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Intercomparison of automated methodologies for determination of ambient isoprene during the PROPHET 1998 summer campaign

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Abstract. The Program for Research on Oxidants: PHotochemistry, Emissions, and Transport (PROPHET) 1998 summer campaign, conducted at the University of Michigan Biological Station, provided a unique opportunity to compare isoprene measurement techniques that were automated, sampled and analyzed on-line, and provided relatively fast time resolution. Assessment of the data quality for fast isoprene measurements is important because isoprene dominates the surface chemistry at many rural sites and even some urban environments. An informal intercomparison was conducted by evaluating ambient isoprene mixing ratio data generated by five different instruments: quadrupole ion trap (QIT) MS, the chemiluminescent-based fast isoprene sensor (FIS), and three gas chromatograph/mass spectrometry (GC/MS) techniques. The GC/MS methods were deployed and maintained by Purdue University (GC/MS-P), the National Center for Atmospheric Research (GC/MS-NCAR), and the Rosenstiel School of Marine and Atmospheric Science (GC/MS-RSMAS). The FIS was deployed and maintained by NCAR, Hills-Scientific.com and Washington State University, while the QIT was implemented by Purdue University. The GC/MS-P was chosen as the reference method to evaluate the agreement of the data set. The data were evaluated for time-matched samples through regression analysis, ratio analysis, and percent difference analysis relative to GC/MS-P. For measurement data in the central 90th percentile relative to the median, the mean percent difference was 21% for GC/MS-NCAR, 41% for QIT , 42% for GC/MS-RSMAS, and 88% for the FIS. Potential sources of disagreement, especially for low-concentration data, such as variations in sampling time, interferences, method precision and accuracy, and limited cross-calibration, are discussed.

1. Introduction

Biogenic hydrocarbons are released into the atmosphere in amounts that are much larger than the total nonmethane hydrocarbon (NMHC) burden from all anthropogenic sources [*Fehsenfeld et al.*, 1992]. The global emissions of biogenic volatile organic compounds (BVOC) are estimated to be 1150 Tg/yr, of which 44% is isoprene (2-methyl-1,3,-butadiene) [*Guenther et al.*, 1995]. Because of isoprene abundance and reactivity with the hydroxyl radical ($k_{isoprene + OH} = 1.10 \times 10^{-10}$ cm^3 $molecules^{-1}$ s^{-1}) [*Stevens et al.*, 1999], it dominates boundary layer tropospheric chemistry in most forested regions and even some urban environments [*Trainer et al.*, 1987; *Chameides et al.*, 1988; *Biesenthal et al.*, 1997]. Isoprene's role in local ozone production, radical concentrations, and nitrogen oxide chemistry is well documented [*Fehsenfeld et al.*, 1992; *Trainer et al.*, 1991; *Chen et al.*, 1998]. Because of its high reactivity, and radiation and temperature-dependent emission rate, isoprene concentrations can be highly variable with time, with a lifetime that can be as short as 17 min at midday [*Monson and Fall*, 1989; *Goldstein et al*, 1998, *and references therein*]. Over the last 20 years, much progress has been made toward understanding isoprene's biogenic synthesis, diurnal profile, and impact on tropospheric ozone and NO_x chemistry. However, recent measurements have revealed temporal characteristics that are not completely understood and need further investigation, in particular, the relatively rapid decay exhibited at sunset [*Yokouchi*, 1994; *Goldan et al.*, 1995; *Biesenthal et al.*, 1998; *Hurst et al.*, this issue], as well as possible nighttime isoprene sources [*Guenther*, 1999].

Clearly, isoprene measurement techniques that are accurate, sensitive, selective, and exhibit high temporal resolution are critical for informative investigations of bioshpere/atmosphere interactions. Isoprene's OH reactivity can make it an important reactive BVOC even at low parts per

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trillion concentrations, making accurate determinations a necessity at limits of detection that are difficult to achieve. Hence the challenge is to improve the speed and limits of detection of the isoprene measurement while maintaining accuracy. To this end, the atmospheric chemistry community is moving away from grab sampling, which is labor intensive and inherently slow, to automated methods [*Biesenthal et al.*, 1997; *Riemer et al.*, 1998; *Guenther and Hills*, 1998]. Intercomparisons are necessary in order to evaluate the methodologies that have potential to deliver accurate and high-resolution data coverage. Unfortunately, there have been very few field intercomparisons to establish the reliability of current methods for the determination of NMHCs and no studies that have compared on-line ambient isoprene measurements. Among the informal studies are *Donahue and Prinn* [1993] (on-line sampling and quantitation with (GC/FID)) and the *Atlas et al.* [1993] (canister grab sampling followed by GC/FID quantitation) assessment of (NMHC) measurements conducted in the marine boundary layer. The latter comparison showed significant disagreement for olefins. The *Schreffler* [1993] study compared automated, on-line analysis to canister grab sampling and suggested a negative systematic bias for canisters. A rigorous, multilab, formal NMHC intercomparison referred to as Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE) is in progress [*Apel et al.*, 1994; 1999]. In the work of Apel [1994], NOMHICE Task 2, 28 laboratories were involved, with most investigators using GC/FID methodology, while a few used GC/MS. A 16 component NMHC National Institute for Standards and Technology (NIST) mixture, containing isoprene, was circulated between the labs. For all laboratories, isoprene results exhibited, on average, a -3% difference from the reference method; however, isoprene showed the largest data scatter of all components tested, with a standard deviation of 85%. The results from these studies are somewhat troubling in that they have shown that current NMHC methodologies may have large measurement uncertainties, particularly during field studies.

In 1997, a research program was initiated at the University of Michigan Biological Station aimed at understanding the relationship between tropospheric chemistry and forest ecosystems. This program, PROPHET, provided a unique opportunity to compare automated, on-line isoprene measurement methodologies during the 1998 summer campaign. Here we describe an informal intercomparison involving five separate instruments representing three techniques: the chemiluminescent-based fast isoprene sensor [*Guenther and Hills*, 1998], which utilizes ozone-induced chemiluminescence to measure isoprene with a response time of 0.5 seconds, a QIT method based on selective chemical ionization and MS/MS provides isoprene determination without chromatography [*Colorado et al.*, 1998], and three automated GC/MS methods. The GC/MS-P method involved Tenax based preconcentration, while the GC/MS-NCAR and GC/MS-RSMAS methods utilized cryogenic preconcentration techniques. Isoprene mixing ratio determinations from August 1 to August 15, 1998, were used to evaluate the methodologies at this forested, rural site. This paper contains

Table 1. Methods Overview

Affiliation	Instrumentation (Method Abbreviation)	Preconcentration Method	Sample Volume / Sampling Time / Data Frequency	Chromatography	Detection Scheme
Washington State, NCAR Hills-Scientific.com	chemiluminescent Fast Isoprene Sensor (FIS)	none	33 mL / 0.5 s / 10 Hz signal averaged to 1 min	none	ozonolysis of alkenes, PMT detection of emission at 500 nm
Purdue	quadrupole ion trap mass spectrometer (QIT)	-150 °C silanized glass bead trap	150 mL / 5 min / 12 min	none	vinyl methyl ether CI - MS/MS Varian 2000 QIT
Purdue	GC/MS (GC/MS-P)	Tenax trap at 10 °C KI ozone trap	300 mL / 5 min / 40 min	Poraplot column, 30 m, 0.32 mm ID	HP 5972 MSD EI in scan mode
NCAR	GC/MS (GC/MS-NCAR)	-10 °C chilled tube (H_2O removal) -145 °C glass bead trap -186 °C cryofocusing fused silica precolumn	300 mL / 3 min / 30 min	DB-624, 60 m, 0.25 mm ID, 1.4 um film	HP 5973 MSD EI in selective ion mode
RSMAS	GC/MS (GC/MS-RSMAS)	-150 °C silcosteel trap and CO_2 removal -180 °C cryofocusing Silcosteel trap	100 mL / 1 min / 30 min	DB-624, 20 m, 0.18 mm ID, 1.0 um film	HP 5971A MSD EI in selective ion mode

a description of all techniques involved, data reduction, and discussion of the relative agreement and proposed sources of error for each method.

2. Experimental Summary

2.1. Field Study Site

The PROPHET field site is located at the University of Michigan Biological Station (UMBS), Pellston, Michigan (45°32.3′ N and 84°40.0′W). UMBS resides on 9000 acres of northern hardwood forest containing mostly aspen (sp. *Populus tremuloides*) and birch (sp. *Betula alba*) with an undergrowth of white pine (sp. *Pinus strobus*). The average canopy height is 20 m. The site is located between two small lakes, Burt Lake and Douglas Lake, and is 30 km due east of Lake Michigan and 50 km due west of Lake Huron. A detailed description of the site and meteorology can be found in the works of *Carroll et al.* [this issue] and *Cooper et al.* [this issue]. At the PROPHET site, there is a 31 m walk-up scaffold tower that supports a 5 cm diameter Pyrex glass manifold with an inlet positioned at 35 m. A blower attached to the end of the manifold samples air at a rate of 160 standard liters per second, yielding a residence time of 1-2 s. The sample is drawn to the base of the tower and into the PROPHET laboratory where the GC/MS-P, QIT, GC/MS-NCAR, and GC/MS-RSMAS sampled via 0.635 cm PFA Teflon tubing affixed to ports in the manifold. The FIS was located at the base of the Ameriflux tower, which is located 132 m from the PROPHET tower. The FIS sampled at a height of 31 m through 1.3 cm PVC pipe, with a sample line residence time of 4 seconds. The sample variation between the towers must be considered when performing an intercomparison with the FIS. Potential sample variation between the FIS inlet and that for the other methods would have to occur on a spatial gradient of 132 m. Both sampling systems are positioned ~ 10 m above the canopy, and therefore the subcanopy micrometeorological effects should not be relevant to sample variability. Because of the proximity and sampling height of both towers, the sampling ports should experience the same flow regimes, chemistry, and radiation. To estimate an upper limit of the isoprene horizontal variability, assuming an air parcel of significantly different isoprene concentration moves over one tower before the other, 1-min-integrated FIS data was utilized. The average wind speed measured at PROPHET 1998 was 2.6 m/s; hence on average, an air parcel should take 51 s to transport between the towers when the wind direction is parallel to a line between the two towers. The mean isoprene concentration change using the central 90th percentile of the FIS data was 16% per minute. Therefore the average isoprene concentration change per minute multiplied by the average time for an air parcel to transport between the towers yields 14%. This small but potentially significant source of sample variation must be considered when comparing the FIS data set with data taken at the PROPHET tower.

2.2. Methods Description

Table 1 lists an overview of the five isoprene methods utilized during the 1998 PROPHET campaign. Note that all instrumentation is automated, and samples were analyzed on-line. The fastest data collection was performed by the FIS with a 10 Hz data frequency. For the purposes of the intercomparison the FIS data were reported as 1-min-integrated samples. The GC/MS methods data frequency range from 30 to 40 minutes. A description of each method is provided below. The QIT and FIS systems will be described in some detail, as this was the first field deployment of the QIT and the first time the FIS was used to determine isoprene mixing ratios in ambient air.

2.2.1. Quadrupole ion trap. This method is based on chemical ionization (CI) in a QIT mass spectrometer. The intention is to utilize a reagent, vinyl methyl ether (VME), which reacts selectively with atmospheric alkenes, for example, isoprene. The utility of VME as a selective CI reagent for olefinic compounds is well documented [*Ferrer-Correia et al.*, 1976; *van Doorn et al.*, 1978]. Isoprene reacts with ionized VME via a Diels-Alder 4+2 cycloaddition, yielding a stable adduct at $m/z = 94$, which is then isolated in the QIT. Collisionally activated dissociation (CAD) of the isolated ion produces a $m/z = 79$ ion which is quantified [*Colorado et al.*, 1998]. Helium served as the carrier, bath, and collision gas. To achieve adequate detection limits, an automated sampling system was built around a Varian 3400 GC equipped with a liquid-nitrogen-cooled cryotrap. Along with sample preconcentration, a method to remove water from the sample was necessary to avoid unwanted ion molecule reactions and the accumulation of water in the QIT. To this end, a hydrophobic membrane inlet was implemented. Sample air was drawn through a 76.2 cm by 0.635 cm Silcosteel tubing that encased a 100 μm diameter tubular dimethyl silicone membrane through which helium was continuously purged at 30 mL/min. Analytes permeated through the membrane into the helium stream and were swept into a cold trap. For this study, sample air was passed over the membrane at a rate of 300 mL/min for 5 min. As discussed by *Colorado et al.*, [1998], the effective sample volume is determined by the rate of permeation of the analyte through the membrane. For isoprene this effective flow rate is ~ 30 mL/min. Therefore for a 5 min sampling period the actual sample size for isoprene is 150 mL. The cold trap consisted of 0.318 cm stainless steel tubing packed with silanized glass beads and cooled with liquid nitrogen to -150°C. After sample concentration the sample was heated to 200°C and swept with helium into the Varian GC column. The GC was equipped with a 30 m DB-1 capillary column held isothermally at 150°C, providing little or no separation of cryotrapped components. The DB-1 capillary column was initially used to provide the flexibility to perform fast chromatographic separations during the PROPHET field study. However, during this campaign the separation capacity was not needed nor utilized, and in retrospect, a deactivated fused silica column could have been used as a transfer line.

Unfortunately, the membrane inlet did not adequately remove water from the sample, and as a result, the instrument would periodically malfunction. Elevated levels of water in the ion trap can cause a high-pressure environment, inefficient ion-trapping conditions, and even electrical arcing. On August 1, a Nafion drying tube (Perma Pure Inc. model 110-48S) was inserted into the sampling line to dry the sample air. While the Nafion dryer did provide water reduction, it also introduced isoprene carryover effects that raised the magnitude and variability of the blank, hence the limit of detection rose from 120 parts per trillion (ppt) to 600 ppt. Calibration was conducted using a gas phase standard of 4.75 ppm isoprene in grade 5.0 nitrogen. Compressed gas

standards were prepared at Purdue using deactivated 29.5 L aluminum cylinders. The isoprene standards were diluted in zero air using MKS flow controllers to produce isoprene concentrations in the 0.25 ppb to 5.00 ppb range. Five point calibration curves were generated weekly.

2.2.2. Fast isoprene sensor. The FIS was deployed jointly by Washington State University, Hills-Scientific.com, and NCAR. The FIS has been used to monitor real-time isoprene concentrations in both cuvette [*Monson et al.*, 1991, 1992] and boundary layer flux studies [*Guenther and Hills*, 1998; *Bowling et al.*, 1998; *Westberg et al.*, this issue]. As a flux sensor, measurements are obtained through a cross correlation between the vertical wind speed fluctuations, measured using a sonic anemometer, and isoprene mixing ratio fluctuations measured by the FIS [*Dabberdt et al.*, 1993; *Guenther and Hills*, 1998; *Westberg et al.*, this issue]. However, prior to this study, the FIS has not previously been used as an ambient mixing ratio sensor. The potential to use the FIS as a mean atmospheric sensor is attractive due to its fast response (0.5 s), linearity, and continuous measurement mode. It should be noted that the FIS was specifically deployed for isoprene flux measurements and the decision to use the FIS mixing ratio data for this intercomparison was made after the completion of PROPHET 1998 field campaign.

The FIS (model FIS-97, Hills-Scientific.com) is based on the reaction between a primary alkene and ozone. Sample air (~ 4 L/min) is continuously pulled into a mirror-finished stainless steel cell, where it reacts with an ozone/O_2 stream (4% O_3 in O_2 at 0.8 L/min). The HCHO reaction product is electronically excited and emits 500 nm light upon relaxation to ground state. The emission is monitored with a single-photon sensitive photomultiplier detector. The reaction cell residence time based on cell volume and flow rate is ~ 0.4 s, which approximates the measured 1/e response time of 0.5 s [*Hills and Zimmerman*, 1990; *Guenther and Hills*, 1998]. In this study, photon pulses were integrated in the detector at 0.5 s and averaged for 1 min, producing 1 min data frequency.

Because of an emphasis during PROPHET 1998 on eddy covariance isoprene flux measurements, a method independent of instrument zero, FIS calibrations were performed at most once per day. During PROPHET 1998 the FIS was in ambient measurement instrument mode 23 hours each day and in calibration mode for 1 hour per day. In calibration mode, inlet air is directed through a platinum converter at 380°C which removes > 99.9% of ambient isoprene [*Guenther and Hills*, 1998]. Instrument zero is recorded for 10 min followed by a series of dynamically generated isoprene standards. The standards (0-30 ppbv) are generated using a built-in dynamic dilution system which adds a mass-flow-controlled stream of an isoprene standard (6 ppm nominal isoprene in 5.0 nitrogen, +/- 3% primary analysis, Scott-Marrin Corp.). The isoprene standard is periodically calibrated against NIST propane, standard reference material 1601.

2.2.3. GC/MS (Purdue). Purdue University employed a Hewlett-Packard 5890 Series II GC and a Hewlett-Packard 5972 MSD equipped with an automated sampling system driven by Labview 4.1 software [*Biesenthal et al.*, 1997; *Starn et al.*, 1998a]. The sample was passed through a potassium iodide trap to remove ozone. Subsequently, analytes were preconcentrated on a Tenax-TA (2,6-diphenyl-p-phenylene oxide polymer) adsorbent trap cooled to 5°-10°C with chilled water that flows through an aluminum block containing the Tenax-TA packed in a short 0.635 cm stainless steel tube. Desorption occurred by heating the Tenax trap to 250 °C under reverse helium flow of 0.88 mL/min and refocusing the analytes on a 10°-15°C PoraPLOT-Q capillary GC column. The analytes were then chromatographically separated using a programmed temperature ramp. Detection was carried out by the HP MSD using scan mode from *m/z* 30 to *m/z* 170. Isoprene was quantified using the peak area of the *m/z* = 67 [$C_5H_7^+$] selected ion chromatogram. The sampling frequency was once every 40 min. The isoprene standard of 4.73 ppm isoprene in 4.8 nitrogen was generated in house at Purdue and was contained in a 29.5 L deactivated aluminum cylinder. Calibration samples were produced by dynamic dilution of the gas phase standard with zero air. Full calibration curves were generated weekly during the field campaign.

2.2.4. GC/MS (NCAR). NCAR utilized a cryotrapping preconcentration method in which a 300 mL air sample was drawn through a chilled tube at -10°C to remove water and then into a glass bead trap at −145°C in which the analytes were concentrated. After collection of the sample, 50 mL of helium was passed through the trap to remove residual gases. The glass bead trap was heated to 120°C transferring the compounds to a length of fused silica precolumn held at −186 °C. The sample was injected by heating the precolumn to 120 °C. The analytes were separated on a 60 m, 0.25 mm ID HP-624 capillary column. Single ion monitoring by a HP 5973 MSD was utilized for quantitation of *m/z* = 67 [$C_5H_7^+$]. The sampling frequency was every 30 min. The NCAR standard was prepared gravimetrically in a treated aluminum cylinder. The instrument was calibrated by one point calibration and periodic full calibration curves. The cylinder was referenced to a NIST propane standard reference material 1601 by GC/FID using previously determined relative sensitivities.

2.2.5. GC/MS (RSMAS). A 100 mL sample was collected at 100 mL/min in a silcosteel trap held at − 150°C. After the volume was collected, the trap was flushed with dry helium to remove CO_2, after which the trap was heated to 100°C and refocused in a silcosteel trap held at − 180°C. The cryotrap was then heated to 100°C and the sample was transferred to a 20 m DB-624 capillary column. Detection was accomplished using a HP 5971A MSD in a single ion monitoring mode. Quantitation was obtained by determination of the peak area for *m/z* = 67 [$C_5H_7^+$]. Data frequency was every 30 min. RSMAS utilized the NCAR standard for calibration.

During the study there was limited crossanalysis of standards. When cross analysis was performed between Purdue and NCAR, the standards agreed to within 15%. Some of the disagreement in reported isoprene concentrations could be caused by a systematic error in the calibration attributed to the uncertainty in the standards used by each investigator. This issue will be addressed in section 3.

3. Results and Discussion

3.1. Overview

The analysis of results will focus on the isoprene mixing ratio data for August 1 to August 15, 1998. Plates 1 and 2 display all isoprene concentration data obtained during this time period. Although some data are below calculated detection limits, these determinations are shown in Plates 1 and 2, as this data contributes to the comparison of the methods when isoprene levels were below 750 ppt (e.g., at

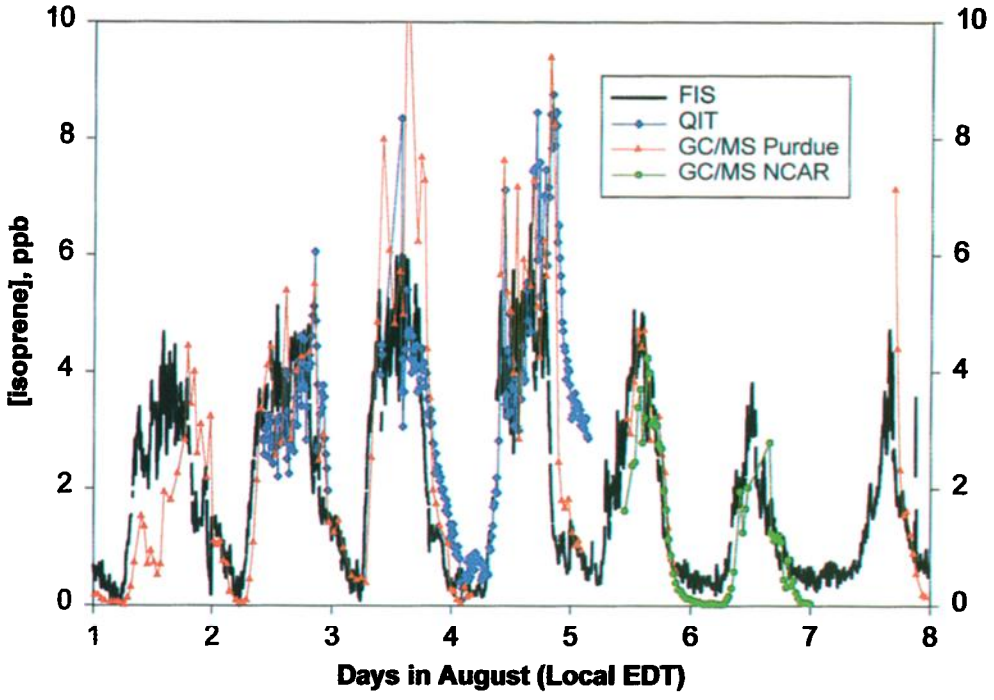

Plate 1. Ambient isoprene concentrations for August 1 to 8, 1998. The measurement data are shown as circles connected with straight lines. The FIS data are 1 min data smoothed with a 30 min running average and displayed as a solid black line. The timescale on the abscissa is eastern daylight time, which is local PROPHET time.

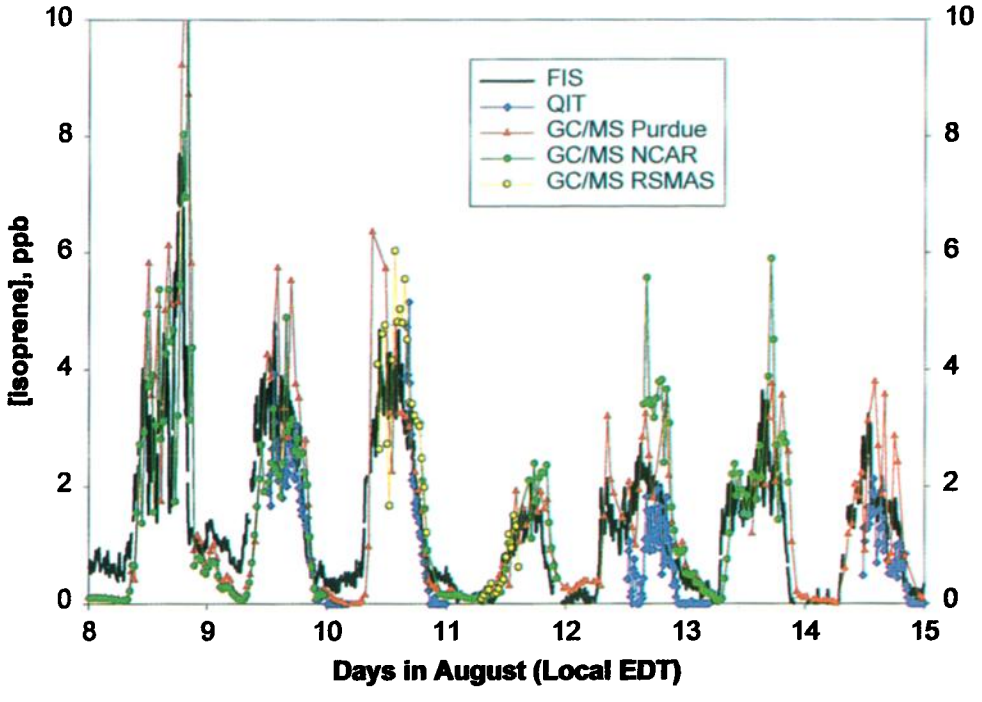

Plate 2. Ambient isoprene concentrations for August 8 to 15, 1998. The measurement data are shown as circles connected with straight lines. The FIS data are 1 min data smoothed with a 30 min running average and displayed as a solid black line. The timescale on the abscissa is eastern daylight time, which is local PROPHET time.

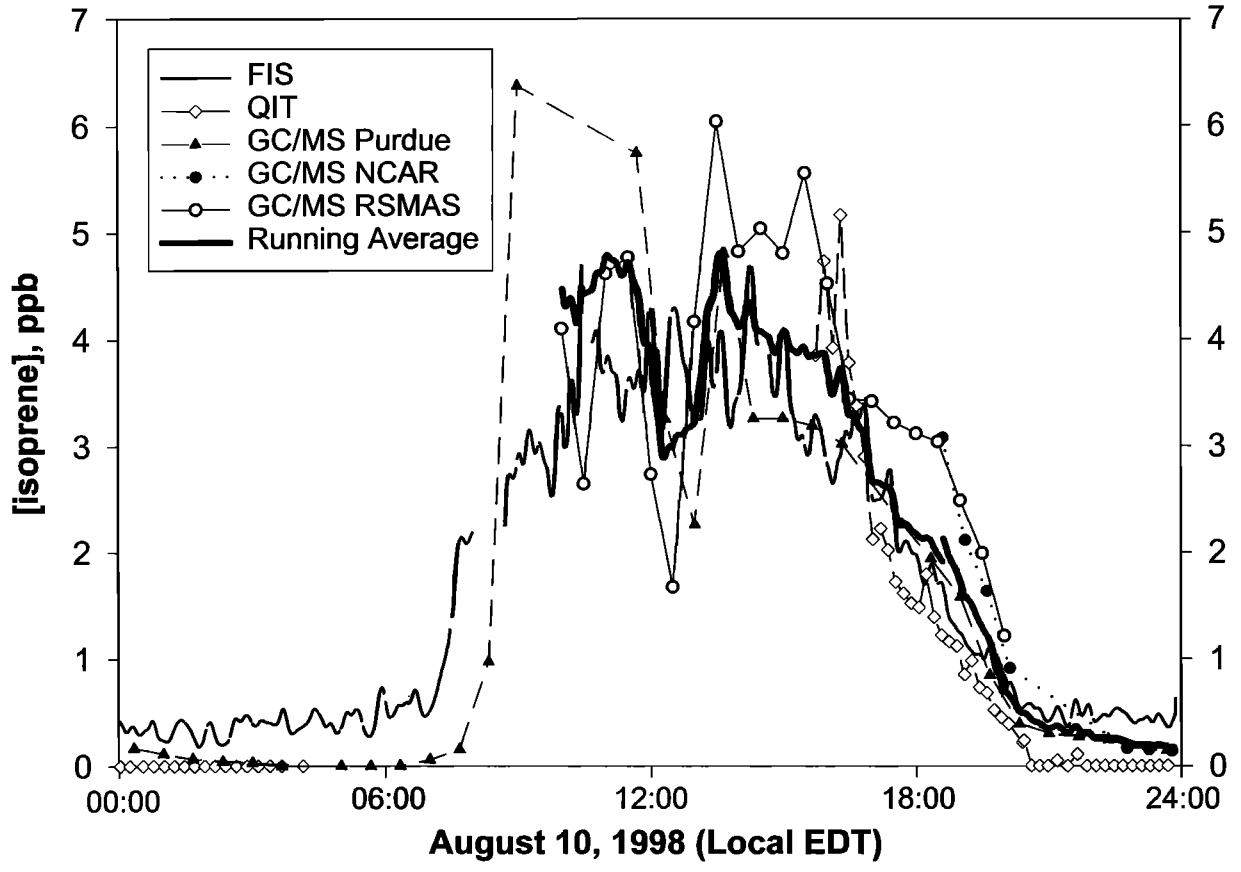

Figure 1. Ambient isoprene concentrations for August 10, 1998. This plot represents typical isoprene data agreement during the 1998 summer PROPHET campaign. The thick line is a running mean of the measurement data when three instruments were acquiring data simultaneously. The average was determined by making a linear regression between data points and assigning an interpolated value every minute and subsequently, calculating the mean of all methods every minute.

typical nighttime concentrations). All data presented in Figures 1 and 2 are presented without data-smoothing techniques, with the exception of the FIS data. As mentioned above, the FIS data were acquired at 10 Hz for eddy covariance flux measurements but were averaged for 1 min for this intercomparison. Subsequently the FIS data were smoothed with a 30 min running average for presentation in Plates 1 and 2 and Figures 1 and 2.

As shown in Plates 1 and 2, the expected diel profile, which is dominated by the correlation of isoprene emission rates with temperature and irradiance [*Monson and Fall*, 1989; *Fehsenfeld et al.*, 1992; *Guenther et al.*, 1995], is well captured by all the methods. The daytime concentration exceeds 4 ppb on most days and often decays to detection limits on several nights. The isoprene concentrations decay rapidly between the hours of 1800 to 2200 EDT. This nighttime decay phenomenon, which exemplifies the need for sensitive and rapid isoprene measurements, is discussed in detail by *Hurst et al.* [this issue] and has been previously observed at numerous sites [*Yokouchi*, 1994; *Goldan et al.*, 1995; *Biesenthal et al.*, 1997; *Starn et al.*, 1998b].

Data for individual days, August 10 and August 12, are shown in expanded scale in Figures 1 and 2. Interpolation between each data point allowed us to estimate isoprene concentration data for each minute for all techniques. All of the interpolated data were averaged to produce a running mean. The average residual between the measurement data and the running mean from all methods was determined. The running mean and average residual was determined only when three or more methods were running simultaneously. On August 10 the mean of the average residual for all methods was 0.46 ppb and on August 12 it was 0.92 ppb. These days represent a range of measurement agreement; that is, Figure 1 is representative of agreement for most of the data set, while Figure 2 displays the largest observed disagreement among the methods for this study.

3.2. Ambient Isoprene Variability

The determined precision of each method, estimated uncertainties, and detection limits for each method are listed in Table 2. Variability in the determined isoprene concentrations is greatest during the daytime. This can be attributed, in part, to large biogenic emissions impacted by features such as stomatal closure during midday, high reactivity of isoprene with the variable OH radical concentrations, turbulent mixing in the vertical direction, and advection of spatially heterogeneous air parcels. In Figure 3 we present the 1 min FIS data for the afternoon of August 2 with the 5% estimated precision shown as error bars. The short-term variability in the determined isoprene mixing ratios exceeds the expected precision of the FIS. Also, the daytime

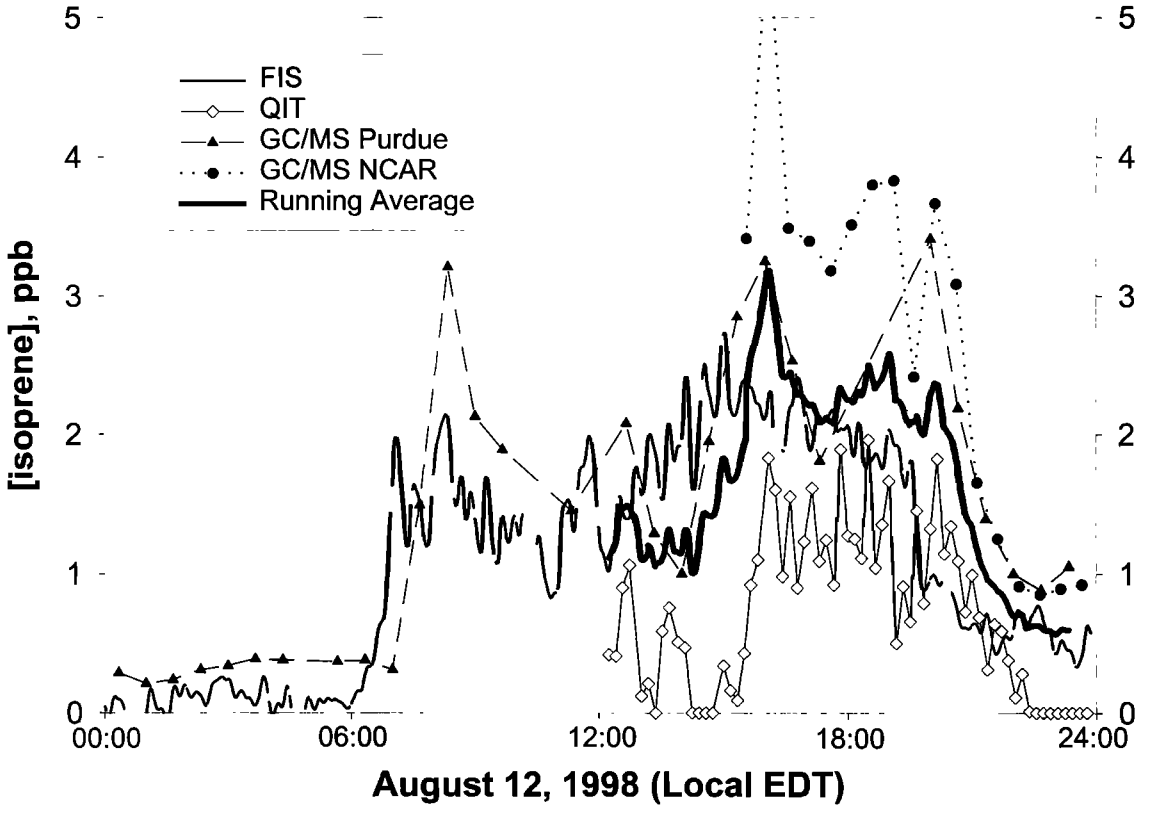

Figure 2. Ambient isoprene concentrations for August 12, 1998. This plot represents the largest variability of isoprene determinations during the coarse of the 1998 summer PROPHET campaign. The thick line is a running mean of measurement data when three instruments were acquiring data simultaneously. The average was determined by making a linear regression between data points and assigning an interpolated value every minute and subsequently, calculating the mean of all methods every minute.

variability shown by the GC/MS-P and GC/MS-NCAR in Plates 1 and 2 far exceeds the stated precision of the instruments, ~ 1%, and thus we conclude that the daytime mixing ratio variability, shown in Plates 1 and 2, clearly results from the actual ambient isoprene mixing ratio variation and not from the imprecision of the methods. The fine temporal structure of the isoprene mixing ratio displayed in Figure 3 illustrates the need to employ fast response methods in order to capture these features. Such an ability would aid in understanding environmental factors that influence isoprene emission rates.

3.3. Quantitative Intercomparison

To evaluate the relative performance for each method, a reference method was needed. All methods were considered to be designated the reference method; however, three methods (GC/MS-RSMAS, GC/MS-NCAR, and the QIT) were excluded because they did not provide continuous data coverage over the 2 weeks of the intercomparison. The FIS displayed continuous 1 min data coverage but was not originally deployed for ambient isoprene determinations, and the method is known to have artifacts when isoprene

Table 2. Analytical Performance of Methodologies

Affiliation	Precision*	Uncertainty in Determination	Limit of Detection†
FIS	5 %	+/- 10 %	200 ppt
QIT	10 %	+/- 20 %	600 ppt
GC/MS-P	1 %	+/- 10 %	15 ppt
GC/MS-NCAR	1 %	+/- 6 %	1 ppt
GC/MS-RSMAS	11 %	+/- 15 %	10 ppt

* Precision is determined by calculating the coefficient of the variance for replicate analysis.

† Detection limits defined as 3 times the standard deviation of the blank divided by the sensitivity.

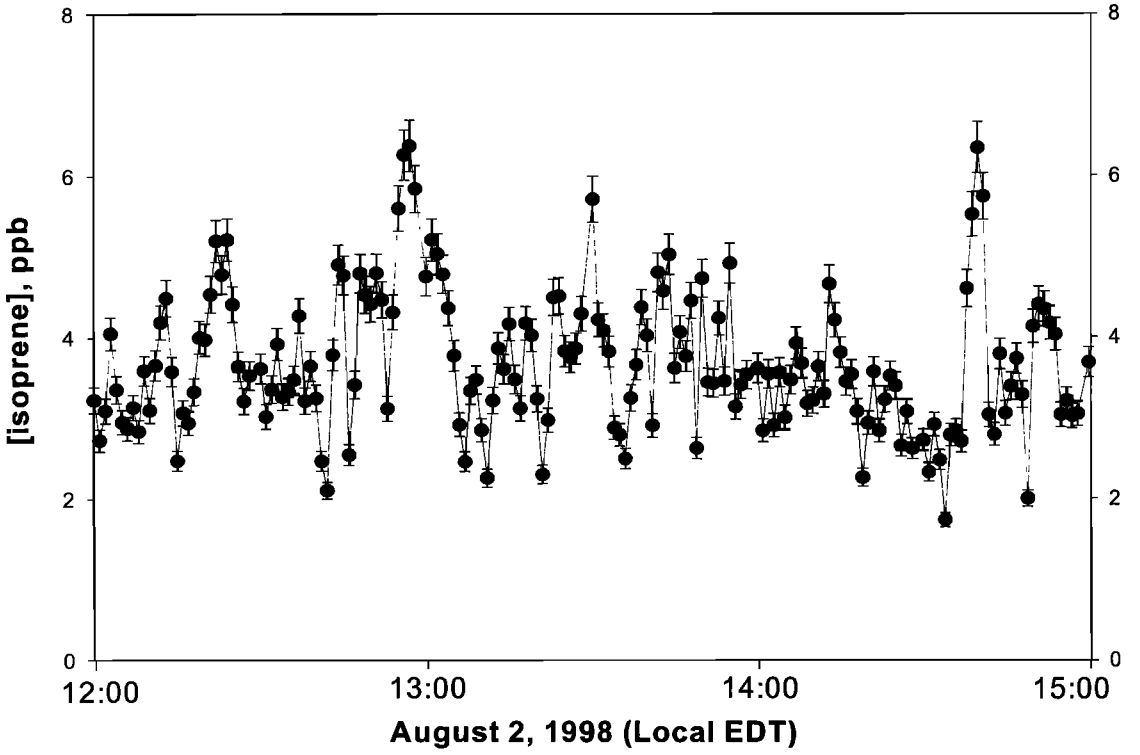

Figure 3. Fast isoprene sensor 1 min data with the estimated precision error bars of 5% for the afternoon of August 9.

concentrations are low. The GC/MS-P was chosen as the reference method because it had the longest deployment and most consistent data coverage during the study as it was acquiring data in each of the 6 weeks of the study. Most importantly, this GC/MS method provides data with no apparent interferences and low instrumental noise levels that result in detection limits of ~ 15 ppt. For these reasons the GC/MS-P isoprene data set has also been utilized for other manuscripts relative to the 1998 PROPHET study [e.g., *Hurst et al.*, this issue; *Faloona et al.*, this issue].

To conduct the intercomparison, data were compared if samples were acquired within 2.5 min of the midpoint of the GC/MS-P sampling time. This time frame is a reasonable balance between having enough data to quantitatively compare methods and a small enough time window to ensure sample homogeneity. All investigators reported their data with a time stamp corresponding to the center of the sampling time. The number of time-matched data points were 288 for the FIS, 30 for the QIT, 19 for the GC/MS-NCAR, and 6 for the GC/MS-RSMAS. For the regression analysis and ratio analysis, below, the FIS data were generated by averaging the 1 min data in order to correspond to the 5 min sampling time of the GC/MS-P. Therefore the comparison of the FIS and GC/MS-P was conducted on samples taken simultaneously. The GC/MS-NCAR, GC/MS-RSMAS, and QIT had sampling times of 3, 1, and 5 min, respectively. A regression analysis of the 1 minute and 5 minute FIS data against the GC/MS-P demonstrated little difference for the two approaches. Regression analysis for 1 min data compared to the GC/MS-P produced a slope of 0.46 and an r^2 of 0.59, while the 5 min FIS data produced a slope of 0.47 with an r^2 of 0.63. This analysis indicates that the +/- 2.5 min timeframe is small enough that only a minimal amount of the disagreement should be attributed to sampling time differences.

Plate 3 displays a log-log plot of isoprene concentrations determined by the FIS, QIT, GC/MS-NCAR, and GC/MS-RSMAS versus the GC/MS-P. Data below the detection limit of the FIS and the QIT are displayed with cross hairs, although these data were not used in the regression analysis. This plot demonstrates excellent agreement among the GC/MS methods, relative to the 1:1 line. The linear regression of the GC/MS-NCAR data produced a slope of 0.98 with an r^2 of 0.97. The GC/MS-RSMAS produced a slope of 1.08 and an r^2 of 0.95. The GC/MS-P and QIT utilized separate calibration standards made at Purdue, while the GC/MS-NCAR and GC/MS-RSMAS systems were calibrated using standards prepared at NCAR. The agreement between the GC/MS methods indicates that there was no significant bias caused by systematic calibration errors. A limitation of this intercomparison is that standards were rarely cross-analyzed. However, the data do not demonstrate a consistent bias. Calibration errors should produce a systematic offset in the comparison data, which is not apparent in this data set. The QIT has a larger degree of data scatter relative to the GC/MS methods as indicated by the r^2 value of 0.48. This scatter can be attributed to higher measurement uncertainty and more variable blank for the QIT relative to the GC/MS methods. The variability in the QIT blank produced a detection limit of 600 ppt, compared to the GC/MS-P detection limit of 15 ppt. The FIS exhibits a positive bias, on average, for concentrations below 0.75 ppb (nighttime data). This is expected when isoprene concentrations are low relative to interfering species [*Guenther and Hills*, 1998], as discussed below.

A percent difference analysis was conducted for all methods versus the GC/MS-P. All time-matched data were used for this comparison. The calculation was performed using equation (1).

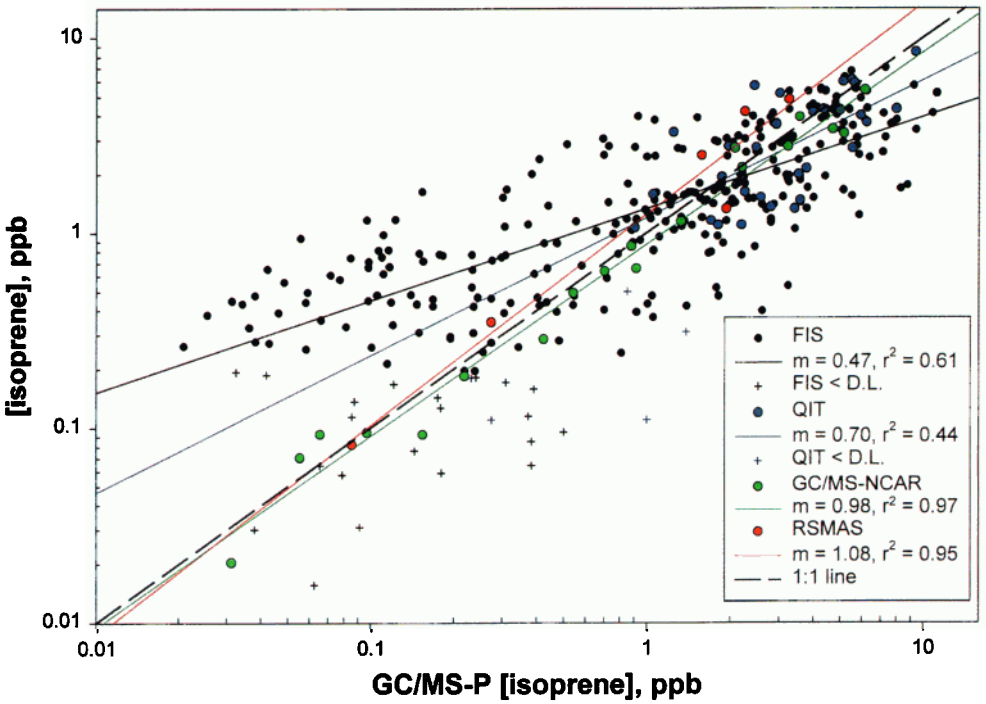

Plate 3. Log – log plot of the FIS, QIT, GC/MS-NCAR, GC/MS-RSMAS isoprene determinations versus the GC/MS-P isoprene determination. The linear least squares fit (llsf) of each data set is displayed with the representative color. The slopes of the llsf line and the correlation coefficient are shown in the legend. The FIS and QIT data below the calculated detection limit are shown with cross symbols but were not used in the regression analysis.

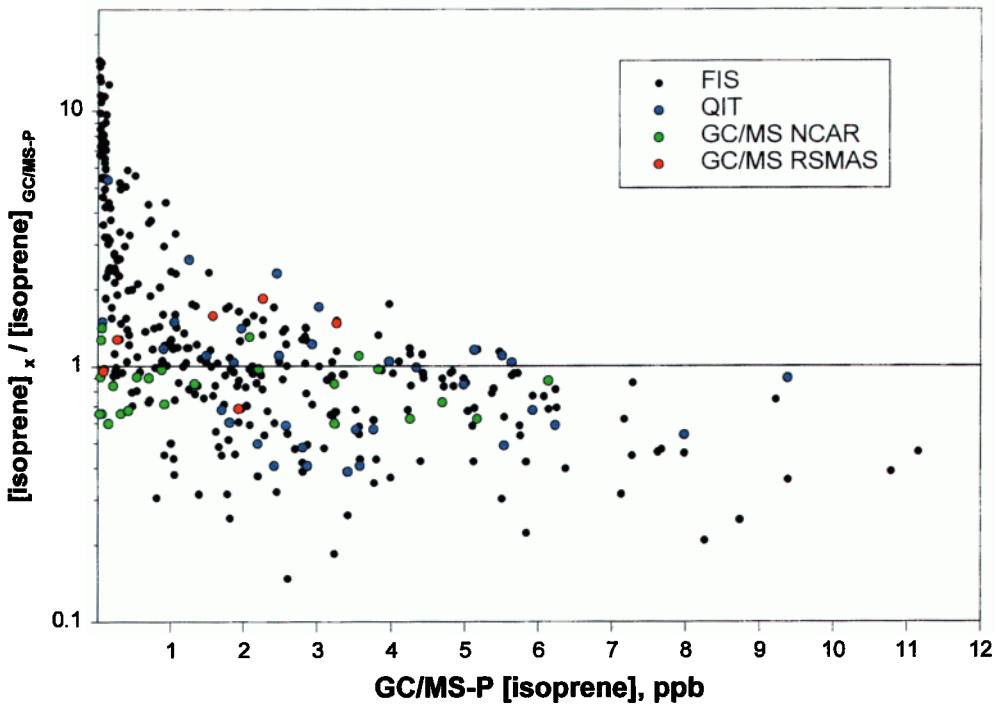

Plate 4. Ratio plot of $[isoprene]_x/[isoprene]_{GS/MS\text{-}P}$ versus $[isoprene]_{GC/MS\text{-}P}$. The horizontal line at 1 represents the value of a perfect agreement between all methods relative to the reference method GC/MS-P.

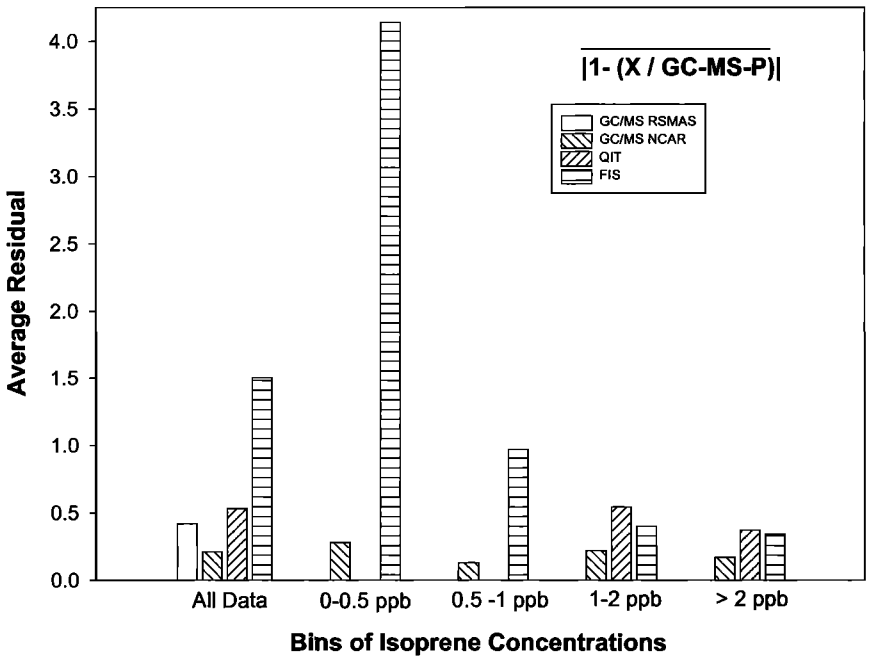

Figure 4. Plot of the average residuals from the value 1 of the ratio $[isoprene]_x/[isoprene]_{GS/MS-P}$ versus $[isoprene]_{GC/MS-P}$. The data are binned in concentrations of 0.0-0.5 ppb, 0.5-1.0 ppb, 1.0-2.0 ppb, and above 2.0 ppb. Because of limited time-matched data for GC/MS-RSMAS its residuals were not binned.

$$\% \text{ difference} = \left| 1 - \frac{[isoprene]_X}{[isoprene]_{GC/MS-P}} \right| \cdot 100 \quad (1)$$

To provide a more meaningful statement of the mean percent difference, the skewness of the percent difference distribution is avoided by only considering the median 90th percentile of the data. The calculated mean percent difference is 21% for GC/MS-NCAR, 41% for QIT, 42% for GC/MS-RSMAS and 88% for the FIS. For a comparison of percent differences, we refer to the results of Task 3 of NOMHICE [*Apel et al.*, 1999]. NOMHICE Task 3 involved circulating 60 commonly observed NMHCs at concentrations of 1-30 ppbv in nitrogen diluent gas in stainless steel canisters to 29 laboratories. Most laboratories utilized GC/FID, while a few utilized GC/MS methods. Reference mixing ratios were determined jointly by scientists from NCAR and from the U.S. Environmental Protection Agency (EPA). The average systematic error for isoprene for all laboratories was 17% high. Participant's results for isoprene were variable as witnessed from the geometric standard deviation of the ratio (the antilog of the mean of the logs of the ratio $[isoprene]_x/[isoprene]_{reference}$). Two thirds of the participant's results fell in the range of 43% low to 75% high compared to reference values. During the NOMHICE Task 3 some of the largest analytical discrepancies were from laboratories that used in-house standards for their calibration and/or syringe sample injection techniques.

While Plate 3 provides an indication of the agreement between methods, direct regressions tend to overweight the high concentration data and make it difficult to compare method performance over the range of observed concentrations. A potentially more informative way to illustrate comparison data is with a ratio plot. Again, the GC/MS-P method was used as a reference method. In Plate 4, we plot the ratio $[isoprene]_x/[isoprene]_{GS/MS-P}$ versus $[isoprene]_{GC/MS-P}$. The scatter in the time-matched data increases as the data approach the detection limit of the methods; this is expected because the uncertainty of the determination increases as the signal to noise ratio decreases. For concentrations above 5 ppb there is an apparent systematic bias for the GC/MS-P relative to the FIS and the QIT. On the ratio plot in Plate 4, there is random scatter about unity for both the University of Miami and the NCAR GC/MS methods. This is not surprising because these methods are similar to the GC/MS-P and should have similar noise, detection limits, and perhaps systematic errors. The most significant difference between the GC/MS-P and the GC/MS-NCAR is the preconcentration method. This result implies that Tenax-based preconcentration and cryogenic preconcentration are equally viable methods for isoprene determinations. The fact that the GC/MS-P method used a KI trap to remove ozone and the NCAR method did not, and the comparative data are in agreement, indicates that there are no significant losses of isoprene due to ozonolysis for the methods that used cryogenic preconcentration.

To quantitatively evaluate the results in Plate 4, we calculated the residual for each data point from unity and determined the average residual within binned concentration ranges. Figure 4 depicts the average residuals for each method as a function of isoprene concentrations in bins of 0.0 – 0.5 ppb, 0.5 – 1.0 ppb, 1.0 – 2.0 ppb, and > 2.0 ppb. The average residual of the ratio for all time-matched data from unity is 0.21 for GC/MS-NCAR, 0.42 for GC/MS-RSMAS, 0.53 for QIT, and 1.50 for the FIS. Because the GC/MS-RSMAS produced only seven time-matched data points the residual analysis was not binned. Also, there was only one data point for the QIT ratio analysis in the bins of 0.0 – 0.5 ppb (4.4) and 0.5 – 1.0 ppb (0.2). There is a large increase in the residual below 0.5 ppb for the FIS. A significant

number of the FIS data points in the 0.0-0.5 ppb bin are near the detection limit, hence the implied systematic error and/or scatter can be related to the increased contribution of the uncertainty in the blank. It is also possible, however, that as isoprene concentrations approach the detection limit, the contribution of normally minor interferences becomes significant. Potential interferences for all methods are discussed below in section 3.4.

3.4. Interferences

All three of the GC/MS methods chromatographically separate and then quantify isoprene at $m/z = 67$ [$C_5H_7^+$] from electron impact ionization. Thus interferences would have to coelute with isoprene and produce a signal at mass 67. There is little chemical noise in the chromatograms at $m/z = 67$, and therefore the blanks in the GC/MS methods are dictated by instrumental noise, column bleed, and memory effects, all of which are minimal. For these reasons the GC/MS methods (perhaps in contrast to GC/FID) achieve low part per trillion detection limits, 1-15 ppt, with a small likelihood for systematic error, other than from uncertainty in the calibration standards.

The QIT method was employed to evaluate the selectivity of the VME chemical ionization. As discussed above, the reaction of ionized VME with isoprene produces an adduct ion at $m/z = 94$, which then undergoes (CAD) to produce $m/z = 79$. Hence a potential chemical interferent could be any mass 68 alkene that reacts with VME to produce a $m/z = 94$ ion, or any molecule of $MW = 94$ that could be ionized by VME via charge transfer but which would then also have to exhibit a loss of $m/z = 15$ during CAD. The lack of a substantial positive bias in the QIT data, as shown in Plate 4, indicates that no chemical interferent exists at this site, or the interfering compounds produce an insignificant signal. However, a significant blank was observed which was caused by the installation of a Nafion dryer into the sampling system on August 1. The QIT detection limit rose from 125 ppt to 600 ppt after the installation of the dryer. This was caused by carryover effects attributed to the isoprene slowly permeating through the Nafion polymer. Unfortunately, the Nafion drying tube limits the current method to hydrocarbon determination because Nafion does not allow reproducible sampling of oxygenated volatile organic compounds [*Burns et al.*, 1983].

Guenther and Hills [1998] identified potential interferences for the FIS by measuring the response factors from a representative list of compounds containing terminal double bonds, i.e., for which ozonolysis produces HCHO as a product. The relative interferences have the potential to be quite high during the nighttime when the isoprene concentrations are below 750 ppt. For the FIS the data agreement above 1 ppb is quite good, but on several nights, a bias below 750 ppt (relative to the GC/MS-P) is observed, suggesting the possibility of chemical interferences. The limited data coverage for potential interferences, largely methyl vinyl ketone (MVK), methacrolein (MACR), propene, and ethene does not allow for a rigorous investigation of the source of the discrepancy. Of the 13 full nights examined in this intercomparison, 5 nights demonstrate a positive FIS bias, 4 nights show no nighttime offset, 2 nights demonstrate a small negative FIS bias, and 2 nights do not have sufficient isoprene data coverage to make the comparison. In Figure 5 we present the calculated signal contribution from MVK, MACR, propene, and ethene for the night of August 5, obtained by multiplying their mixing ratios by their respective response factors as reported by *Guenther and Hills* [1998], and summing to produce the total offset. This value is plotted in Figure 5 with the difference between the FIS and the GC/MS-P isoprene determinations. For this night, which is comparable to other nights where a positive FIS bias was observed, the calculated response from the sum of these compounds is comparable to the observed FIS-GC/MS-P offset. However, on several nights the predicted FIS offset, predicted from the presence of terminal alkenes, does not occur in the ambient data. Since this bias should consistently be observed, this implies the possibility of another source of error. The nighttime offset could have been due to zero drift

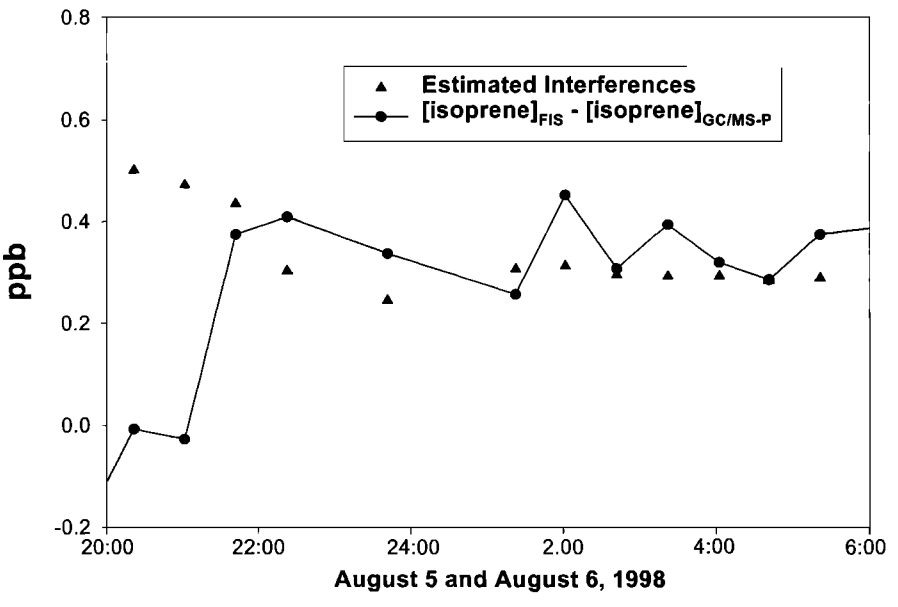

Figure 5. FIS offset relative to the GC/MS-P and the predicted summed contribution of methyl vinyl ketone, methacrolein, propene, and ethene to the FIS signal for the night of August 5 and the morning of August 6.

of the FIS which might have been corrected by more frequent calibration, especially at night. The sensor was being operated in eddy covariance mode during PROPHET (a calibration-insensitive mode). At low concentrations, even a small error in the zero offset could cause a large error in the ambient isoprene FIS data. This may explain why the offset is not consistent. While the interfering species should produce a signal, the zero offset could be in error either in a positive or negative direction, which would cause the expected bias relative to the GC/MS-P to vary randomly. More experimentation should be conducted in order to quantify potential interferences of the FIS during a field study. The FIS has proven to be a reliable isoprene flux measurement instrument and has the potential to be a fast time isoprene mixing ratio sensor for rural sites, at least for conditions when isoprene is the dominant component of the terminal alkene burden.

4. Conclusions

This study represents a quantitative comparison of five automated, field-deployed isoprene measurement methods during the 1998 PROPHET campaign. This informal intercomparison is unique in that it is an evaluation of the entire method from calibration to quantitation. Each group utilized different standards that were not cross-calibrated, therefore the standards had the potential to contribute to the lack of agreement. Overall, all methods demonstrate relatively good agreement in that the diel profiles, decays, and onsets were captured; however, the relative differences at isoprene concentrations below 1 ppb are significant. Also, a bias between the QIT and FIS methods relative to the GC/MS-P for data above 5 ppb was observed. As nighttime atmospheric chemistry garners more attention, the accuracy and frequency of measurements below 1 ppb will become increasingly important.

The FIS has been utilized effectively as an atmospheric flux sensor and laboratory cuvette monitor. During this study, the FIS provided continuous data coverage with a sampling frequency of 1/min. Consequently, the FIS should be considered a reliable on-line sampling method for the determination of isoprene mixing ratios when isoprene dominates the terminal alkene budget, i.e., during the daytime. Unfortunately at night, when isoprene concentrations are low, other alkenes can contribute significantly to the total signal. Accordingly, caution should be exercised in interpreting FIS concentration data below 1 ppb and/or during nighttime analysis. Also, future studies should involve consistent nighttime calibrations to minimize the potential for error caused by zero drift.

The QIT successfully demonstrated that selective CI chemistry, coupled with MS/MS technology, can provide a discriminating determination of isoprene without chromatography. However, this first field deployment did expose a limitation of the method. Humidity in the sample leads to water accumulation in the ion trap, which can cause electrical arcing, coulombic space charge problems, and a high-pressure environment, all of which can trigger system failures. Under the current configuration a Nafion drying tube is a necessary part of the QIT sampling unit to remove water from the sample stream. Future work needs to be done to improve the sample interface in order to make the QIT a robust method. Possible alternatives to the Nafion drying tube are a *U*-tube condenser (water trap) or use of a Tenax polymeric preconcentration trap.

Regression analysis of the GC/MS methods demonstrate excellent agreement for ambient sample analysis. The GC/MS-P demonstrated excellent data coverage throughout the study and displayed consistent agreement with the GC/MS-NCAR for all isoprene concentrations. While the FIS and QIT methods showed promise during PROPHET 1998, the GC/MS methods appear to be the most accurate, while providing the highest degree of precision and lowest detection limits. We note that although the time resolution of the GC/MS methods for this study, 30 min or longer, could not capture the fine temporal features of a molecule of high reactivity such as isoprene, this could be greatly improved simply by optimizing the chromatography to focus on rapid elution of isoprene, followed by high-temperature column purging before the subsequent analysis.

Finally, this informal intercomparison and the analysis of other NMHC intercomparison studies reveals limitations of the data sets. On the basis of this experience, we have identified the following recommendations. These recommendations may seem obvious, yet typically present a challenge during the competing pressures of a field study. A single instrument analysis should include the following: (1) Determination of analytical precision should be conducted in the field, not in the laboratory. (2) High-quality gas phase standards, applied at the sample inlet, are essential for accuracy in the field. (3) Standards should be characterized with certified, traceable standards, preferably from NIST. (4) Calibration curves, with replicate and frequent blanks, representing the range of concentrations for the ambient concentrations of the analyte should be obtained in the field. When multi-method analysis is available, the following should also apply: (5) Standards should be regularly cross analyzed. (6) Every effort should be made to sample simultaneously from the same inlet to facilitate unambiguous comparison.

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