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Development of an Automated Cylindrical Ion Trap Mass Spectrometer for the Determination of Atmospheric Volatile Organic Compounds

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Volatile organic compounds released from the biosphere are known to have a large impact on atmospheric chemistry. Field instruments for the detection of these trace gases are often limited by the lack of instrument portability and the inability to distinguish compounds of interest from background or other interfering compounds. We have developed an automated sampling and preconcentration system, coupled to a lightweight, low-power cylindrical ion trap mass spectrometer. The instrument was evaluated by measuring isoprene concentrations during a field campaign at the University of Michigan Biological Station PROPHET lab. Isoprene was preconcentrated by sampling directly into a short capillary column precooled without the aid of cryogenics. The capillary column was then rapidly heated by moving the column to a preheated region to obtain fast separation of isoprene from other components, followed by detection with a cylindrical ion trap. This combination yielded a detection limit of ~80 ppt (parts per trillion) for isoprene with a measurement frequency of one sample every 11 min. The data obtained by the automated sampling and preconcentration system during the PROPHET 2005 campaign were compared to those of other field instruments measuring isoprene at this site in an intercomparison exercise. The intercomparisons suggest the new inlet system, when coupled with this ion trap detector, provides a viable field instrument for the fast, precise, and quantitative determination of isoprene and other trace gases over a variety of atmospheric conditions.

Recent research in atmospheric chemistry has shown that biological volatile organic compounds (BVOCs) released from the biosphere have significant impacts on climate, air quality,

and ecosystems.¹ Plants are estimated to emit greater than 1.2×10^{12} kg of these BVOCs per year to the atmosphere.¹ Many individual compounds emitted by plants contributing to this total have now been identified.^{1,2} However, an estimated 5×10^{11} kg of this total is made up of one dominant species, isoprene (2-methyl-1,3-butadiene, C_5H_8). The emission rate of this biogenic compound is primarily driven by temperature and light levels, with possible links to plant stresses such as high temperature, lack of water, and local ozone concentrations.^{3–6}

Isoprene possesses two carbon–carbon double bonds, making it extremely reactive when released into the atmosphere,^{7,8} as these bonds are susceptible to attack by atmospheric oxidants. For example, the reaction of isoprene with OH is the major loss route for isoprene, occurring with a rate constant of 1×10^{-10} cm³ molecule⁻¹ s⁻¹, almost that of the molecular collision frequency.⁹ Assuming an OH radical concentration of 1×10^6 molecules cm⁻³, the corresponding isoprene lifetime is 2.3 h.¹⁰ Isoprene has also been implicated in regional events of elevated tropospheric ozone^{11–13} owing to the following mechanism:

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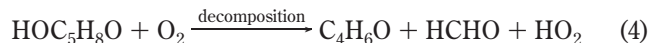
[‡] Departments of Earth and Atmospheric Science, Purdue University.

[§] Purdue Climate Change Research Center.

[‡] Griffin Analytical Technologies.

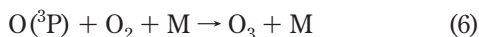
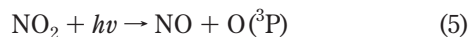
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(where $\text{C}_4\text{H}_6\text{O}$ = methyl vinyl ketone or methacrolein).

The oxidation of NO to NO_2 by peroxy radicals such as the isoprene peroxy radical ($\text{HOC}_5\text{H}_8\text{O}_2$) produced as an intermediate in reactions 1 and 2 quickly generates photochemical ozone in the sunlit troposphere via reactions 5 and 6.¹⁴



Wide varieties of reactive BVOCs are emitted by different plant species, making the total flux of BVOCs extremely species dependent. These emission rates could be influenced in the future where biodiversity is likely to be reduced and atmospheric CO_2 levels are likely to be much higher than present.¹⁵ As carbon dioxide levels in the atmosphere and global average temperatures continue to rise, it will be important to know how plants respond to these changes. For example, several authors have recently highlighted that certain species of plants that emit isoprene may reduce emissions when exposed to elevated CO_2 environments, whereas there may be an inverse effect for other BVOCs.^{16,17} Clearly, many questions remain unanswered as to ecosystem responses with respect to global climate change and BVOC emission rates at local, regional, and global levels. This necessitates the need for fast, precise, and accurate methods of measuring BVOC concentrations.

Over the past decade, there have been many techniques reporting measurements of isoprene at concentrations of a few parts per billion (ppb) or less. Most have been traditional GC-based methodologies, involving preconcentration of airborne VOCs, either cryogenically or onto sorbent materials such as Tenax followed by thermal desorption of the trapped samples onto a cryo-cooled GC column.^{18,19} Detection often involves use of a flame ionization detector (FID) or a mass spectrometer.^{20,21} Although these methods are highly reliable, one potential drawback of these systems is that the temporal resolution offered by the preconcentration/GC-based methods is unable to capture

short-term variations in isoprene concentrations that result from its relatively short atmospheric lifetime and the close correlation between isoprene emission rates and rapid variations in local meteorological conditions.²² This is compounded by the problem of coelution of peaks and other potential interferences. In addition, GC instruments are often bulky and difficult to transport to remote field sites and often require significant supplies of cryogens to obtain effective preconcentration prior to chromatography.

One instrument that does direct detection with adequate response time for flux measurements is the fast isoprene sensor or FIS, (Hills Scientific, Boulder, CO).^{23–25} This instrument detects isoprene with a fast response time (0.4 s) using the chemiluminescent reaction of alkenes with ozone. Chemiluminescence photons are generated by reacting alkenes in ambient air with known high levels of ozone (generated internally by an ozone generator), which are then detected with a photomultiplier tube. In environments where isoprene is the dominant alkene, the FIS response can be assumed to be due to the reaction of isoprene only. However, this assumption is not valid in environments where other alkenes have significant ambient concentrations, as the chemiluminescent reaction of ozone with species such as propene, ethylene, and monoterpenes, as well as isoprene oxidation products can be important.^{23,26}

New developments in mass spectrometry techniques such as proton-transfer reaction mass spectrometry (PTR-MS)²⁷ have also led to improved temporal resolution in the measurement of BVOCs. The PTR-MS technique utilizes proton-transfer reactions involving the hydronium ion (H_3O^+) to ionize airborne trace gases. The intensity and mass-to-charge ratio (m/z) of the subsequent product ion (typically $[\text{M} + \text{H}^+]$) is then measured by mass spectrometry. Recent measurements by several authors have shown the applicability of using PTR-MS detectors as general field instruments^{28,29} and for the specific measurement of isoprene concentrations and fluxes.^{30,31} Although the PTR-MS method has many advantages over chromatographic methods, there are still several drawbacks associated with these systems. PTR-MS systems often have inadequate selectivity, as these instruments respond to all species with a particular m/z and/or molecules of high molecular weight that fragment to yield the target ion. Hence, these instruments cannot distinguish among the large number of

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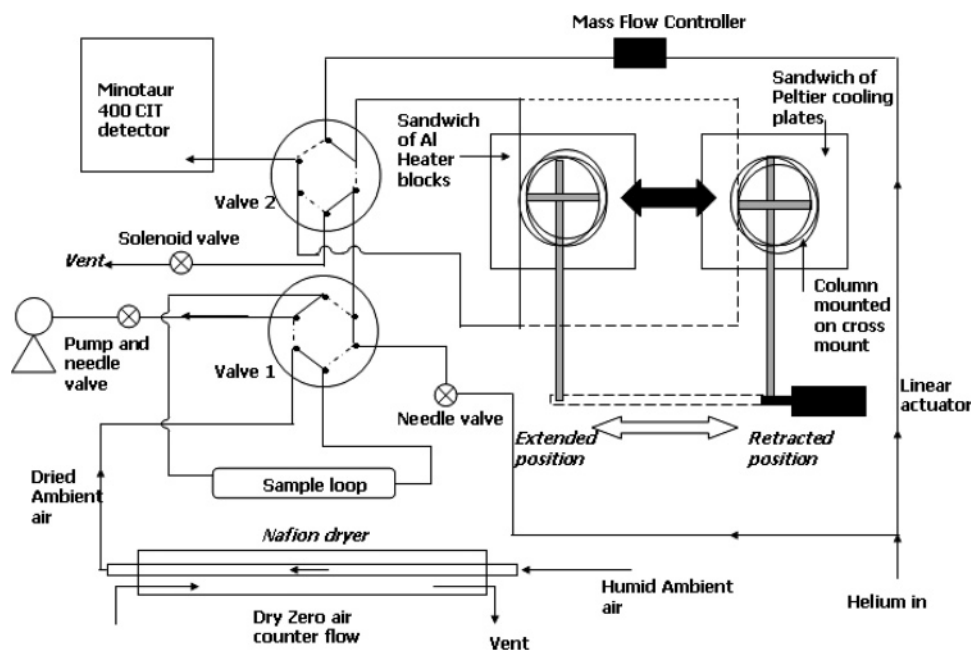


Figure 1. Schematic diagram of the inlet system and CIT detector showing the sample dryer, preconcentrator, and heaters.

individual isomeric terpenes, xylenes, aldehydes, and ketones and thus can suffer from interference problems.³²

Patterson et al.³³ described recent developments of miniature cylindrical ion trap (CIT) mass spectrometer systems, capable of multidimensional mass analysis (MSⁿ). The cylindrical design makes this trap simpler to manufacture (compared with hyperbolic ion traps) and miniaturize while using low power, making this trap feasible as a field-portable detector. CIT technology offers enhanced ion collection efficiency and the ability to generate a mass spectrum of ions within the trap at a much faster rate than the ion collection time associated with using a linear quadrupole. Using this custom-made trap combined with internal electron impact ionization, Riter et al.³⁴ showed that a CIT was capable of MSⁿ analysis while retaining high sensitivity to VOCs, even at sub ppb concentrations. A cylindrical trap-based mass spectrometer instrument is now commercially available (Griffin Analytical Technologies LLC, West Lafayette, IN). However, prior to this work the device had not yet been proven to be a viable instrument for the measurement of atmospheric trace species.

In this article, a new instrument is described that combines a rapid short-capillary column preconcentration system interfaced with a CIT mass spectrometer. The small preconcentrator and portable detector represent a fully automated sampling inlet system that provides rapid preconcentration and separation of analytes in ambient air without the aid of a cryogen. The laboratory characterization of the CIT is described, and field measurements of ambient isoprene concentrations above a forest site in northern lower Michigan are reported. These field data are compared to isoprene concentrations obtained from other measurement tech-

niques and analyzed in the context of environmental variables that control the concentration–time dependence of isoprene at this forest site.

EXPERIMENTAL SECTION

Sample Acquisition. The instrument described herein was designed to be as small, automated, portable, and efficient as possible and to avoid use of cryogenics such as liquid nitrogen or dry ice. In many GC systems, sample turnaround times are limited by the necessity to heat or cool the column to achieve both preconcentration of the desired target molecule and separation of the species of interest from other molecules. Although the selectivity offered by a CIT detector made high-resolution separation unnecessary, it was still necessary to preconcentrate the sample to achieve adequate detection limits for quantitative atmospheric BVOC determination. To develop a low-power, lightweight analytical method, our approach involved a unique combination of preconcentration within the same short capillary column used for minimal separation. A schematic diagram of the autosampler inlet system is shown in Figure 1.

With the use of two six-port valves (VICI, Houston, TX) to control the flow path, ambient air was pumped through a 1 L PFA Teflon sample volume at 3 L min⁻¹ using a diaphragm pump (Gast Manufacturing, Benton Harbor, MI). Once the volume was filled, valve 1 was turned such that the ambient air sample was flushed out of the sample volume by a 200 mL min⁻¹ flow of ultrahigh-purity ($\geq 99.999\%$) helium into the capillary column, where hydrocarbons were trapped by adsorption to the precooled stationary phase. The preconcentration capillary column was a 2 m long fused-silica Q-PLOT column, i.d. 0.32 mm (RESTEK, Bellefonte, PA), mounted on a custom-made cross-shaped holder machined from aluminum. The diameter of the column spool was 10 cm. At the ends of each of the arms of this cross-shaped mount, 0.25 cm grooves were machined into the aluminum to enable secure mounting of the column. The sample volume flush rate needed to be high enough so that the time taken to transfer the

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sample to the preconcentrator column was short enough to ensure fast sampling turnaround, yet low enough to maintain effective trapping of the analytes. The optimum flush flow rate was determined experimentally to be 200 mL min⁻¹.

To maximize the collection efficiency for isoprene, the capillary column mount moves to within a "sandwich" design Peltier cooler consisting of two 120 V Peltier-based thermoelectric cooling plates (Melcor, Trenton, NJ), maintained at 5 °C. These Peltier coolers were attached to two heat sinks in the form of machined aluminum blocks (10 cm × 8 cm × 1 cm) and were housed in machined PFA mountings of similar dimensions to the blocks to thermally isolate the system from ambient air. Optimum cooling temperatures inside the air gap between the aluminum blocks were maintained by regulation of the dc current supplied to the Peltier plates by a solid-state relay (Crydom, San Diego, CA) regulated by thermocouple (J1 type) feedback to a temperature controller (Omega Engineering, Stamford, CT).

As air flowed from the sample volume into the precooled column, VOCs were trapped at the head of the column. This procedure ensured good precision as each sample volume was determined by the fixed 1 L sample volume. Molecules that were not retained by the column (e.g., air, CO₂) were vented through an open 24 V dc solenoid valve (Parker Hannifin Corporation, Cleveland, OH). After a total flush time of 5.5 min (just over 1 L of sample internal volume at 200 mL min⁻¹), the solenoid valve was closed and the six-port valves turned such that helium flowed through the column and into the CIT. The flow rate was controlled using a mass flow controller (MFC) (MKS Instruments, Wilmington, MA) as shown in Figure 1. The column was then moved from the cold block to the heated block to allow rapid component separation and elution to occur. Movement of the column assembly between these locations was controlled using a 24 V dc linear actuator (Fergelli, Bellingham, WA). The column mount was connected directly to the actuator by attaching one end of the mount to the end of the linear actuator using a "D" shell clamp and aluminum connecting arm. The linear actuator device provided motion in a single plane parallel to the temperature-controlled areas, and thus the column mounting was attached at 90° to this direction of motion. The initiation of the stroke was controlled remotely using the Griffin 400 software. The stroke length was fixed at 15 cm by internal limit switches. The travel time between the two limits was less than 5 s.

Once the column was moved to the heated area, heat transfer from two machined aluminum blocks (of equal dimensions to the blocks kept cooled) rapidly heated the column. As before, one block was positioned above the other in a "sandwich" design. With the aid of 0.2 cm diameter threaded bolts fitted through holes tapped in the blocks, the relative height of the blocks was adjusted to obtain a small air gap, while still allowing free motion of the column assembly into and out of the heater block. To aid thermal isolation from the surroundings the heated blocks were mounted in Teflon housings with fiberglass insulation placed between the block material and the housing. The blocks were resistively heated to a constant 140 °C temperature using two 150 W internal cartridge heaters (Melcor), regulated using an Omega temperature controller, solid-state relay, and J1 type thermocouple feedback. Column temperatures in excess of 90 °C were achieved within 60 s of the start of the heat cycle.

Cylindrical Ion Trap Mass Spectrometer. The CIT described here is a commercially available instrument called the Griffin 400. The Griffin 400 CIT technology has undergone several design modifications and refinements since its inception.^{33,34} The trap and instrument electronics have been enclosed in a ruggedized case with a shock-resistant platform to minimize impact and vibration damage to the internally self-contained vacuum system consisting of a turbo molecular pump and related components. The ruggedized unit has dimensions of 48 cm × 49 cm × 46 cm and has a total weight (including pumps) of 32 kg. The unit can operate on either 120 or 240 V.

The Griffin 400 utilizes a CIT operated at a drive frequency of 1.6 MHz. The resultant mass range for this system is m/z 40–425 with unit mass resolution, thus covering the mass range of most gas-phase atmospheric VOCs. The electronics and software are capable of generating fully arbitrary waveforms utilized here for ion isolation and resonant ejection. The Griffin 400 was tested for the isoprene molecular ion, m/z 68, and the scan function was optimized as follows. Separated species were allowed to enter the ion trap by way of the flow path shown in Figure 1. Helium flow through the column (in the same direction as sampling) and into the ion trap was maintained at 2 mL min⁻¹. Once molecules eluted from the end of the column, they entered the vacuum region of the Griffin 400 instrument. The instrument employed internal electron ionization (EI), with a 50 μ A maximum emission current to generate ions within the CIT volume. The initial ionization period lasted 15 ms, followed by a 2 ms cooling step in which ions were allowed to cool through collisions with helium buffer gas provided as carrier gas through the GC. The analyte ion was isolated for a period of 50 ms by utilizing a broadband excitation prior to final mass analysis at 10 kTh s⁻¹. Detection of the ions was via a channeltron electron multiplier (Detector Technology Inc., Palmer, MA).

Although capable of MSⁿ, the Griffin 400 was set up to scan in single ion monitoring mode (SIM) exclusively. As the dominant ion in the isoprene EI spectrum was the parent mass m/z 68 amu, SIM operation maximized instrument sensitivity. During routine operation, the instrument's duty cycle was such that one isoprene sample was recorded every 11 min. Analyte peaks were wide by conventional standards (>60 s at full width, half-maximum). The intention of the limited chromatography was only to rapidly separate isoprene from air, water, and other molecules present in higher concentrations than the target molecule. Most of the selectivity in this method was derived from the mass spectrometer.

The Griffin 400 platform has been designed to accept internal hardware modifications so that it can be connected to other commercial instruments such as commercial GCs with minimal user input required. All Griffin 400 and related instrument functions were controlled using a PC-based software system (Griffin Systems Software), to allow automated control and data acquisition with little or no user input. Communication between the mass spectrometer and the preconcentration system was achieved through multiple level and signal control lines. A 12 V dc power supply was added to provide power to the linear actuator, two relays were added to control the flow switching valves for the system, and a 24 V dc line was added to control the solenoid valve. By using a preset time and control sequence, the software enabled precise command over sample acquisition such that the

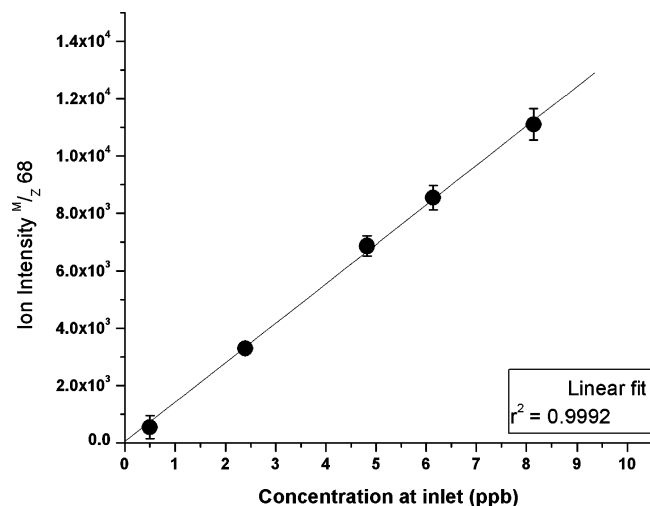


Figure 2. Typical calibration curve for the Griffin 400 mass spectrometer under field conditions. The error bars represent the 1s standard deviation of the detected counts for replicate measurements.

coupled Griffin 400 and capillary inlet served as an automated sampler allowing the complete system to operate unattended for extended periods.

Field measurements using this ion trap mass spectrometer and GC system were made at the PROPHET (Program for Research on Oxidants: PHotochemistry, Emissions, and Transport) research lab located at the University of Michigan Biological Station (UMBS) near Pellston, Michigan (45°32' N, 84°40' W). The PROPHET laboratory is located within a mixed deciduous/coniferous forest, at the base of a 31 m walk-up scaffolding tower. A Pyrex sampling manifold that extends to 34 m above the surface, or 10 m above the forest canopy, is used to draw sample air into the laboratory with a 1–2 s manifold residence time. A detailed description of the PROPHET site can be found elsewhere.³⁵

RESULTS

The preconcentrator and CIT detector were calibrated for isoprene using a gas-phase standard. A cylinder of isoprene in nitrogen was made in the atmospheric chemistry lab at Purdue University by the injection of a known quantity of liquid isoprene (99% Sigma-Aldrich) from a calibrated syringe (Hamilton, Reno, NV) into a pre-evacuated cylinder through a heated stainless steel transfer line. The cylinder was then pressurized to 500 psig pressure with ultrapure nitrogen (99.999%, Airgas) to obtain an isoprene mole fraction within the cylinder of 6.1 ppm. The preconcentrator and CIT detector were then calibrated using this gas-phase standard diluted to ambient concentration ranges of 0.5–8.0 ppb with isoprene-free zero air using a calibrated MFC (MKS Instruments, Wilmington, MA.). A typical calibration curve obtained during the field study is shown in Figure 2. A five-point calibration curve can be obtained in under 1 h. The precision of the overall system was measured by flowing a constant 3 ppb of isoprene into the instrument inlet that was then sampled in replicate. The measured peak heights revealed a precision of $\pm 5\%$ (1s).

To determine the limit of detection (LOD) of the ion trap, blank samples containing zero air were evaluated. For these zero-air

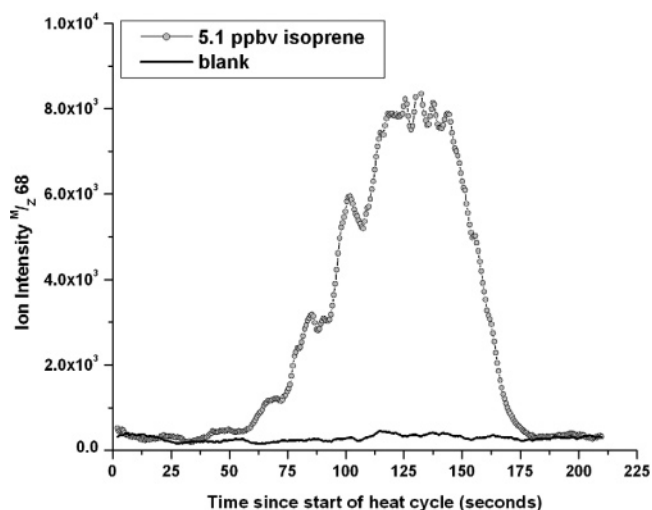


Figure 3. Comparison of the detected isoprene signal (m/z 68) for 5.1 ppb isoprene and the signal from a zero-air blank.

experiments, only random noise at m/z 68 was detected. Zero-air samples were obtained before and after every calibration. These data indicated no carry over of analyte between samples. A plot of the typical blank signal along with the detected counts at m/z 68 for a sample loading of 5 ppb isoprene is shown in Figure 3. Propagation of errors from preparation of the standard resulted in an overall calibration uncertainty of $\pm 8\%$ (1s). The estimated LOD for the ion trap for isoprene, in the current configuration, was defined as 3 times the standard deviation of the blank counts of replicate samples of zero air. During each calibration the LOD for the instrument was determined in this way. The average LOD ($3s_{\text{blank}}$) was 78 parts per trillion (ppt) over the course of the nine calibrations performed during the field campaign.

As with many analytical techniques, mass spectrometers often exhibit large humidity-dependent sensitivities in their performance.^{36–39} Experiments designed to determine the sensitivity of this system to changes in sample humidity were performed. A known concentration isoprene standard was mixed with an additional zero-air flow that was humidified by passing it through an impinger bottle filled with 18 M Ω water. By keeping the total flow rate constant and varying the relative flows of dry and humid air, the desired levels of relative humidity in the final air stream were achieved.

In Figure 4 we show a plot of detected isoprene counts, for a fixed isoprene concentration of 8 ppb, as a function of varying sample air relative humidity. As shown in Figure 4, as the humidity of the sample air increased, the detected isoprene signal decreased. This humidity response is similar to that experienced by Colorado et al.³⁶ To obviate this humidity response, sample air was allowed to flow through a 2 m long Nafion dryer (Perma Pure, Toms River, NJ) prior to the sample volume (see Figure

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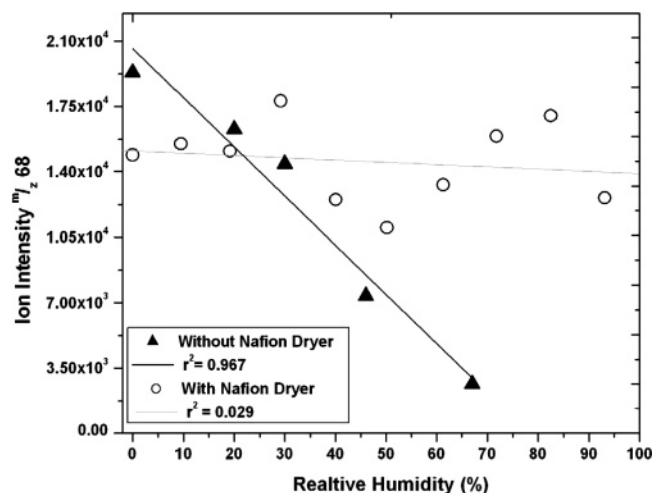


Figure 4. Comparison of the detected isoprene signal, at 8ppb concentration, with changing humidity in the sample air. Open circles represent data for dried sample air. Black triangles represent data for undried sample air.

1). This dryer tubing consisted of an outer tube of PFA and an inner tube made of the Nafion copolymer. Sample air was passed through the inner tube of the dryer, while additional dry air was passed through the outer tube with a flow direction counter to that of the inner tube flow. The semiporous Nafion membrane allowed the removal of water vapor from the inner tube to the outer tube, while quantitatively retaining isoprene. These data show that with the addition of the Nafion dryer, no significant change in the response of the detector for isoprene over a wide range of relative humidity was observed, even when the air approached saturation, i.e., >80%. The Nafion dryer was subsequently included and used in all field measurements.

Measurements using the automated sampler and Griffin 400 CIT were made at the PROPHET tower from July 7, 2005 until the end of the summer measurement campaign on August 17. Samples were obtained from above the forested canopy via the PROPHET lab glass manifold at a frequency of one sample every 11 min. The instrument sampled continually over the campaign period, stopping for occasional down periods to allow for calibrations and/or other instrument performance checks. Over the course of the campaign, the instrument was calibrated nine times using our gas-phase standard. The average sensitivity (slope of the calibration curve) was found to vary by 11% (at 1s) over the course of the field campaign.

The period from July 7 to August 17 was marked by a period of hot, dry weather with temperatures in excess of 30 °C, intermixed with cooler, rainy periods. The isoprene sampling system provided excellent data coverage during this period providing an ideal opportunity to investigate the field performance of the instrument over these changing conditions. A plot of isoprene concentrations for the campaign is shown in the four-panel plot in Figure 5. The results show ambient isoprene concentrations that ranged from the instrument LOD of 78 ppt at night to >10 ppb during the day, i.e., covering over 2 orders of magnitude similar to data observed at the PROPHET site in several previous studies.³⁵

Comparison of Reported Concentrations with Other Instruments. During the summer of 2005, several other investiga-

tors measured isoprene fluxes and thus, concentrations, at the field site offering the ability to compare data from our instrument with results from instruments that detect isoprene by independent methods and that use different calibration systems. Isoprene concentrations were compared to measurements made by a FIS operated by Washington State University (WSU)^{23–25} and a PTR-MS instrument operated by the National Center for Atmospheric Research (NCAR) as described in detail by Karl et al.³¹ Both the FIS and PTR-MS were operated in flux mode with rapid analysis times (<1 Hz) and consequently higher signal-to-noise (S/N) ratios owing to the very quick sample acquisition. Detection limits for the PTR-MS were below 1 ppt for isoprene at this time resolution.³¹ The LOD for the FIS (in flux mode, 10 Hz) was <500 pptv.²⁴ To compare the performance of the instruments it was necessary to compare the gas-phase standards used to calibrate each system. All three systems used cylinders containing isoprene diluted in an inert carrier gas as gas-phase standards. To perform the comparison, the CIT system was calibrated using the Purdue University standard, as normal. The standards from NCAR and WSU were then measured, and the concentrations of isoprene in these standards determined relative to the Purdue standard. The calculated mole fraction for each standard was within the uncertainty of the CIT instrument (8% at 1s). From the exercise we concluded that any differences between the atmospheric isoprene concentrations determined by these three instruments were not because of errors in calibration.

The PTR-MS instrument sampled air from just above the canopy (~24 m), whereas the FIS sampled from 34 m and the CIT system sampled from 35 m. These instruments operated for the majority of the campaign with the FIS measuring eddy covariance fluxes and the PTR-MS measuring virtual disjunct eddy covariance fluxes of isoprene. In addition, a second flux technique was tested during a portion of this time by WSU personnel, providing additional isoprene concentration data along with canister samples collected by NCAR. For the WSU instrument, air was subsampled into inert Tedlar bags as part of a disjunct eddy accumulation (DEA) isoprene flux system, jointly developed by WSU and NCAR and deployed for the first time at this field campaign.⁴⁰ Hourly averaged isoprene concentrations were determined from the Tedlar bags using a gas chromatograph equipped with a photoionization detector (GC-PID). NCAR also obtained isoprene concentration data from gas samples taken using pre-evacuated stainless steel electropolished and conditioned 2 L canisters (C.W. Sinks and Associates). The isoprene concentrations within these canisters were determined postcampaign at the gas analysis lab at NCAR using a GC-FID instrument.

Concurrent measurement of isoprene from the CIT, PTR-MS, and FIS instruments were available from July 29 to August 16. During this time there was also occasional sampling using the WSU DEA system and the NCAR canisters. A comparison of isoprene concentrations obtained by the CIT, FIS, PTR-MS, DEA, and the NCAR canister samples is shown in Figure 6. Generally, all instruments captured the diel cycle in isoprene concentration and reveal isoprene concentrations that are comparable. These data show that there is substantial daytime variability, largely due

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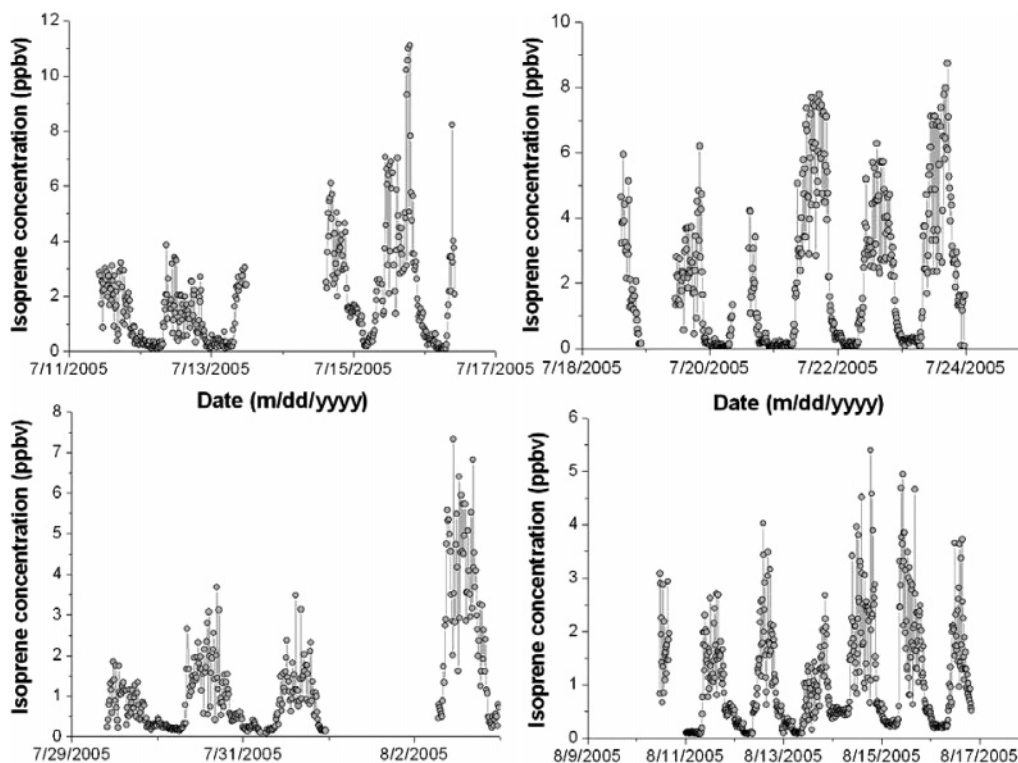


Figure 5. Isoprene concentrations measured during a 4 week experiment in summer 2005 at a forest site in northern Michigan using the new inlet system and CIT detector.

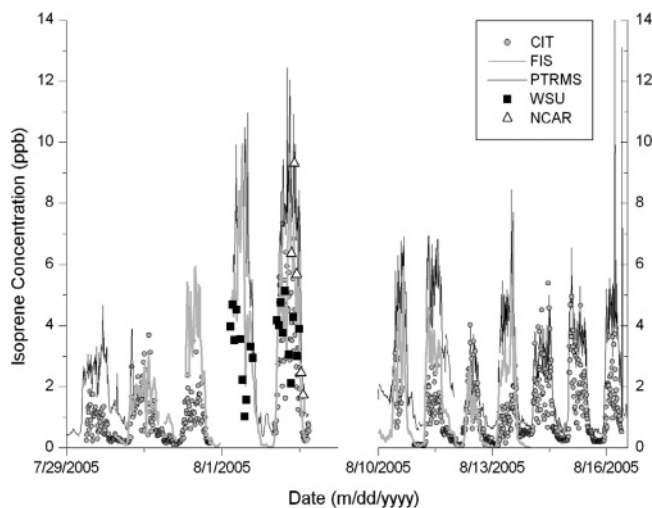


Figure 6. Comparison of all concurrent measurements of isoprene, summer 2005, at the PROPHET site. Data are from the CIT, PTRMS, FIS, and additional samples made by Washington State University's DEA sampler (WSU) and the National Center for Atmospheric Research (NCAR) canister samples.

to variations in the emissions, along with variations in vertical transport (Figures 5 and 6), as discussed below.

The CIT, FIS, and PTR-MS were able to record isoprene concentrations at a much faster rate than the DEA system or the NCAR canister samples, and hence they operated in automated mode, capturing data from all hours of the day. Through averaging the FIS and PTR-MS data into 10 min averages, concurrent and centered on the time during which the CIT sampled, a comparison was made between the isoprene concentrations reported by these instruments. A plot of the profile of these time-of-day-averaged concentration data is shown in Figure 7A. These data show that

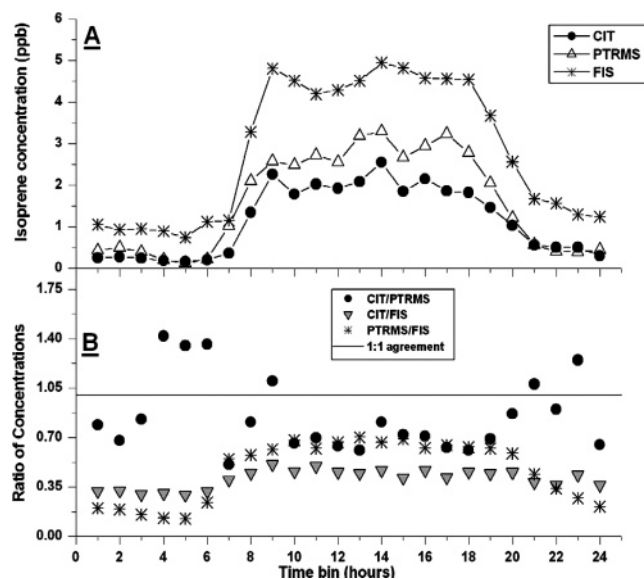


Figure 7. Plot of binned isoprene concentrations reported by instruments measuring during PROPHET summer 2005. Part A shows data sorted according to time of day in 1 h bin increments limited to times where all instruments reported data (see text), then hourly averages obtained. Part B shows the bin-averaged ratio of the CIT isoprene concentration to other groups reporting isoprene concentration data.

there is substantial day/night variability, largely due to variations in the emission rate over the diel cycle.

Generally, the CIT consistently reported the lowest concentration, the FIS consistently reported the highest concentration, while the PTR-MS instrument reported concentrations between these two. Overall, the PTR-MS data were more similar to those reported by the CIT. However, because of the significant isoprene vertical

gradient, with isoprene concentrations decreasing exponentially with height above the canopy,⁴² we expect the PTR-MS daytime concentrations, measured at 24 m, to be consistently higher than those determined by the CIT system measuring at 32 m. Better agreement between the PTR-MS and the CIT is observed at night, despite lower concentrations. Isoprene emissions cease, and the vertical gradient is substantially relaxed as some vertical mixing continues.⁴¹ These trends are shown in Figure 7B. This plot shows the ratio $[\text{isoprene}]_{\text{CIT}}/[\text{isoprene}]_{\text{PTR-MS}}$ varies around 1.0 during nighttime, but with greater variability since the absolute concentrations are often close to the limits of detection for both instruments, as shown in Figures 5 and 6. During daytime hours, this ratio ranged between 0.6 and 0.8, largely reflecting the vertical gradient of isoprene between the PTR-MS inlet at the top of the canopy and the CIT inlet 10 m above.⁴²

The agreement between the CIT and FIS instruments was not very good. Even though these instruments measured at similar heights, daytime ratios of $[\text{isoprene}]_{\text{CIT}}/[\text{isoprene}]_{\text{FIS}}$ were approximately 0.4, with nighttime ratios slightly lower (~ 0.3). Reasons for the disagreement are not well understood at this time. There is a possibility that the FIS is responding to other BVOCs such as isoprene oxidation products or terpenes. However, we believe this is minimal, at least during daytime.^{24–26} There is also the potential for unknown alkenes to cause interferences. The influence of fluxes of unidentified but reactive biogenic molecules has recently been postulated as the cause of imbalances in the OH budget at this forest site.⁴³ If there are unknown terpenes or sesquiterpene species present at the PROPHET location, they could possibly cause interference in the FIS data. If there are “missing” fluxes of BVOCs, their emission rate would likely have large temperature dependences.⁴³ The interference of these species would therefore be largest during daytime hours when temperatures and, hence, fluxes are highest. The influence of temperature on the ratio of the CIT/FIS isoprene concentration data was therefore investigated. These data showed no statistically significant temperature trend in the CIT/FIS ratio.

As a result of the issues described above, it is clear that the CIT data are more directly compatible with the GC-FID data obtained by the Tedlar bags used in the WSU DEA system and the NCAR canister samples, acquired at the same height as the CIT. In Figure 8 (top) we compare the temporal characteristics of the measured $[\text{isoprene}]$ for the CIT, NCAR, and WSU's DEA system for August 2, 2005. For this day, as shown in Figure 5, all three instruments offered good data coverage. However, while there appears to be reasonably good agreement between these instruments on this day, due to the temporal variability in $[\text{isoprene}]$, a simple comparison of isoprene concentration versus time can be confusing. A better display of the comparative measurements is to calculate the ratio $[\text{isoprene}]_{\text{CIT}}/[\text{isoprene}]_X$, where X represents either the WSU or NCAR measurement, as shown for the same data in Figure 8 (bottom). To calculate this ratio, we averaged the CIT data into hourly bins equal to the time

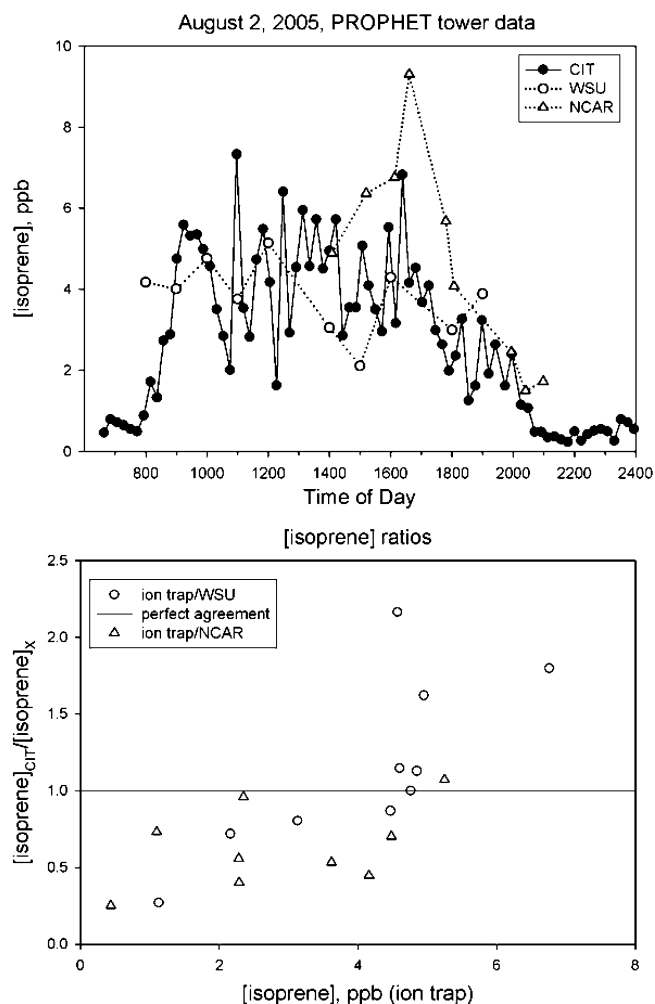


Figure 8. Plot of isoprene concentrations on August 2, 2005. Part A shows the hourly averaged CIT and DEA average concentrations together with the “grab sample” canister data, while Part B shows the ratio of CIT to other instruments as a function of CIT concentration. Data show that the general agreement for these instruments was good but show possible evidence of a concentration dependence of the CIT/WSU ratio.

resolution of the WSU Tedlar bags. As the CIT measures only once every 11 min, such averaging was not always possible when comparing the NCAR canister samples, which typically took between 1 and 30 min to complete the fill. For comparison of these ratios, CIT isoprene concentrations were interpolated to a time equal to the midpoint of the canister fill time. The ratios are then plotted as a function of $[\text{isoprene}]_{\text{CIT}}$.

As shown in Figure 8B, it appears that there is a concentration dependence to these ratios, for the CIT/WSU data. When $[\text{isoprene}]$ is low, the CIT data are considerably low relative to $[\text{isoprene}]_{\text{WSU}}$, although there is very little data from WSU (and NCAR) for this day at low concentrations. The CIT instrument still has quite good precision for the low-concentration data, and the very low nighttime concentrations are well documented.⁴² There could be contributions from losses in the CIT inlet system at low $[\text{isoprene}]$, although the calibration curve shows no evidence for this. There could be issues for blanks for the WSU DEA system at low concentrations, but it is difficult to determine if this is the case from the existing data set. On the high-concentration end, there are insufficient data to enable determi-

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nation of whether the ratios are statistically significantly greater than unity. For the CIT/NCAR data, there is no apparent concentration dependence. Furthermore, there is some danger in this analysis given the fact that sample times were not identical, and given the high temporal variability in the actual [isoprene], due to the strong vertical gradient and the short-term fluctuations in vertical scale turbulence.

Control of Daytime Isoprene Concentration. As there is considerable temporal variability in [isoprene] above the forest canopy, it is useful to test our understanding of what controls that variability in order to assess our understanding of the performance of the instrument. The rate of change of isoprene concentration above the canopy at this site can be explained by considering vertical scale turbulent transport from the emission source (the canopy) into a layer situated at tower height, transport upward out of the layer by turbulent diffusion, and losses of isoprene from within the layer by reaction with ozone and OH. The reaction of isoprene with the nitrate radical (NO_3) and dry deposition of isoprene to the canopy are considered negligible.⁴² Thus, for this highly reactive species, the concentration of isoprene at time t can be described by

$$[\text{isop}]_t = [\text{isop}]_0 + \left(\frac{\text{flux}}{Z} - k_{\text{OH}+\text{isop}}[\text{OH}][\text{isop}] - k_{\text{O}_3+\text{isop}}[\text{O}_3][\text{isop}] - k_Z \frac{d^2[\text{isop}]}{dz^2} \right) \Delta t \quad (\text{I})$$

where $[\text{isop}]_0$ is the initial isoprene concentration as measured by the CIT. The flux term is the isoprene flux from the canopy as measured by the FIS in the eddy covariance mode at 34 m. In flux mode, the FIS instrument has previously been demonstrated to produce reliable data.^{24,25} Z is the height of the assumed layer into which the flux from below is emitted. This was set at 10 m, the distance from the canopy height, where the PTR-MS measurements were made, to the CIT and FIS measurement height. The $k_{\text{OH}+\text{isop}}$ and $k_{\text{O}_3+\text{isop}}$ terms represents the rate constants for the OH + isoprene⁹ and the O_3 + isoprene reaction,⁴⁴ k_Z represents the vertical scale eddy diffusion coefficient, and $d^2[\text{isop}]/dz^2$ is the vertical scale isoprene gradient (calculated using an e-folding height of 175 m⁴²) over the layer height (Z).

The first 4 days of week 4 of the 2005 campaign (August 10 until August 14) offered the most complete data coverage of the parameters described in eq I. Using a combination of PTR-MS data at canopy height (24 m), CIT isoprene concentrations, FIS fluxes at 10 Hz, ozone concentrations (A. Hogg, private communication), measured at the layer height (34 m), and literature data for the average diel profile of OH,⁴⁵ we can calculate [isoprene] versus time and examine the factors controlling isoprene concentrations at this site. By describing how the parameters in eq I change over the diel cycle, and by binning concentration data reported for week 4 of the campaign into hourly bins, the variation in each parameter described in eq I can be considered. Then, the solution to this equation can be discussed.

Averaged eddy covariance fluxes measured by the FIS are shown in Figure 9A, plotted as a function of hourly time bins.

Using vertical wind measurements at 34 m above ground height, 10 m above the canopy, the eddy diffusivity, k_z , for this site needed to be calculated and substituted into eq I. k_z is calculated using eq II, as described by Lenschow,⁴⁶ where μ is the friction velocity measured at 34 m,

$$k_z = \mu k_{\text{VC}}(Z - d) \quad (\text{II})$$

k_{VC} is Von Karman's coefficient (0.4), and d is the displacement height ($\sim 0.75 \times$ canopy height). The average eddy diffusivity was calculated for week 4 and then binned as shown in Figure 9B.

As described above, the isoprene concentrations measured at 34 m differ from those at canopy height (24 m) due to the flux divergence, in part from isoprene oxidation by OH over the time scale of vertical transport from the canopy to the sampling height 10 m above. The decrease in isoprene concentration with height can be described by a simple exponential decay, i.e.,

$$[\text{isoprene}]_z = [\text{isoprene}]_0 e^{-(kZ)} \quad (\text{III})$$

where k = the reciprocal of the e-folding height (using an e-folding height of 175 m⁴²) and Z is the height above the canopy (10 m). Equation III was solved such that hourly averages of flux divergence were obtained as tangents of the hourly averaged isoprene decay curve. The isoprene concentration gradients as a function of time were then calculated. The final term in eq I was then calculated as the product of the gradient and k_z divided by the height scale (10 m).

With the use of data from Tan et al.,⁴⁵ Figure 9D shows the magnitude of the chemical loss rate for isoprene over the diel cycle (scale inverted to show losses as negative). Overall, the chemical loss of isoprene is dominated (>90%) by the reaction of isoprene with the OH radical (reaction 1), even during the early morning and late evening, with loss rates being greatest at solar noon.

In Figure 9E, we present the calculated average [isoprene] at tower height, from the parameters expressed in Figure 9A–D. The data are compared with the average isoprene concentration at 34 m as measured by the CIT during week 4 of the campaign, as shown in Figure 9F. Comparison of parts E and F of Figure 9 shows that the overall shape of the measured isoprene diel cycle is captured by solving eq I. At sunrise, photosynthesis begins within the forest canopy, and the trees begin to emit isoprene. The air mass above the canopy is very stable at this time, showing little convective activity, and thus the eddy diffusivity is small. At the start of the day, chemical loss of isoprene is low, as OH concentrations are small and the kinetics of the reaction between ozone and isoprene are relatively slow.^{41,43} The net result is a rapid increase in isoprene concentration in the morning but before a slower increase up to 1 p.m., since vertical mixing, emission rate, and chemistry all increase together. Approximately 2 ppb of isoprene persists above the forest even into the later evening hours, but it is seen to begin to decay after 6 p.m. local time.

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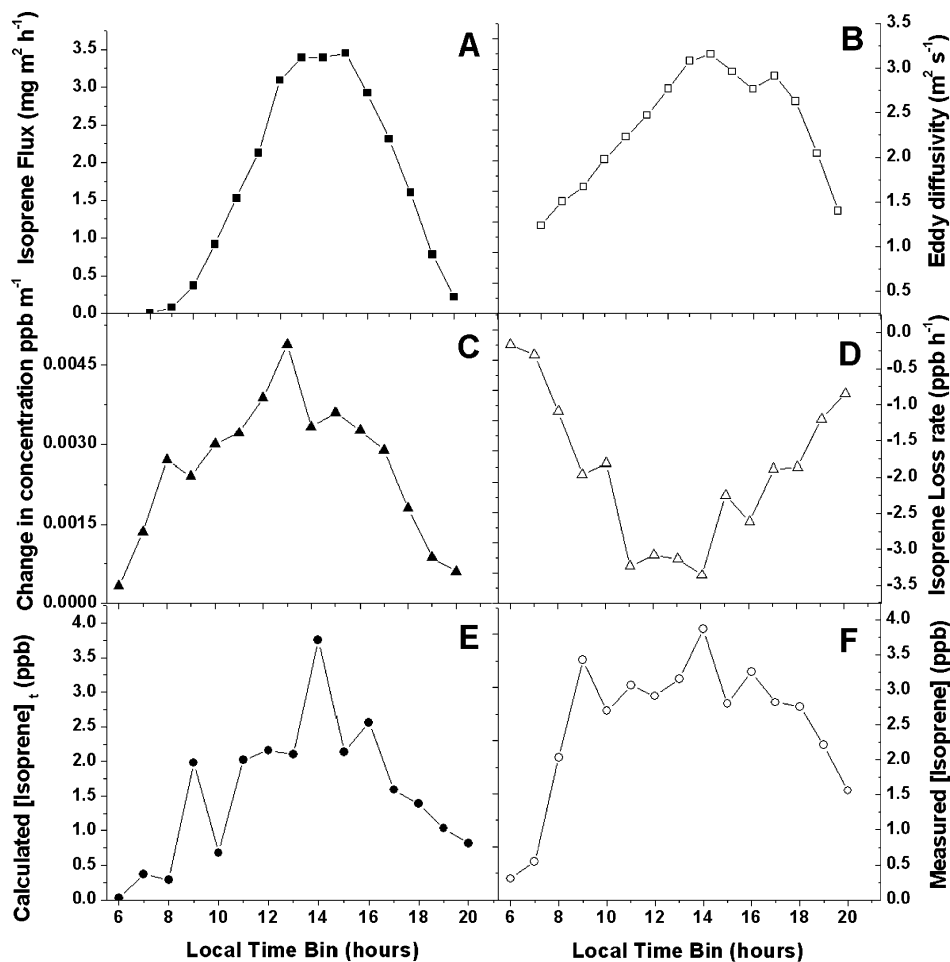


Figure 9. Change in factors influencing isoprene concentration at the PROPHET site during the 2005 campaign. These data show that the temporal changes can be explained by changes in eddy diffusivity (A), measured isoprene flux (B), flux divergence between canopy and tower heights (C), and chemical loss rate (D) over time. Bin averages of isoprene concentrations measured in situ (E) show similar trends to the solution of an equation linking how local chemistry and turbulent diffusion change over time (F) (see text).

After 6 p.m., emission rates and vertical mixing rates abate together. Here, the emission of new isoprene into the air above the canopy effectively falls to zero while at the same time, the atmosphere becomes more stable as the nocturnal boundary layer begins to form.⁴² Loss of existing atmospheric isoprene (from the sampling height) then occurs through a combination of vertical mixing and chemical loss, yielding the characteristic nighttime decay observed during this measurement period and during previous studies.^{26,42}

SUMMARY AND FUTURE WORK

A new CIT instrument was characterized in this study, and continuous, automated ambient measurements of isoprene were successfully performed at the PROPHET site during the summer of 2005. Although this field study has shown the potential of CITs for rapid determination of BVOCs, we focused only on isoprene here. In principle, multiple species could be determined with appropriate mass analysis. For future deployments of the instrument, improvements to the CIT detector could be made to further utilize the advantages of this technology. During this work the instrument was operated in SIM mode, the amplitude of the dc and rf voltages being set to observe only m/z 68. This mode provided the highest sensitivity for isoprene specifically as more

mass spectrometric sampling time was spent on this mass. However, the CIT system has the potential for multidimensional MS^n analysis that has the ability to determine both the parent ion and fragments of these ions. This analytical capability could be used in future experiments to detect other compounds of interest, especially isobaric ions, such as the isoprene oxidation products methyl vinyl ketone and methacrolein.

In addition to modifications to the CIT detector, improvements to the preconcentrator system could increase sample frequency and allow for detection of more species. In particular, the performance of this system could be improved by faster transfer to the preconcentration column and by faster heating of the column. This would improve both the time resolution and the LOD. One solution would be to resistively heat the preconcentrator column during injection, rather than physically transferring the column from one temperature zone to the other. This would almost certainly increase the rate of heat transfer to the column, sharpening the peaks and thus improving S/N. Achieving sampling temperatures lower than 5 °C for the column may also lead to sharper analyte peaks.

Although there are still developments and improvements possible in the CIT-MS and the inlet and preconcentration measurement system, in its current configuration this instrument

produced good precision data that were in good agreement when compared to the isoprene concentrations reported by other independent instruments, specifically the GC data. In addition, the CIT and preconcentrator platform demonstrated excellent stability of calibration and good reliability. We therefore conclude that during its first field campaign at the PROPHET site, the new instrument performed well. This gives further weight to the potential of this device as a field-portable mass spectrometer instrument for the fast and accurate measurement of atmospheric VOCs.

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