difference
Case 1	14.1	3.62	-13.5
	14.4	3.13	
Case 2	16.3	4.07	-0.74
	16.9	4.04	
Case 3	12.2	1.47	-11.6
	12.3	1.30	
Case 4	23.1	2.60	-19.2
	23.3	2.10	
Case 5	27.6	11.77	-3.57
	27.2	11.35	
Case 6	25.9	5.78	-24.2
	26.4	7.18	

Note: % difference based on first emission data set.

3.2 Analysis

In this research, a concentration was achieved by adsorption on Tenax-TA sorbent followed by use of an automated desorbing and cryogenic focusing system (Model 5010GT, Tekmar, Cincinnati, OH). Conditions for sampling and analysis were specifically developed, and used for monoterpene measurements. Both the GC-ITD (Perkin Elmer Model 8420, Ion Trap Detector (ITD): Finnegan) and GC-FID (Perkin Elmer Model 8500) analytical systems were equipped with Tekmar 5010 sample introduction systems enabling automated transfer of VOCs from sorbent traps or Tedlar bags to the GC. Because the same source (manufacturer) and similar models of gas chromatographs (PE, GC-8420 and GC-8500) were selected for use, almost identical GC capillary columns were installed so that the same analysis parameters could be used in both systems (GC/ITD/Tekmar and GC/FID/Tekmar). This similarity in analytical systems made it possible to easily compare and interpret the mass spectrometric and flame ionization chromatograms acquired from both systems. More specific details of the configurations and operating conditions for the GC and desorber systems were described elsewhere (Kim, 2001; Kim, 1995).

Samples of compounds under investigation were

obtained from commercial sources. These compounds included α -pinene (99% purity), camphene (85% purity), β -pinene (99% purity), myrcene (77.2% purity), Δ^3 -carene (95% purity), d-limonene (97% purity) and p-xylene (99% purity). All of these chemicals were purchased from Aldrich Chemical Company

(Milwaukee, MD). A mixture of d-limonene and β -phellandrene (60 and 40% purity respectively) was donated from Dr. Janet Arey of the University of California, Riverside. Calibration standards were prepared by making individual monoterpene hydrocarbons and p-xylene dissolved in ACS reagent grade me-

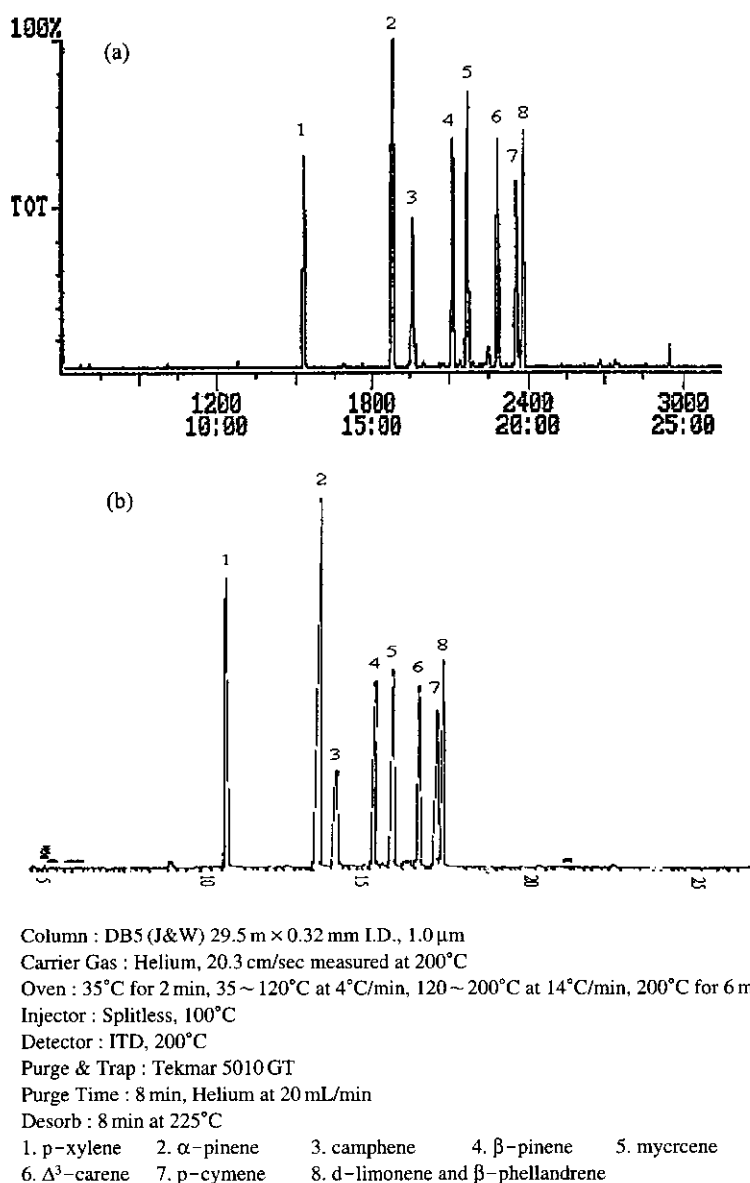


Fig. 3. Typical gas chromatogram for a standard mixture of terpene compounds and p-xylene Internal standard for the GC/ITD/Tekmar system (a) and GC/FID/Tekmar system (b).

thanol (optima grade, Fisher). 1 μ l of standard solution was spiked into Tenax tubes, followed by purging the tubes with 150 mL pure He to elute the solvent. Initially, each individual organic compound was injected into the GC/ITD and GC/FID systems using the respective Tekmar thermal desorbers in order to establish relative retention times and acquire mass spectral cracking patterns (see Fig. 3). *p*-xylene (99% purity) was selected as an appropriate stable and reproducible, non-interactable internal standard in both laboratory and field.

Initially, the EPA default desorb temperature of 190°C was used in conjunction with a 5 minute desorb time, however, these conditions caused incomplete desorption of monoterpenes from Tenax sorbent. When a mixture of the same amounts of α -pinene, β -pinene, *d*-limonene was injected into a GC column at the predetermined (EPA default) Tekmar desorb conditions, the GC peak areas (i.e., FID response) for these

compounds were considerably different, due to terpene losses and residuals retained by the Tenax sorbent. The desorb temperature (190°C) was increased to 225°C and the desorb time increased to 8 minutes. With these modified thermal desorb conditions, it was found that no measurable terpene residuals were left on the Tenax sorbent and the FID sensitivities for the same amount of the three terpene compounds tested were very similar.

From studies of Tenax sorbent in stainless steel and glass sampling tubes it was determined that adsorption of monoterpene hydrocarbons on Tenax-TA (60/80 mesh, Alltech, Deerfield, IL) in a glass tube container was the most reproducible and efficient method for the recovery and analysis of monoterpene hydrocarbons. This observation was particularly true when these sampling tubes were used in conjunction with a commercial thermal desorption and cryofocusing system (Tekmar 5010GT) coupled to a GC.

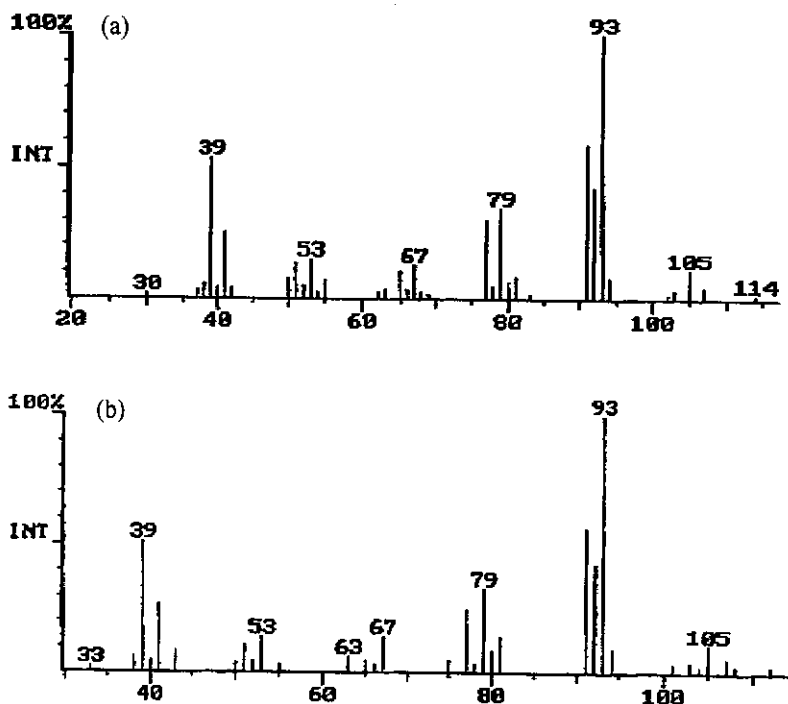


Fig. 4. Mass spectral cracking pattern for α -pinene from a standards (a) and field samples (b) using perkin elmer 8500GC/ITD/Tekmar system.

Monoterpene hydrocarbon collection sampling tubes were prepared by filling individual pyrex glass tubes (o.d. 1.27 × 18.1 cm long) (Southern Scientific, Micanopy, FL) with about 900 mg of Tenax-TA held in place with silanized glass wool (Supelco, Bellefonte, PA). The preconditioned sample tubes, were then individually inserted into the Tekmar desorber system oven. The tube was purged for 5 minutes and baked at 250°C for 20 minutes. After conditioning the sampling tube twice, it was then checked for the presence of impurities (background). The preconditioned clean sample tubes were stored in sealed trap sampling containers (#14-1463-000, Tekmar, Cincinnati, OH) during storage and transport. Sampling containers were stored in an ice-cooled insulated box during transport to and from the field site.

Helium carrier gas flow rate selection for the GC systems and temperature programming of the DB-5 capillary columns were optimized for rapid, high resolution separation of biogenic hydrocarbon sample components. In the analyses of biogenic hydrocarbons using the GC-FID/ITD systems, identical temperature programs for the column ovens were used. The DB-5 columns were held at 35°C for 2 minutes and then ramped at 4°C per minute to 120°C. At 120°C the ramp rate was increased to 14°C per minute up to 200°C and finally the columns were held at 200°C for 6 minutes.

Field Blanks and calibration checks using calibration standard #3 were run before and/or after field sample runs in order to check GC response and retention time precision and to establish whether any impurities were present in field samples as a result of contamination. It is seen that recovery (accuracy) is within 100 (5% and precision (RSD < 2%) was very good. The Control charts also showed that the analysis instrument was in control all of the time.

Field samples were quantified using the Tekmar/GC/FID system. Occasionally, field samples were analyzed with the Tekmar/GC/ITD system to verify the terpene content from mass spectral cracking patterns and relative retention times. The precision of retention time data (% relative standard deviation, RSD, < 0.25

%, n = 55) for standard and field samples injected to the GC/FID system were excellent for every sample component injected to the system during the project period. Identical mass spectral data and relative retention times are found between standards and field samples, as shown in Fig. 4.

4. CONCLUSIONS

A portable vegetation enclosure chamber was designed and constructed of Tedlar in order to estimate more accurate and precise NVOC emission rates of either small whole plants or the branches of large trees. The enclosure chamber was initially tested in the laboratory, and also successfully evaluated in the field.

Overall precision for this enclosure measurement (including the VOC analysis and components of the emission measurement) was estimated as RSD < 10% (n = 9). The overall errors associated with the enclosure method in a laboratory system might be relatively small (say < ± 15%); however, they might be rather large (say ± 40%) in a field-based system.

The proved VET technique was applied to two different pine species: slash and loblolly pines. Two consecutive samples were collected on each sampling day from the two pine species during the test period. If the emission rates are constant, then the monoterpene concentrations in the enclosure bag should be also consistent after an exposure period of 35 minutes to allow for equilibrium. Slash pine studies showed that the absolute percentage differences between the first and second samples varied from 0.33% to 29%. The percent differences between consecutive emission samples for loblolly pines varied from 0.74% to 24.2%.

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REFERENCES

- Altshuller, A. (1983) Review: Natural volatile organic substances and their effect on air quality in the United States. *Atmospheric Environment*, 17, 2131–2165.
- Arnts, R.R., W.B. Peterson, R.L. Seila, and B.W. Gay (1982) Estimates of alpha-pinene emissions from a loblolly pine forest using an atmospheric diffusion model. *Atmospheric Environment*, 16, 2127–2137.
- Chameides, W.L., R.W. Linsay, J. Richardson, and C.S. Kiang (1988) The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. *Science*, 241, 1473–1475.
- Coeur, C., V. Jacob, and P. Foster (1999) Aerosol formation from the gas-phase reaction of hydroxyl radical with the natural hydrocarbon bornyl acetate. *Atmospheric Environment*, 33, 1615–1620.
- Dimitriadis, B. (1981) The role of natural organics in photochemical air pollution. *J. Air Pollut. Control Assoc.*, 31, 229–235.
- Guenther, A., C.N. Hewitt, D. Erickson, R. Fall, and C. Beron (1995) A global model of natural volatile organic compound emissions. *J. Geophys. Res.*, 98, 12609–12617.
- Guenther, A.B., P.R. Zimmerman, L. Klinger, J. Greenberg, C. Ennis, K. Davis, W. Pollock, H. Westberg, E. Allwine, and C. Geron (1996) Estimates of regional natural volatile organic compound fluxes from enclosure and ambient measurements. *J. Geophys. Res.*, 101, 1345–1359.
- Guenther, A., J. Greenberg, P. Harley, D. Helmig, L. Klinger, L. Verling, P.R. Zimmerman, and C. Geron (1996) Leaf, branch, stand landscape scale measurements of volatile organic compound fluxes from U.S. woodlands. *Tree Physiology*, 16, 17–24.
- Isebrands, J.G., A.B. Guenther, P. Harley, D. Helmig, L. Klinger, L. Vierling, P. Zimmerman, and C. Geron (1999) Volatile organic compound emission rates from mixed deciduous and coniferous forests in Northern Wisconsin, USA. *Atmospheric Environment*, 33, 2527–2536.
- Johnson, J.D. (1984) A rapid technique for estimating total surface area of pine needles. *For. Sci.*, 30, 913–921.
- Khalil, M.K.A. and R.A. Rasmussen (1992) Forest Hydrocarbon Emissions: Relationships Between Fluxes and Ambient Concentrations. *J. Air Waste Manage. Assoc.*, 42, 810–813.
- Kim, J.C., E.R. Allen, and J.D. Johnson (1995) Terpene emissions in a southeastern pine forest, in proceedings (Paper#95-WA74A.03) of 88th Annual Meeting of AWMA, San Antonio, Texas, June 18–23.
- Kim, J.C. (2001) Factors controlling natural VOC emissions in a southeastern US pine forest, *Atmospheric Environment*, 35(19), 3279–3292.
- Lamb, B.K., H.H. Westberg, T. Quarles, and D.L. Flyckt (1984) Natural Hydrocarbon Emission Rate Measurements from Selected Forest Sites. EPA-600/S3-84-001: U.S. EPA.
- Lamb, B.K., H.H. Westberg, G. Allwine, and T. Quarles (1985) Biogenic hydrocarbon emissions from Deciduous and coniferous trees in the United States. *J. Geophys. Res.*, 90, 2380–2390.
- Lamb, B.K., H.H. Westberg, and G. Allwine (1986) Isoprene emission fluxes determined by an atmospheric tracer technique. *Atmospheric Environment*, 20, 1–8.
- Lamb, B.K., A. Guenther, D. Gay and H.H. Westberg (1987) A national inventory of biogenic hydrocarbon emissions. *Atmospheric Environment*, 21, 1695–1705.
- Lamb, B.K., D. Gay, H. Westberg, and T. Pierce (1993) A Biogenic hydrocarbon emission inventory for the U.S.A using a simple forest canopy model. *Atmospheric Environment*, 27A, 1673–1690.
- Novak, J.H. and J.A. Reagan (1986) A Comparison of Natural and Man-made Hydrocarbon Emission Inventories Necessary for Regional Acid Deposition and Oxidant Modeling. In the 79th Air Pollution Control Association Annual Meeting. U.S. EPA.
- Pio, C.A. and A.A. Valente (1998) Atmospheric fluxes and concentrations of monoterpenes in Resin-Tapped pine forests. *Atmospheric Environment*, 32, 683–691.
- Rasmussen, R.A. (1972) What do the hydrocarbons from trees contribute to air pollution?. *J. Air Pollut. Control Assoc.*, 22, 537–543.
- Roselle, S.J. (1994) Effects of biogenic Emission uncertainties on regional photochemical modeling of control strategies. *Atmospheric Environment*, 28, 1757–1772.

- Seila, R.L., R.R. Arnts, F.L. Kuntz, F.L. Mowry, K.R. Knoerr, and A.C. Dungeon (1982) Measurement of Loblolly Pine Terpene Emissions. EPA/600/S3-82-010: U.S. EPA. pp. 1-4.
- Singh, H.B. and P.B. Zimmerman (1991) Atmospheric distributions and sources of non-methane hydrocarbons. *Advances in Environmental Science and Technology: Gaseous Pollutants*, ed. J.O. Nriagu, 117-235. Wiley, New York.
- Tingey, D.T., M. Manning, L.C. Grothaus, and W.F. Burns (1979) The influence light and temperature on isoprene emission rates from live Oak. *Physiologia Plantarum*, 47, 112-118.
- Winer, A.M., J. Arey, R. Atkinson, and S.M. Aschmann (1992) Emission rates of organics from vegetation in California's Central Valley. *Atmospheric Environment*, 26, 2647-2659.
- Winer, A.M., J. Arey, S.M. Aschmann, and R. Atkinson (1989) Hydrocarbon Emissions from Vegetation found in California's Central Valley. Contract #A732-155, Air Resour. Board, Sacramento.
- Winer, A.M., D.R. Fitz, and P.R. Miller (1983) Investigation of the Role of Natural Hydrocarbons in Photochemical Smog Formation in Calif., Contract #A0-056-32, Air Resour. Board, Sacramento.
- Zimmerman, P.R. (1979a) Testing of Hydrocarbon Emissions from Vegetation, Leaf Litter and Aquatic Surfaces, and Development of a Methodology for Compiling Biogenic Emission Inventories. EPA-450/4-79-004: U.S. Environmental Protection Agency (U.S. EPA).
- Zimmerman, P.R. (1979b) Determination of Emission Rates of Hydrocarbons from Indigenous Species of Vegetation in the Tampa/St Petersburg Florida Area. EPA-904/9-77-028: U.S. EPA.