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Quantitative Determination of Biogenic Volatile Organic Compounds in the Atmosphere Using Proton-Transfer Reaction Linear Ion Trap Mass Spectrometry[†]

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Although oxidation of biogenic volatile organic compounds (BVOCs) plays an important role in tropospheric ozone and secondary organic aerosol production, significant uncertainties remain in our understanding of the impacts of BVOCs on ozone, aerosols, and climate. To quantify BVOCs, the proton-transfer reaction linear ion trap (PTR-LIT) mass spectrometer was previously developed. The PTR-LIT represents an improvement over more traditional techniques (including the proton-transfer reaction mass spectrometer), providing the capability to directly quantify and differentiate isomeric compounds by MS/MS analysis, with better time resolution and minimal sample handling, compared to gas chromatography techniques. Herein, we present results from the first field deployment of the PTR-LIT. During the Program for Research on Oxidants: Photochemistry, Emissions and Transport (PROPHET) summer 2008 study in northern Michigan, the PTR-LIT successfully quantified isoprene, total monoterpenes, and isomeric isoprene oxidation products methyl vinyl ketone and methacrolein at sub-parts per billion (nmol/mol) levels in a complex forest atmosphere. The utility of the fast time response of the PTR-LIT was shown by the measurement of rapid changes in isoprene, methyl vinyl ketone, and methacrolein, concurrent with changing ozone mole fractions. Overall, the PTR-LIT was shown to be a viable field instrument with the necessary sensitivity, selectivity, and time response to provide detailed measurements of BVOC mole fractions in complex atmospheric samples, at trace levels.

A major uncertainty in the future of climate change is related to the fate and behavior of the biosphere, particularly due to

nonlinear interactions between climate and biogeochemical cycles.¹ Models of future climate states diverge significantly based on the treatment of the future biosphere.^{2,3} Forest ecosystems, particularly in the tropics, emit large quantities of biogenic volatile organic compounds (BVOCs),⁴ which comprise ~90% of global VOC emissions at 1150 Tg C/year.⁵ While BVOC emissions are predicted to increase, the response of biogenic emissions to climate change is highly uncertain, due to complex feedbacks involving warming, drought, nutrient (e.g., N) inputs, land use changes, tropospheric ozone (O₃), aerosols, and carbon dioxide (CO₂) concentrations.^{6,7} The atmospheric oxidation of BVOCs (in the presence of NO_x) produces ozone (a greenhouse gas) and secondary organic aerosol (SOA), which influence climate through both direct and indirect effects.¹ While biogenic SOA formation has been shown to significantly impact aerosol optical thickness and, thus, direct radiative forcing,⁸ the mechanisms of BVOC oxidation leading to SOA formation are poorly

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understood.^{5,9} BVOCs typically have an atmospheric lifetime of minutes to hours¹⁰ and exist as complex mixtures with individual BVOC mole fractions ranging from a few ppb (nmol/mol) down to sub-ppt (pmol/mol) levels.¹¹ Only a small fraction of atmospheric VOCs have been identified with many likely existing as isomers, further complicating measurement.⁵ Thus, study of the impacts of BVOCs on ozone, aerosols, and climate requires measurement techniques that are sensitive, selective, and possess fast time response.

Global emissions of isoprene (2-methyl-1,3-butadiene, C₅H₈), estimated at ~400–600 Tg C/year,¹² are greater than for any other nonmethane BVOC and represent approximately one-third of total nonmethane VOC emissions.⁵ Isoprene thus contributes significantly to global SOA concentrations, despite low aerosol production yields (~1–3%) from its oxidation;¹³ global annual mean surface SOA concentrations due to isoprene are predicted to increase by ~30% from year 2000 to 2100.¹⁴ Isoprene has a short atmospheric lifetime (~1 h to 1 day) due to fast reactivity with tropospheric oxidants.¹⁰ The dominant first-generation products in the reaction of isoprene with OH radicals in the presence of NO are the structural isomers methyl vinyl ketone (CH₃C(O)CH=CH₂; MVK) and methacrolein (CH₂=C(CH₃)CHO, MACR), in addition to formaldehyde (CH₂O).¹⁵ The oxidation pathways for these isomers differ with MACR producing peroxyacetylnitrate (MPAN) and MVK producing peroxyacetylnitrate (PAN), for example.¹⁶ The contribution of isoprene oxidation to local ozone production can be estimated using MVK or MACR mole fractions since NO₂, which leads to the formation of O₃ upon photolysis, is generated in the oxidation of isoprene in the presence of NO.^{17,18}

Proton-transfer reaction mass spectrometry (PTR-MS) is frequently used to quantify atmospheric VOCs in real time at parts per trillion levels.^{19,20} While many publications to date have used PTR-MS for measurement of [MVK + MACR], PTR-MS cannot differentiate between such isobaric species (i.e., analyte ions with the same nominal mass) and isomers based solely on precursor

ion mass. Generally, gas chromatography (GC) is employed for the separation and determination of MVK and MACR, for example, in the ambient atmosphere; however, the sampling frequency of ~30–40 min is suboptimal given fast isoprene oxidation kinetics,²¹ and analyte manipulation is required prior to injection. During GC sample preconcentration, artifacts can be introduced due to interactions between VOCs and reactive gases, such as O₃, which can produce MVK and MACR from trapped isoprene, for example.²² Thus, Mielke et al.²³ developed a proton-transfer reaction linear ion trap (PTR-LIT) mass spectrometer, which, similar to PTR-MS, utilizes chemical ionization of VOCs using a soft ionization source (H₃O⁺), providing ionization of most VOCs.²³ Collision-induced dissociation (CID) of ions within a linear ion trap is utilized to differentiate and quantify isobaric and isomeric species.²³ Higher ion collection efficiencies of the linear ion trap compared to a quadrupole ion trap improve the limit of detection (LOD), which is important for atmospheric measurements.²³ Previously, Mielke et al.²³ obtained a PTR-LIT LOD of ~100 ppt for MVK and MACR, using the ratio of *m/z* 41 to *m/z* 43, CID fragments of the precursor ion *m/z* 71, for ~2 min averaging. During a smog chamber isoprene-NO_x irradiation experiment, the PTR-LIT showed quantitative agreement with GC/MS measurements of MVK and MACR mole fractions and provided increased temporal resolution of the reaction progress.²³ However, to date, the PTR-LIT, while highly promising, has not been tested in the low concentration, complex, and dynamic matrix of the ambient atmosphere.

Herein, we describe the first field-based measurements using the PTR-LIT during the Program for Research on Oxidants: Photochemistry, Emissions and Transport (PROPHET) summer 2008 field intensive at the University of Michigan Biological Station (UMBS). We report quantification of isoprene, MVK, MACR, and total monoterpenes above the mixed forest canopy. The MS² capability of the PTR-LIT was also utilized to test for interferences by other species at *m/z* 69 and 71 in the quantification of isoprene and MVK + MACR, respectively, in MS¹ mode.

EXPERIMENTAL SECTION

Atmospheric BVOC oxidation chemistry was studied during the summer 2008 intensive in northern Michigan at the PROPHET tower site at UMBS (45° 30' N, 84° 42' W).²⁴ The mixed forest is primarily composed of red maple (*Acer rubrum*), red oak (*Quercus rubra*), paper birch (*Betula papyrifera*), white pine (*Pinus strobus*), and big tooth aspen (*Populus grandidentata*), which emit BVOCs, including isoprene, monoterpenes, and sesquiterpenes.²⁵ Atmospheric measurements were made ~12 m above the average canopy height (~22 m) using a 5 cm diameter Pyrex sampling manifold (flow rate of ~3300 sLpm) leading to the laboratory at the base of the tower. With sampling from the main manifold through 70 °C heated Teflon tubing, the residence time from the PROPHET manifold inlet at ~34 m to the PTR-LIT was ~2.5 s. A

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Rotronic Instrument Corp. MP100 probe measured temperature and relative humidity. Ozone mole fractions were determined using a Thermo Electron Corp. model 49C ozone analyzer. NO_x mole fractions were determined from June 22 to July 28 using a home-built chemiluminescence instrument, following Ridley and Grahek.²⁶

The PTR-LIT, described in detail by Mielke et al.,²³ consists of a hollow cathode ion source producing H₃O⁺, ion drift tube, linear quadrupole ion trap, and a secondary electron multiplier. Ambient air is introduced into the drift tube where molecules (M) with higher proton affinities than H₂O (7.22 eV) undergo proton-transfer reactions to produce mainly MH⁺ ions with little fragmentation. Protonated molecules are injected into the linear ion trap, where they accumulate and can either be scanned out without further manipulation (MS¹ mode) or undergo CID (MS² mode), prior to detection by the secondary electron multiplier. During MS² mode, the ion trap is filled, a narrow range of ions (usually 1 Da) is isolated, the ions undergo CID via dipolar excitation in the presence of helium, and the resulting fragments are scanned out of the ion trap. For comparison between the quantification of [MVK + MACR] in MS¹ and MS² modes, the PTR-LIT was alternately operated in MS¹ mode for 40 min (during which time all masses were monitored) and then MS² mode for precursor ions at *m/z* 71 (corresponding to MVK and MACR) for 20 min. As described by Mielke et al.,²³ the ratio of *m/z* 41 to 43, resulting from CID of the ions at *m/z* 71, enabled differentiation of MVK and MACR. CID of precursor ions at *m/z* 69 (primarily protonated isoprene) was intermittently performed to examine for possible isoprene interferences from other species.¹⁹ For these MS² experiments, the CID product *m/z* 41 was used to quantify isoprene. During PROPHET, trap filling, ion manipulation, and scan-out times were 2 s, 100 ms, and 250 ms, respectively, providing a sampling rate of ~0.4 Hz. To ensure quantification of low mole fractions during these first PTR-LIT field measurements, 250 data points were averaged, yielding a duty cycle of ~10 min.

The PTR-LIT sampled ambient air continuously from July 7 to August 13 with down time only for calibration. From July 7 to July 19 (period 1), the PTR-LIT was operated such that only ions at *m/z* 67–73 were isolated for the quantification of isoprene, MVK, and MACR. From July 19 to August 13 (period 2), the PTR-LIT utilized a scan function that encompassed *m/z* 55–210, which allowed the quantification of total protonated monoterpenes (C₁₀H₁₇⁺) at *m/z* 137. The similarities in the PTR-LIT CID fragmentation patterns of structurally similar monoterpenes do not allow differentiation between individual monoterpenes in complex mixtures.²⁷ Calibrations for isoprene, MVK, and MACR were performed every 1–3 days using separate standard cylinders, prepared in the Shepson lab;²⁸ total monoterpenes were quantified based on their relative sensitivity compared to isoprene, as determined previously from a multicomponent

standard.²⁷ To calculate [MVK + MACR] in MS¹ mode, the calibration slopes for MVK and MACR standards were weighted based on the MVK/MACR ratio. Figure S-1 in the Supporting Information illustrates the linear calibration curves for isoprene, MVK, and MACR. The humidity dependence of the PTR-LIT for the quantification of isoprene, MVK, and MACR was investigated by adding the standard gas to air at six different relative humidities from 0–100%. Absolute humidity was quantified by a LI-COR 7000 CO₂/H₂O gas analyzer.

RESULTS AND DISCUSSION

One challenge in operating a PTR-MS under ambient atmospheric conditions can be the changing humidity of the sample air.¹⁹ Reactions between sample and H₃O⁺ reagent ions in the PTR drift tube can significantly depend on the humidity of the sampled air, particularly for VOCs with proton affinities only slightly higher than that of water, such as formaldehyde.¹⁹ Previously, Warneke et al.²⁹ found that the PTR-MS operating conditions determined the magnitude of the humidity dependence on the observed isoprene signal. During the PROPHET study, the PTR-LIT humidity response for isoprene, MACR, and MVK was examined (Table S-1 in the Supporting Information). The slopes of normalized signals versus absolute humidity were not significantly different from zero for absolute humidities of 5.9–24.5 mmol/mol for isoprene, MACR, and MVK. This encompasses the humidity range observed during the PROPHET study (8.9–23.6 mmol/mol), demonstrating no need to scale ion signals for changing ambient humidity as has been completed for certain PTR-MS field studies.³⁰ While not examined in this study, the PTR-LIT humidity dependence for monoterpenes, as measured by the signals at *m/z* 137, is expected to be minor (<15% error in mole fraction) based on previous PTR-MS studies,³¹ given the PTR-LIT *E/N* ratio (electric field strength to number density of buffer gas) of 95 Td.

During periods 1 and 2 of the PROPHET study, the MS¹ LODs, defined as 3σ of the blank (noise) for ~10 min averages, were 93–110, 140–200, and 110 ppt for isoprene (*m/z* 69), (MVK + MACR) (*m/z* 71), and total monoterpenes (*m/z* 137), respectively. Given these LODs, 95%, 96%, and 77% of the observed isoprene, (MVK + MACR), and total monoterpene data, respectively, were resolved. LODs were lower in MS² mode, as observed during previous laboratory studies, due to the high CID efficiency, lower standard deviation in the noise of the blanks for the product masses, and higher scan-out (detection) efficiency for lower mass ions.²³ MACR and MVK LODs, based on *m/z* 41 to 43 ratios, were 67–120 and 120–130 ppt, respectively, during the PROPHET study for ~10 min averaging. Required averaging times are dependent on the ambient concentration and the LOD of the analyte of interest. For example, during PROPHET, 88% of the observed MS² MVK data were above the LOD; based on Poisson statistics, averaging of 55 data points (~2.2 min averaging) would have resolved

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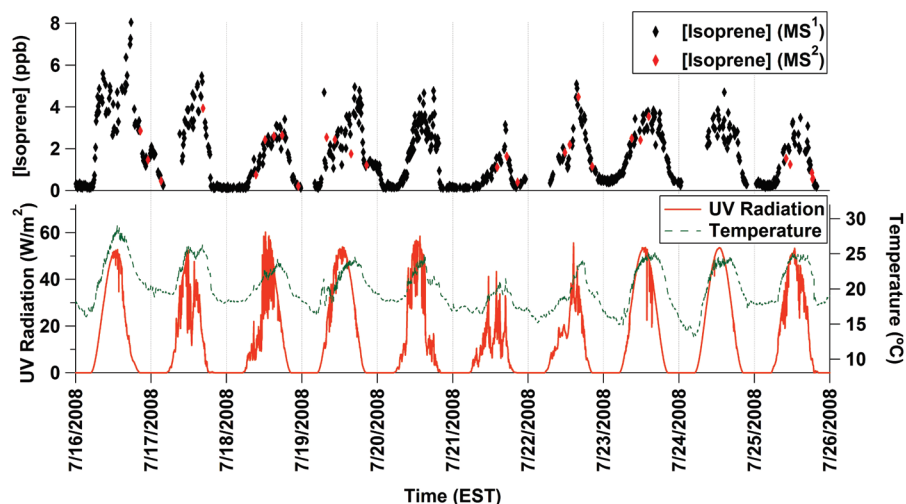


Figure 1. Temporal profiles of isoprene mole fractions measured by the PTR-LIT in MS¹ (m/z 69) and MS² (m/z 41) modes, as well as broadband ultraviolet (UV) radiation and ambient temperature. Date labels indicate 0:00 EST.

75% of the MS² MVK data. Therefore, future deployments of the PTR-LIT will employ reduced averaging for improved time resolution, which will also be possible in environments characterized by higher analyte mole fractions.

In the ambient atmosphere, m/z 69 is generally representative of isoprene, particularly in BVOC-impacted environments, as determined by comparisons between PTR-MS and GC measurements.¹⁹ When 2-methyl-3-buten-2-ol (C₅H₁₀O or MBO), which is emitted from several species of North American pine trees,³² is protonated during PTR-MS, it loses H₂O to yield m/z 69. However, MBO likely did not contribute significantly to m/z 69 at UMBS, since the white pine trees at UMBS do not emit MBO.³² For isoprene calibration standards, the m/z 69 CID products were observed at m/z 41 and m/z 39 with an average m/z 39/41 ratio of 0.19 ± 0.03 . For the 66 MS² data points obtained for the m/z 69 precursor ion during the PROPHET 2008 study, the average m/z 39/41 ratio was 0.21 ± 0.02 , i.e., not statistically different. Figure 1 illustrates good agreement between isoprene mole fractions alternately determined based on MS² m/z 41 and based on MS¹ m/z 69. The observed diurnal pattern with mid-day maxima is due to correlation of isoprene emission rates with temperature and irradiance,³³ as observed in Figure 1. The mean mid-day (10:00–14:00 local time (EDT)) isoprene mole fraction for PROPHET 2008 (2.0 ± 0.1 ppb) is similar to the mean mid-day summer 1998 mole fraction (1.9 ± 0.4 ppb) at the same location as measured by GC/MS.³⁴ Figure 2 illustrates the distribution of isoprene MS¹/MS² ratios, calculated using interpolated MS¹ mole fractions, as described in the Supporting Information. A p -value of 0.22 was obtained for a one-sample t test with a mean of 1, suggesting the isoprene MS¹/MS² ratios are likely normally distributed about 1. This implies that there were no interferences with isoprene at m/z 69, unless the contributing species had the same CID fragmentation pattern. Furan (C₄H₄O), which can also be present at m/z 69,

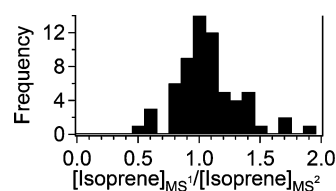


Figure 2. Histogram of isoprene MS¹/MS² mole fraction ratios (bin width of 0.1).

is known to have a comparable MS¹(m/z 69)/MS²(m/z 41) ratio; however, furan reacts rapidly with OH and is only present in fresh biomass burning plumes,³⁵ which did not impact the PROPHET study. In environments where isoprene and furan coexist, differentiation may be possible using the isoprene CID fragment m/z 67 (which does not exist in the furan CID spectrum). Together these analyses demonstrate that the signal at m/z 69 was indeed representative of isoprene concentrations during PROPHET 2008.

During a previous smog chamber study, Mielke et al.²³ used the PTR-LIT to independently quantify MVK and MACR using CID products at m/z 41 and m/z 43 from the m/z 71 precursor ions, for relatively high concentration laboratory experiments. During PROPHET, CID of ions at m/z 71 yielded a mass spectral pattern indicative of MVK and MACR present. Since the independent quantification of MVK and MACR is important, an essential test of the PTR-LIT derives from the comparison of the MS² [MVK] + [MACR] data with [MVK + MACR] from the MS¹ mode (emulating the PTR-MS) for any systematic differences. As shown in Figure 3, good agreement is achieved for the comparison of [MVK + MACR] determined from PTR-LIT MS¹ mode and [MVK] + [MACR] via the MS² mode during PROPHET 2008. As described in the Supporting Information, the MS² [MVK] + [MACR] mole fraction was systematically lower than the MS¹ mole fraction on average for July 7 to July 19, likely due to variation in the determined calibration sensitivity for this period. However, in addition, operating in MS² mode was found to decrease precision of the [MVK] +

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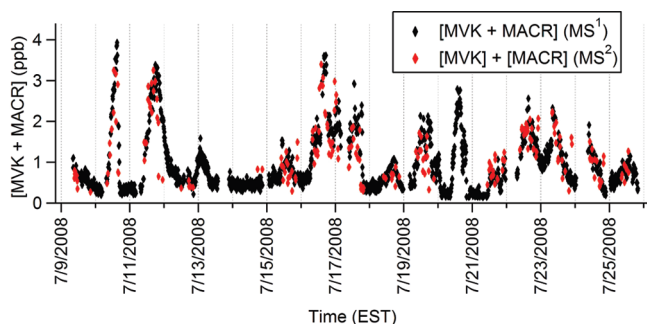


Figure 3. Temporal profiles of MVK + MACR mole fractions measured by the PTR-LIT in MS¹ (*m/z* 71) and MS² (*m/z* 41/43 ratio) modes. Date labels indicate 0:00 EST.

[MACR] measurement by 6%, likely due to the added complexity of CID measurements.

Similar to the isoprene diurnal trend, maxima in [MVK + MACR] generally occurred at mid-day due to the fast oxidation of isoprene by OH in the presence of NO_x.¹⁸ For periods of concurrent NO_x and PTR-LIT measurements, NO_x mole fractions, ranging from 0.03–3.10 ppb, were typical of the rural boundary layer,³⁶ such that oxidation of isoprene was NO_x-limited rather than VOC-limited.¹⁸ Previously, the production rate of MVK has been shown to have a maximum at ~4–6 ppb NO_x.¹⁸ The mean mid-day (10:00–14:00 local time) MVK and MACR mole fractions were 0.73 ± 0.08 and 0.43 ± 0.05 ppb, respectively, yielding a mean [MVK + MACR]/[isoprene] ratio of 0.60 ± 0.02 . Considering the relative rates of production of MVK and MACR, the predicted slope of [MVK] versus [MACR] is 1.5 ± 0.2 .³⁷ As shown in Figure S-3 in the Supporting Information, when a y-intercept was allowed, the observed slope for the mid-day data was 1.1 ± 0.1 , slightly lower than observed in 1998 (slope = 1.35);³⁴ however, when forced through zero, the slope was 1.6 ± 0.1 , which should be the case if isoprene oxidation is the only source.

A significant advantage of the PTR-LIT is the ability to measure MVK and MACR mole fractions with high time resolution. Previously, a cylindrical ion trap mass spectrometer showed high temporal variability in isoprene mole fractions at UMBS.³⁸ While GC techniques generally possess lower LODs, the current PTR-LIT provides increased time resolution (<10 min) compared to GC/MS (30–40 min) for the measurement of MVK and MACR in the field.^{21,24} As an example from the 2008 PROPHET study, Figure 4 shows the temporal variations of isoprene, MACR, MVK, and O₃ mole fractions for July 10, exemplifying the short-term variability that is possible for these species. Since reaction of OH with isoprene results in the formation of O₃, local ozone production from isoprene oxidation can be calculated from isoprene, MVK (or MACR), and O₃ profiles, as detailed in the Supporting Information. For July 10 (Figure 4), O₃ was observed to increase by 7.3 ppb over the course of ~2.8 h, concurrent

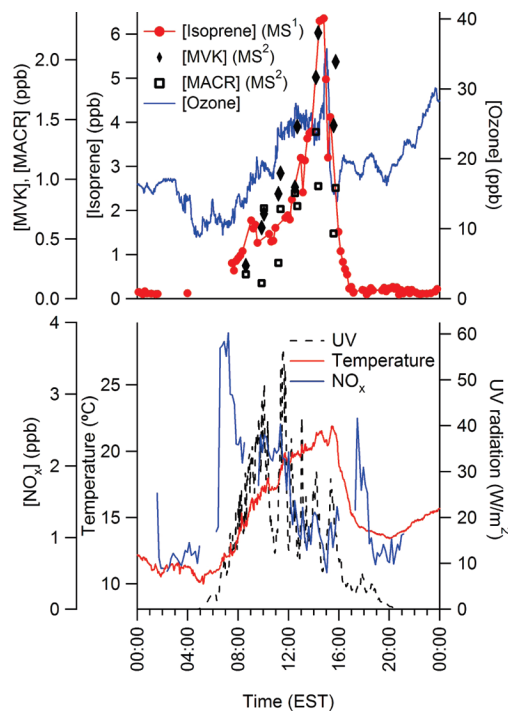


Figure 4. Temporal profile of PTR-LIT isoprene, MVK, and MACR mole fractions, as well as ozone and NO_x mole fractions for July 10, 2008. Ambient temperature and UV radiation are also shown; the variation in UV radiation is due to clouds.

with an increase in MVK of 0.8 ppb. Therefore, ~38% of ozone during this period is estimated to have been produced via local isoprene oxidation above the forest canopy. For similar photochemical episodes on July 11 and July 22, estimates of ~37% and ~16% were calculated, showing the importance of isoprene oxidation in local ozone production. Following the rapid increases in isoprene, MVK, and MACR mole fractions on July 10, rapid losses were observed, as shown in Figure 4. From ~15:02–15:51 EST, the O₃ and isoprene mole fractions rapidly decreased by 22 and 1.7 ppb, respectively, showing the need for rapid measurements to resolve this kind of decay event, which was correlated with temperature and UV radiation. Similar to previous measurements by Hurst et al.,³⁹ isoprene mole fractions decreased from 6.4 to 0.2 ppb over the course of ~2 h (~14:43–16:53 EST). [MVK + MACR] decreased by 3.4 ppb (87%) over the same period. Since this occurred in the daytime, such rapid changes could likely only occur as a result of a very rapid mixing event, i.e., either exchanging isoprene-deficient air from aloft³⁹ or a rapid change in air mass. Such events can be studied with the high time resolution afforded by the PTR-LIT.

Monoterpenes (C₁₀H₁₆) account for ~11% of total VOC emissions globally (~127 Tg C/year), primarily from tropical forests.⁴ The North American upper Great Lakes region, including UMBS, is currently undergoing a transition from deciduous to coniferous forest with dominant big tooth aspen (*Populus grandidentata*, an isoprene, but not terpene, emitter) switching primarily to white pine (*Pinus strobus*, a monoterpene

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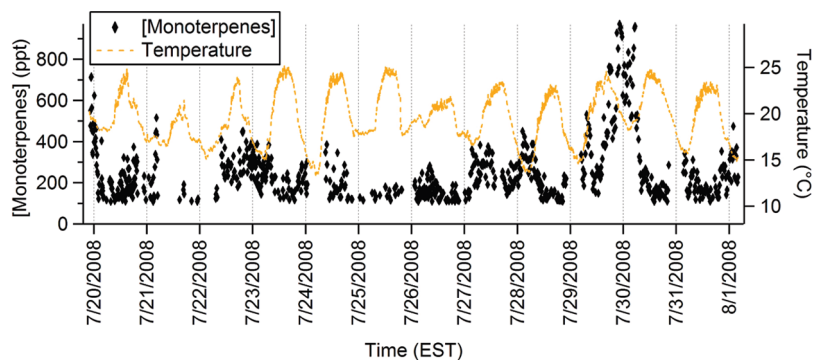


Figure 5. Temporal profile of total monoterpene mole fractions measured by the PTR-LIT in MS¹ (m/z 137) mode, as well as ambient temperature. Date labels indicate 0:00 EST.

and sesquiterpene, but not isoprene, emitter).^{25,40} As the forest composition changes, the mixture of BVOCs will also change, influencing atmospheric processes. Unlike isoprene, most monoterpene emissions are independent of light but exponentially dependent on temperature.¹⁰ The actual concentration is dependent on the flux, as well as oxidation and vertical mixing, which are both suppressed at night. Thus, as shown in Figure 5, total monoterpene mole fractions near the canopy are often greatest at night. During the summer 2008 PROPHET study, total monoterpene mole fractions, measured by the PTR-LIT in MS¹ mode, were found to range from below the LOD (110 ppt) to 970 ppt. For time periods with mole fractions above the LOD (60% of time points), the mean mole fraction was 250 ppt; by including periods with monoterpene mole fractions less than 110 ppt, the mean mole fraction was estimated as 170 ppt. Consistent with the forest succession from aspen to pine, 2008 monoterpene mole fractions were likely higher than the summer 1998 average (50–100 ppt), based on GC/MS measurements.⁴¹ In previous PTR-MS studies, Lee et al.⁴² measured higher total monoterpene mole fractions (by ~30% on average) compared to GC techniques, particularly at night, suggested to be due to the presence of unidentified and unresolved monoterpenes; however, differences between the 2008 and 1998 PROPHET studies were larger on average. Nighttime median monoterpene mole fractions were also higher in 2008 (280 ppt for the 65% of data >LOD; including periods <110 ppt, 200 ppt) compared to 1998 GC/MS measurements (54 ppt).⁴¹ Since monoterpenes are important aerosol precursors,⁴³ the forest ecosystem and associated feedbacks should be changing. This region thus represents a good opportunity to examine the impacts of monoterpene emissions on aerosols and climate.

CONCLUSIONS

The PTR-LIT successfully quantified isoprene, total monoterpenes, and isoprene oxidation products MVK and MACR at sub-parts per billion (nmol/mol) levels in a complex forest atmosphere during

the PROPHET summer 2008 field intensive in northern Michigan. Unlike the traditional PTR-MS, the PTR-LIT provides the capability to differentiate isomeric compounds, such as MVK and MACR. While GC techniques can differentiate and quantify MVK and MACR at sub-parts per billion levels, the PTR-LIT provides improved time resolution (<10 min) compared to GC techniques (30–40 min) during field measurements.²⁴ Furthermore, most GC methods require significant preconcentration of the analyte prior to injection, often leading to systematic errors.²² The utility of the fast time response of the PTR-LIT was shown by measurement of concurrent rapid changes in isoprene, methyl vinyl ketone, and methacrolein, which were observed to be correlated with changes in ozone mole fractions. The change from an isoprene-dominant to monoterpene-dominant environment^{25,40} due to forest succession has implications for regional atmospheric chemistry, such as increasing the regional SOA burden due to the lower volatility and correspondingly higher SOA yields of monoterpenes.⁴³ Future work studying the impacts of BVOCs on oxidative chemistry and SOA formation will benefit from the sensitivity, selectivity, and fast time response of PTR-LIT.

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SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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