Analysis of the isoprene chemistry observed during the New England Air Quality Study (NEAQS) 2002 intensive experiment

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[1]   Isoprene and its first and second generation photochemical products, methyl vinyl ketone (MVK), methacrolein (MACR), and peroxymethacrylic nitric anhydride (MPAN), were measured off the coast of New England during the 2002 New England Air Quality Study (NEAQS) on board the NOAA Research Vessel *Ronald H. Brown*. The results of these measurements were analyzed using a simple sequential reaction model that has been used previously to examine regional oxidant chemistry. The highest isoprene impact was observed in air masses that had passed over an area of high isoprene emission WSW of Boston. The relative concentrations of isoprene and its first generation products show that the photochemistry is consistently "older" than the isoprene photochemistry observed at continental sites. The sequential reaction model was also applied to the aldehyde-PANs (Peroxycarboxylic nitric anhydride) system, and the resulting PPN (peroxypropionic nitric anhydride)/propanal and PAN (peroxyacetic nitric anhydride)/ acetaldehyde relationships were consistent with additional sources of PAN in this environment, e.g., isoprene photochemistry. This isoprene source was estimated to result in approximately 1.6 to 4 times more PAN in this environment relative to that produced from anthropogenic VOCs (volatile organic compounds) alone.

1.   Introduction

[2]   Regional air pollution due to ozone (O_3) has been a persistent problem dating back to the last half of the 20th Century [*National Research Council*, 1991]. The persistence of the problem is due in large part to the fact that the photochemical production of O_3 is driven by a variety of sources of NO_x (NO_x = nitric oxide + nitrogen dioxide) and volatile organic compounds (VOCs). Successful control strategies must take into account these sources in the context of meteorological conditions that contribute to ozone events in a given region. The northeastern United States has been singled out as an important area of concern because of its geographic relationship to anthropogenic NOx source regions, and the presence of significant biogenic hydrocarbon sources.

[3]   The emission of reactive biogenic hydrocarbons (BHC) from vegetation is a major confounding factor in understanding and controlling regional O_3 chemistry [*Trainer et al.*, 1987; *Chameides et al.*, 1988]. Isoprene is the principal reactive BHC in the northeastern United States [*Warneke et al.*, 2004], and has relatively large sources to the west and southwest of the Boston area [*Geron et al.*, 1994]. Isoprene is extremely reactive with atmospheric radicals, OH and NO_3, and very effective in O_3 formation in the presence of sufficient NO_x. Understanding the detailed mechanism of isoprene-NO_x photochemistry is an important part of predicting the effect of this VOC on regional air quality. The first generation products of isoprene oxidation, methacrolein (MACR) and methyl vinyl ketone (MVK), have been used to compare the daytime chemistry occurring in the atmosphere to that predicted from measured rates and branching ratios [*Montzka et al.*, 1993; *Stroud et al.*, 2001a; *Apel et al.*, 2002; *Roberts et al.*, 2003]. This analysis also provided estimates of the time-scale on which the isoprene photochemistry has taken place that ranged from 0.1 to 2 hours. The importance of isoprene-NO_x photochemistry as a source of peroxyacetic nitric anhydride (PAN) has also been demonstrated in Nashville, TN, through the analysis of concurrent measurements of PAN and peroxypropionic nitric anhydride (PPN), and their parent aldehydes [*Roberts et al.*, 2001]. PAN is an extremely important species in the troposphere, as it is the most abundant odd-nitrogen (NO_y) species in the midtroposphere. Its relative stability allows it to be transported over

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long distances, eventually providing a source of NO_x to the remote troposphere.

[4] The data analyzed here were taken during the NEAQS 2002 intensive study aboard the NOAA RV the *Ronald H. Brown*, in the Gulf of Maine. The relationships between isoprene and its first generation products MACR and MVK will be analyzed with a simple sequential reaction model to see if the observations are consistent with the ratios expected from laboratory-determined branching ratios, and to estimate reaction times for this environment. The model will also be used to interpret PAN, PPN, ethanal and propanal measurements to discern the importance of isoprene as a source of PAN.

2. Experimental Methods

[5] The measurements used in the analysis have been discussed in detail elsewhere and will be only briefly summarized here. Methods for the measurement of PANs in this study were described at length by *Williams et al.* [2000], *Roberts et al.* [2002], and *Flocke et al.* [2005] with changes or additions to those methods described below. The basis of the measurement was capillary gas chromatographic separation, followed by electron capture detection. The instrument used a continuously flushed sample loop which was injected every 10 min, on the even 10 min mark, i.e., XX:00, XX:10, XX:20 etc. The inlet consisted of an all-PFA Teflon manifold at high flow (10 SLPM). The inlet was filtered by a 1 μm pore size Teflon filter, which was changed every few days. We have tested filters of this type in the laboratory and found them to pass PAN with 100% efficiency. Moreover, no abrupt change in PANs, either up or down, was associated with the filter changes so we conclude that the filter did not interfere with the measurement. A smaller flow (1 SLPM) was taken from this manifold into the PAN instrument. The PAN thermal decomposition and calibration plumbing were fitted to the small flow inlet as described by *Roberts et al.* [2002]. The inlet equilibration time was estimated to be approximately 1 min. The instrument response to PAN was calibrated routinely, every 5 hours, using a modified acetone/CO/NO photolysis source which is based on the calibrated NO mixing ratio and known conversion efficiency (93 ± 3%). Prior to the cruise, the photolysis source was compared to a diffusion source consisting of a PAN/tridecane/pentadecane mixture in a pressure, temperature and flow controlled capillary cell. The output of the capillary cell was calibrated using an NOy instrument. The responses of the GC system to the two PAN sources were within 5% of each other. The system response to PPN was determined using the diffusion source and NOy instrument prior to the field experiment, and the relative response used during the cruise. Two of the other PAN compounds, PiBN and MPAN, were calibrated by using relative response factors that had been determined in the laboratory, and have been consistent within 5% over several different field campaigns. Detection limits for all of the compounds were 4 pptv and the overall uncertainties were ±(4 pptv + 15%) for PAN and PPN, ±(4 pptv + 20%) for PiBN and MPAN.

[6] Measurements of the volatile organic compounds (VOCs) were made either by gas chromatography/mass spectrometry (GC/MS) or by proton transfer reaction mass spectrometry (PTRMS)   e methods and aspects of the

results of those measurements during this project have been discussed by *de Gouw et al.* [2003] and *Goldan et al.* [2004]. Measurements of NO, NO_2, NO_y, and O_3 were made using methods and procedures described previously by *Williams et al.* [1998].

3. Sequential Reaction Model

[7] The sequential reaction model is a computationally simple scheme that has been successfully applied to a number of tropospheric photochemical systems. It involves a simple reaction scheme in which a parent compound reacts in the atmosphere to form a known product species, at a known rate k_1 and with a known branching ratio α_1, with the subsequent loss of the product species at a known rate, k_2;

$$\text{Parent} => \text{Product} \qquad k_1, \alpha_1 \qquad (1)$$

$$\text{Product} => \text{loss} \qquad k_2 \qquad (2)$$

An expression for the evolution of the ratio [Product]/[Parent] is arrived at by solving the chemical kinetic expression for the formation and loss of the product species [*Bertman et al.*, 1995].

$$[\text{Product}]/[\text{Parent}] = \alpha_1 k_1 / (k_2 - k_1)\{1 - \exp(k_1 - k_2)\text{t}\} \quad (3)$$

Similar expressions have been developed for laboratory kinetics wherein a parent/product pair are being studied [see, e.g., *Baker et al.*, 2004]. A number of publications discuss the application of the sequential reaction model to alkyl nitrate/alkane chemistry [*Bertman et al.*, 1995; *Roberts et al.*, 1998; *Stroud et al.*, 2001b; *Simpson et al.*, 2003], several papers have applied the model to Isoprene-MACR-MVK chemistry [*Stroud et al.*, 2001a; *Apel et al.*, 2002; *Roberts et al.*, 2003], and one publication describes the application of the model to aldehyde-PANs [*Roberts et al.*, 2001].

[8] The analyses of data using the sequential reaction model can reveal interesting and useful things about the associated chemistry. One immediate result is an estimate of the timescale on which the chemistry is occurring, given assumed photochemical quantities such as average [OH] and photolysis rates. Another feature is the extent to which the observed [Product]/[Parent] ratios match those calculated from measured branching ratios of individual reactions. Deviations from the expected kinetic line have revealed the importance of other chemistry in the formation of one or more of the constituents, for example, the large effect of alkoxy decomposition in producing ethyl nitrate in the troposphere [e.g., *Bertman et al.*, 1995], and the significance of isoprene as a source of PAN in Nashville, TN [*Roberts et al.*, 2001]. Limitations of the model include the limited applicability of average photochemical quantities, especially over multiday cycles, and the confounding effects of mixing between air masses of differing ages and origins.

4. Results and Discussion
4.1. Isoprene Methacrolein and Methyl Vinyl Ketone

[9] The daytime photo-oxidation of isoprene is initiated primarily by reaction with OH radical, and produces the first

Table 1. Rate Constants for the Reactions of OH, O_3, and NO_3 With Isoprene, Methylvinyl Ketone, and Methacrolein From the IUPAC Evaluation [*Atkinson et al.*, 2006]
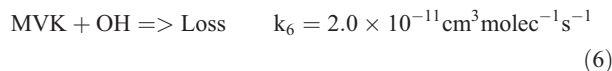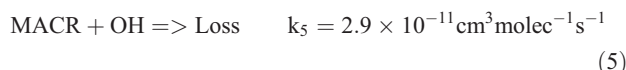
Compound	k_{OH} ($\times 10^{-11}$)	k_{O3} ($\times 10^{-18}$)	k_{NO3} ($\times 10^{-15}$)
Isoprene	10	12.7	700
Methylvinyl ketone	2.0	5.2	<0.6
Methacrolein	2.9	1.2	3.4

generation products methacrolein (MACR) and methyl vinyl ketone (MVK);
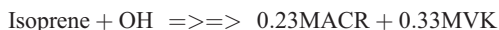
$$\text{Isoprene} + \text{OH} \;=>=>\; 0.23\text{MACR} + 0.33\text{MVK}$$
$$k_4 = 1.0 \times 10^{-10} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1} \tag{4}$$

The rate constant of the reaction is quite high, 1.0×10^{-10} cm^{3}molec^{-1}s^{-1} and the yields have been determined in three different studies, all of which are in good agreement [*Atkinson et al.*, 2006; *Atkinson and Arey*, 2003]. The daytime removal mechanisms of MACR and MVK are dominated by reaction with OH, also relatively rapid reactions, the rates of which are well known [*Atkinson et al.*, 2006, 1983; *Gierczak et al.*, 1997]. Table 1 lists the rate constant recommendations given by the IUPAC evaluation [*Atkinson et al.*, 2006], which will be used in this work.

$$\text{MACR} + \text{OH} => \text{Loss} \quad k_5 = 2.9 \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1} \tag{5}$$

$$\text{MVK} + \text{OH} => \text{Loss} \quad k_6 = 2.0 \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1} \tag{6}$$

Processes such as reaction with O_3 or photolysis are sufficiently slower (<10%) that they may be neglected, at least during the daytime. As a result, the sequential reaction model for Isoprene-MACR and MVK, can be reduced to the above OH chemistry, as described by *Stroud et al.* [2001a], and shown below for MACR/Isoprene;

$$[\text{MACR}]/[\text{Isoprene}] = 0.23*k_4/(k_5 - k_4)$$
$$*\{1 - \exp((k_4 - k_5)[\text{OH}]t)\} \tag{7}$$

Thus equation (7) permits the calculation of the ratio [MACR]/[Isoprene] as a function of time, if an average [OH] is assumed. The analogous equation for [MVK]/[Isoprene] is likewise arrived at, and the two plotted against each other form a line that predicts how the ratios should correlate. The branching ratios for the production of MACR and MVK are a function of NO_x regime. This is because the fate of RO_2 radicals changes from reaction with NO, to reaction with HO_2 or other RO_2 radicals, at about 30 or so pptv of NO. With typical daytime NO_2/NO ratios of 3 to 4, this translates to about 200 pptv of NO_x. 99% of the all NO_x data acquired during NEAQS 2002 was 200 pptv or above, and that corresponding to periods in which MACR and MVK was observed was well above that. Accordingly, the branching ratios appropriate for high NO_x conditions were used in the calculations.

[10] The predicted line is plotted in Figure 1 along with the data points from the NEAQS 2002 study, and summaries of 4 other studies. The ratios in equation (7) change because of the time integral of [OH], $\int[\text{OH}]t$, in practice, an average [OH] is chosen so that a timescale can be placed on the model line. The assumption of a 24 hour average [OH] = 2.6×10^6 molec cm^{-3} results in the times plotted in Figure 1 for the entire kinetic line. This is the average [OH] from the calculation of *Warneke et al.* [2004] for this data set. A 24 hour average is most appropriate for the NEAQS data set considering the transport times between sources and point of observation. The alternate timescale shown in Figure 1 was derived from a daytime average [OH] = 5.2×10^6 molec cm^{-3}, which is the daytime average from *Warneke et al.* [2004], and is most appropriate for the ground site data [*Stroud et al.*, 2001a].

[11] The data in Figure 1 span roughly 5 orders of magnitude, and the timescales associated with the theoretical fit to the data ranged from 0.05 hours (3 min) to more than 10 hours. In general, the lowest ratios were observed at ground sites that were located in the middle of forests. The two studies, SOS 1990 and PROPHET 1998, involved sampling right in the canopy of mixed deciduous forests in the summertime. Transport times in those situations could be as short as tens of seconds. The lowest ratios in the
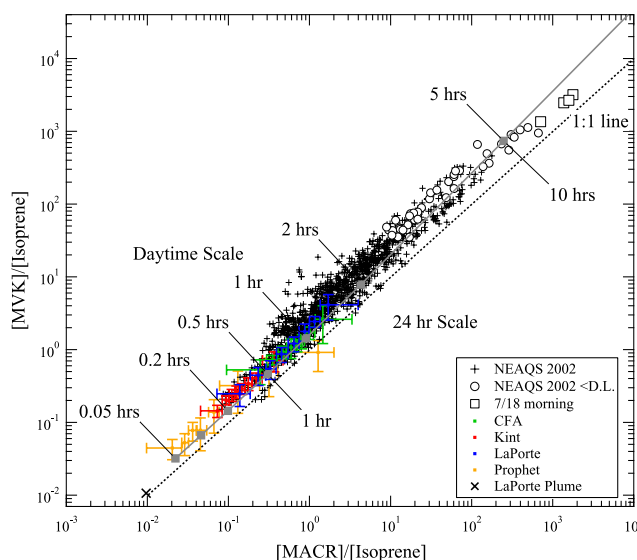

Figure 1. Plot of the ratio MVK/Isoprene versus the ratio MACR/Isoprene. The crosses are all the data from NEAQS 2002 that were above the detection limit. The open circles are those points for which isoprene was below detection limit, but the ratios calculated by using an isoprene mixing ratio equal to one half the detection limit (0.2 pptv). Previously reported daytime data sets are also plotted in 8 bins, with error bars denoting the extent (max and min) of each bin on the horizontal scale and the standard deviation of each bin on the vertical scale. The data sets shown this way are SOS ROSE I, 1990 (red); SOS, Cornelia Fort, 1999 (green); TexAQS 2000, La Porte (blue); and PROPHET 1998 (orange). The model line is plotted in gray, with two different timescales based on [OH]$_{avg}$= 2.6×10^6 molec cm^{-3} (24 hour scale) and [OH]$_{avg}$= 5.2×10^6 molec cm^{-3} (daytime scale).

record were associated with a single sample acquired during TexAQS 2000, as an isoprene plume from a chemical plant impacted the site [*Roberts et al.*, 2003] at 0856 LST. The isoprene was so high in this plume, 33.9 ppbv, that it almost certainly caused complete chemical loss of OH radicals, further suppressing chemistry. The two ground sites that were in suburban locations, Nashville 1999, CFA site and TexAQS 2000, LaPorte site were situated in fields where the nearest trees were several hundred meters away. As a consequence, transport times were on the order of tens of minutes and the isoprene chemistry shows correspondingly longer photochemical times. The possibility that vehicle exhaust sources of MVK and MACR might impact the suburban measurements can be excluded by realizing that the MVK/CO and MACR/CO measurements of *Biesenthal and Shepson* [1997], combined with ambient CO mixing ratios, yield MVK and MACR mixing ratios of a few tens of pptv in the urban/suburban source region, which are negligible relative to the levels measured. The other feature of the data from the ground sites is that the data span at most about two orders of magnitude in either ratio, and considerably less for some data sets (e.g., SOS 1990). This is probably because the sites were surrounded by forests close enough that there was always a contribution from close-in sources, and never an instance when air masses could be observed that had average photochemical ages longer than about 2 hours (daytime scale).

[12] The product ratios observed in the NEAQS measurements covered a much larger range, over 3 orders of magnitude. The lowest ratios were in the same range as those from the suburban sites, but the highest were higher than any reported in surface measurements. Also shown in Figure 1 are points that were calculated from measurements of MACR and MVK that were above detection limit, but for which isoprene was below detection limit. The ratios were calculated by setting isoprene to half its detection limit, 0.2 pptv. When these points are considered the data from NEAQS span about 4.5 decades. The span of the data is such that it is most appropriate to refer to the diurnal-average OH chemistry timescale. The individual NEAQS points cluster slightly above the kinetic line at low to moderate times with some points more than a factor of three above the line. The points added by assuming isoprene = 0.2 pptv, range from just above the kinetic line, to well below the line at the longest times. These added data points extended from the bulk of the NEAQS observations in a direction parallel to the 1:1 line (also shown in Figure 1). The points generated by setting isoprene to 0.2 pptv result in lower limits to the actual ratio on this log plot because of the fact that isoprene could be many times lower than 0.2 pptv, but a measurement only twice as high would have resulted in an actual observation.

[13] The data from NEAQS plotted in Figure 1 include all data, from all sample times, and the ratios extend to photochemical times of 12 hours or so. This brings up the question of what effect the nighttime chemistry involving NO₃ radical might have on the analysis. Nitrate radical measurements made during NEAQS are discussed by *Brown et al.* [2004] and *Warneke et al.* [2004]. NO₃ mixing ratios often approached peak values of 100 pptv or more, and a value of 20−30 pptv can be used as a typical nighttime value. Unde   e conditions, isoprene has a

lifetime of less than 1 hour, while the products, MACR and MVK have lifetimes on the order of days to months [*Atkinson and Arey*, 2003]. The yields of MACR and MVK from the reaction of isoprene with NO₃ are fairly small and are essentially the same, $3.5 \pm 1.4\%$ [*Kwok et al.*, 1996]. As a result, the effect of NO₃ chemistry is to "age" the air mass, by removing isoprene rapidly, with negligible effect on the products. This aging would appear to occur parallel to the 1:1 line for the chemical reasons noted above. This is in fact what is observed.

4.2. Morning of 18 July 2002

[14] An example of this nighttime aging phenomenon can be seen in the data from the early morning of 18 July 2002, which account for the "oldest" points in Figure 1. Figure 2 shows the timeline for the isoprene, MACR, MVK and PANs measurements along with the local wind vector. This air mass was encountered in Massachusetts Bay, approximately 25 km NE of downtown Boston (Figure 3). The local wind speed and direction measured aboard the ship indicates that the air mass in which elevated MACR and MVK were measured was a remnant of the previous day's emissions, in or around the Boston area. The air mass had been transported out to the bay and then back toward land, as indicated by the local wind vector. As a consequence the isoprene within the air mass had experienced both day and almost a full nighttime period of chemical processing. This is supported by the fact that isoprene is absent from the air mass, but the key product species, MACR, MPAN, and PAN are present and in fact are elevated in mixing ratio relative to the air masses on either side of this plume. The data points for the period 0330−0500, LST, were the "oldest" air masses observed in Figure 1, for which MVK and MACR were above detection limit. Another interesting aspect of the 18 July 2002 remnant plume is that the data points lie significantly below the OH kinetic line. This is likely to be due to the effects of O₃ reactions, which were modeled by *Stroud* [2000] to result in a relatively slow change in the ratios, but in the direction that produced points that were systematically lower than the OH kinetic line. The possibility that some of the departure from the OH kinetic line is due to deposition in seawater or on aerosol is unlikely since both MACR and MVK are not very soluble [*Iraci et al.*, 1999].

4.3. Aldehydes and PANs

[15] The sequential reaction system involving the aldehydes and PANs is slightly more complicated than that described above, as detailed by *Roberts et al.* [2001]. The chemistry is initiated by the reaction of the parent aldehyde with OH and proceeds through the intermediate peroxyacyl radical;

$$RCHO + OH + O_2 \rightarrow R(CO)OO + H_2O \qquad k_8 \qquad (8)$$

which will react either with NO₂ to produce a PAN or with NO to be destroyed;

$$R(CO)OO + NO_2 \rightarrow R(CO)OONO_2 \qquad k_9 \qquad (9)$$

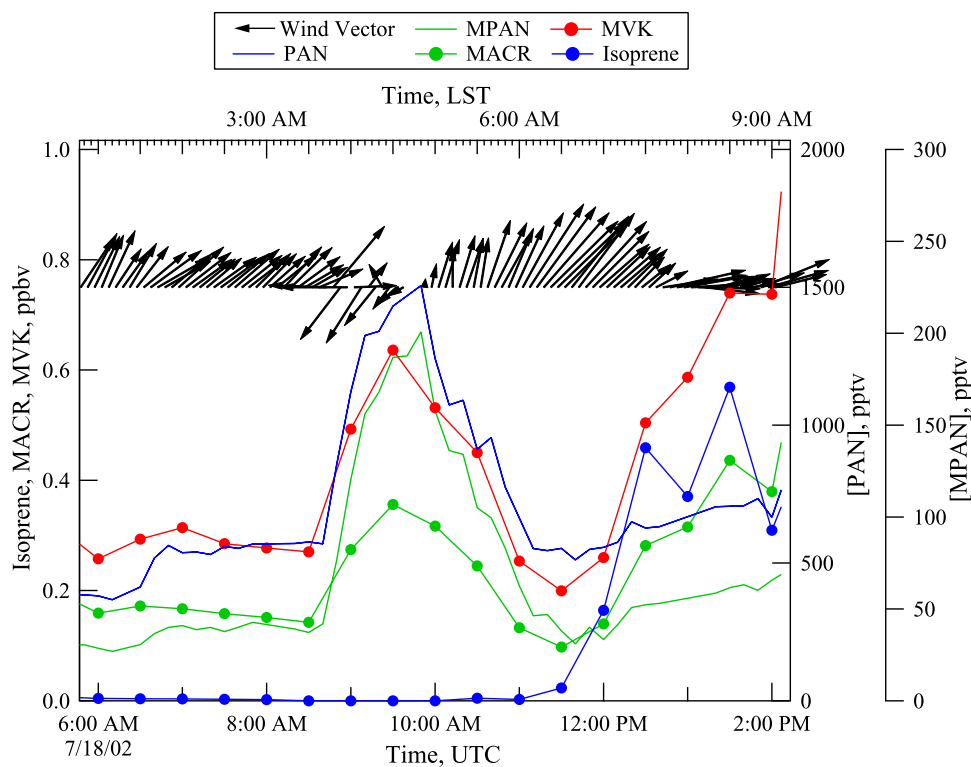$$R(CO)OO + NO \rightarrow R + CO_2 + NO_2 \qquad k_{10} \qquad (10)$$

Figure 2. A timeline plot of Isoprene, MACR, MVK, MPAN, PAN, and MPAN, along with the local wind vector, for the early morning period of 18 July 2002.

PANs are lost primarily through thermal decomposition;

$$R(CO)OONO_2 \rightarrow R(CO)OO + NO_2 \qquad k_{11} \qquad (11)$$

and the net loss is again mediated by reactions (9) and (10). The reaction of PA radical with other radicals or aerosol surfaces is known, but those reactions will be slower than the NOx reactions for NOx mixing ratios above 100 pptv or
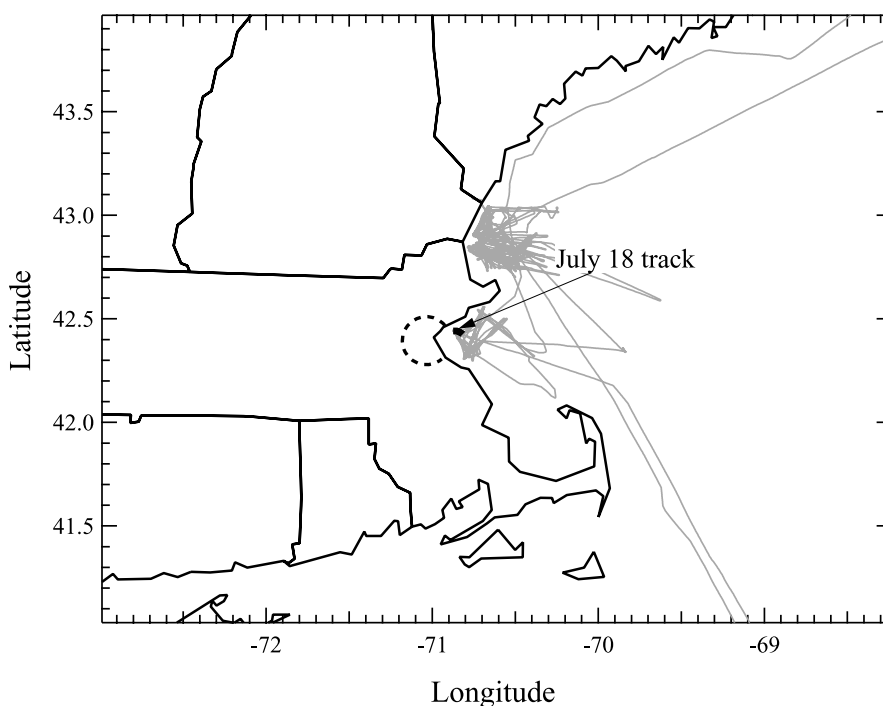

Figure 3. A map of the cruise track for the campaign north of about 41° latitude, with the aforementione d on 18 July 2002 highlighted.
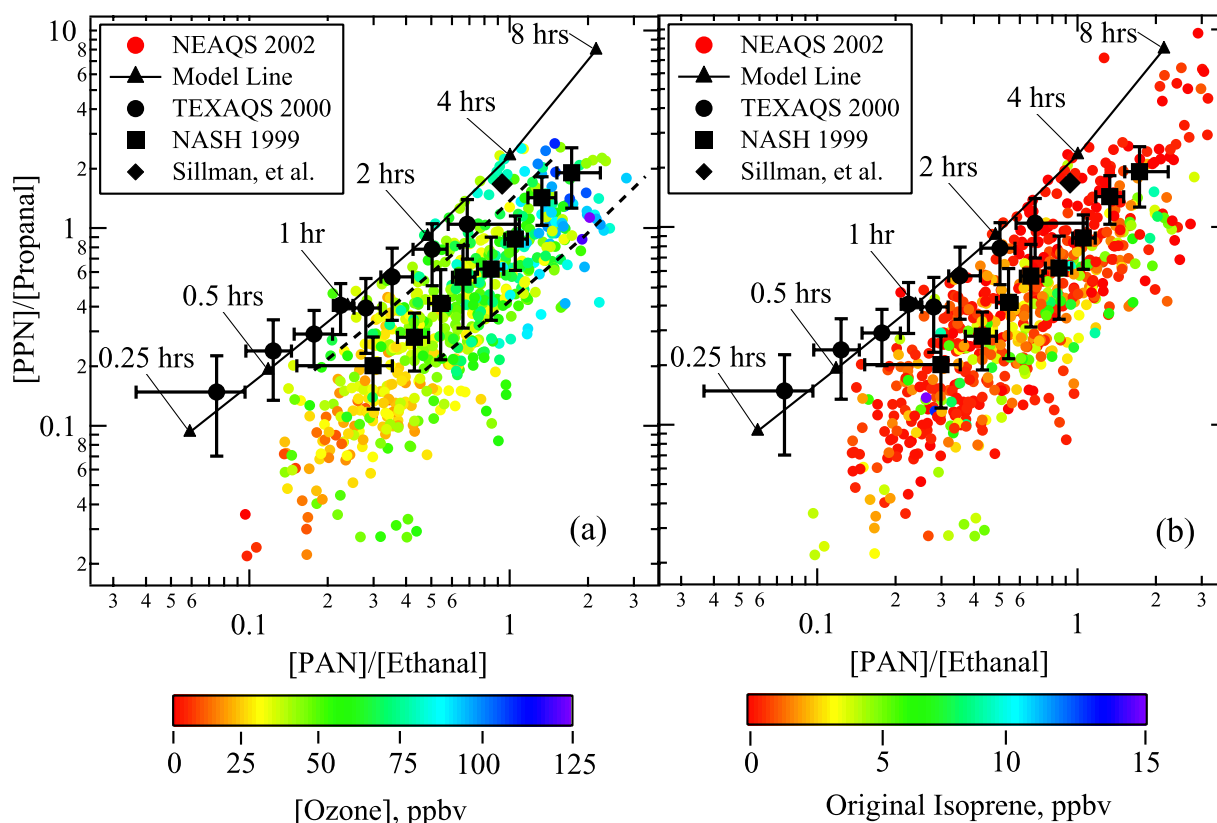
Figure 4. A plot of the ratio of PPN/Propanal versus PAN/Ethanal observed during the NEAQS 2002 study for all ship tracks north of 40°N, colored by (a) O_3 mixing ratio and (b) "original isoprene" as calculated by *de Gouw et al.* [2005]. Also shown are the data from CFA (squares) and LaPorte (circles) plotted in 8 bins, with error bars denoting the extent (max and min) of each bin on the horizontal scale and the standard deviation of each bin on the vertical scale. The point from the calculation of *Sillman et al.* [1990] is shown as a solid diamond. The dashed lines are the central two thirds of the data calculated as the ratio of measured PAN/ethanal to that calculated by the model, between the 0.5 and 4 hour times.

so. The effect of reactions (9) and (10) is to introduce a correction factor, β, to the sequential reaction equation both in the formation of the PAN and in the subsequent loss of the PAN from thermal decomposition;

$$\beta = \{1 + (k_{10}[NO]/k_9[NO_2])\}^{-1}$$

which, when combined with equation (3), yields the following solution;

$$[PAN]/[Ethanal] = \beta * k_8[OH]/(k_{11}(1-\beta) - k_8[OH])$$
$$* \{1 - \exp(k_8[OH] - k_{11}(1-\beta)t)\} \quad (12)$$

The sequential reaction equation for aldehydes → PANs is evaluated using average [OH], average [NO]/[NO₂] and average temperatures. The net effect of varying these parameters is to change the times associated with a given [PAN]/[aldehyde] ratio, with practically no effect on the position of the line [*Roberts et al.*, 2001]. This can be understood in terms similar to that of the isoprene chemistry described above. The position of the kinetic line on the ratio versus ratio plot is determined by the branching ratios and rate constants of the reactions, while the time that is

ascribed to a given ratio changes if the rates of the reactions change, i.e., average [OH], temperature and [NO]/[NO₂].

[16] The plot of [PPN]/[Propanal] versus [PAN]/[Ethanal] for the NEAQS 2002 study is shown in Figure 4a. The NEAQS data are color coded according to the O_3 mixing ratio, and the data from the SOS 1999 study (CFA) and the 2000 TEXAQS study are also shown. The model line shown was calculated for an average [OH] = 6 × 10⁶ molec/cm³, and average temperature of 298 K and an average [NO]/[NO₂] = 0.1. Also plotted in Figure 4 is a point derived from the simple relationship between PAN and ethanal (and PPN and propanal) presented by *Sillman et al.* [1990], which assumes that the PAN compound is in steady state with respect to its production and loss.

[17] The ratios observed during the TEXAQS study are consistent with the sequential reaction model line for the simple aldehyde → PANs chemistry, while those observed in Nashville during the SOS 1999 study were systematically higher in PAN/Ethanal (or lower in PPN/Propanal) relative to the model line. Since PPN and propanal are essentially exclusively anthropogenic in source, this was interpreted by *Roberts et al.* [2001] as strong evidence of isoprene impact on the NOₓ-VOC photochemistry at the CFA site, and the lack of such impact at the TEXAQS 2000 site. This is
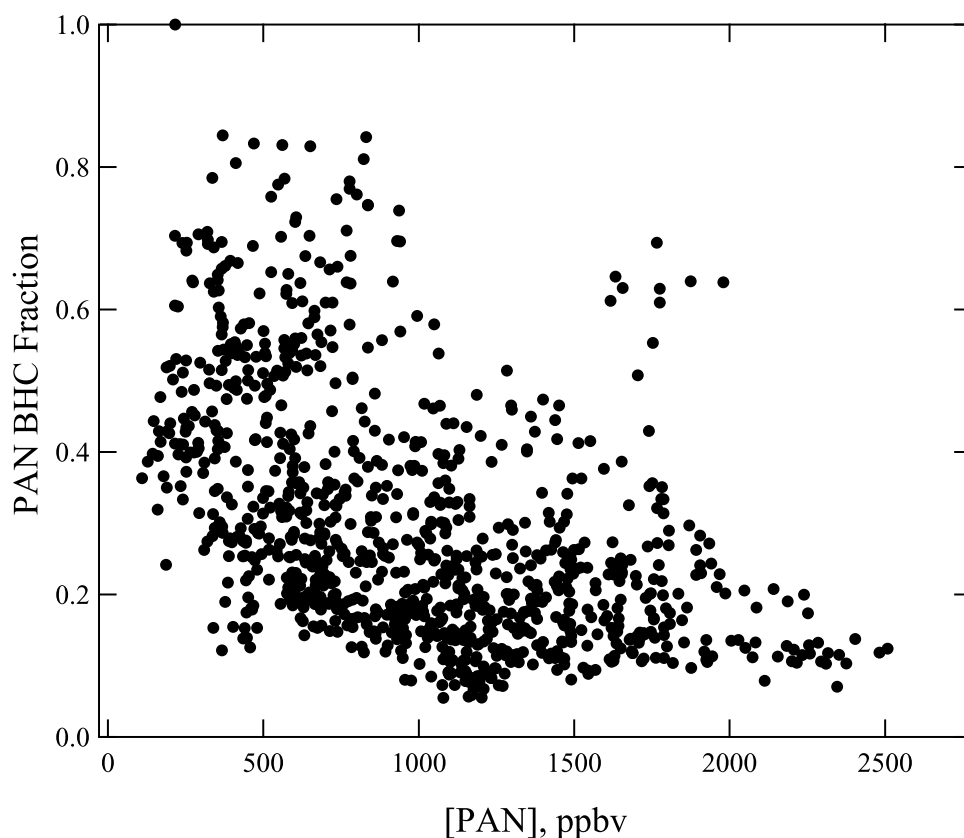
Figure 5. A plot of PAN BHC fraction versus [PAN] for the hours 1000–1900 LST, measured at the Nashville 1999 CFA site.

because isoprene-NO_x photochemistry produces PAN through chemistry that does not produce ethanal as an intermediate, but rather methylglyoxal, which photolyzes, or reacts with OH, to produce $CH_3C(O)$ directly. The NEAQS 2002 data are even further away from the sequential reaction model line, indicating substantial impact of isoprene on those air masses. This aspect of the NEAQS 2002 study is further born out when the data are colored by the "isoprene source" mixing ratio as shown in Figure 4b. This isoprene is estimated from the product/isoprene ratio as described by *de Gouw et al.* [2005] and should be thought of as an indicator of the strength of the isoprene source impacting a given air mass. There is a clear distinction in the data points, with those that had the highest original isoprene occurring furthest from the model line. The extent of the deviation of NEAQS data points from the model line is due to a combination of the impact of isoprene chemistry coupled with the longer photochemical times characteristic of the NEAQS data set relative to the continental data sets as explained above.

[18] The PAN/ethanal ratios shown in Figure 4 range from being on the model line to factors of 5 or so higher than the line, with the average deviation being just a bit more than a factor of 2. As described above the points that had the highest isoprene influence tend to be farthest from the line. The observation-based results presented here are somewhat at odds with other observation-based interpretations of this similar data. *de Gouw et al.* [2005] used indicators of primary   condary AHC chemistry and

BHC chemistry to estimate that PAN is 75% from AHC chemistry. The resolution of this inconsistency may lie in the fact that the kinds of analyses presented by *de Gouw et al.* [2005], *Williams et al.* [1997], and *Roberts et al.* [2002] emphasize the high concentration regimes of the distributions, while the deviation in the PAN/ethanal ratios are seen throughout the distribution. This feature can be seen when the data from Nashville 1999 are plotted as the PAN BHC fraction versus [PAN], Figure 5. The PAN BHC fraction is defined by equation (13);

$$BHC\ Fraction = a[MPAN]/(a[MPAN] + b[PPN]) \qquad (13)$$

where a and b are the coefficients obtained by the linear combination model [*Roberts et al.*, 2002]. Figure 5 shows BHC fractions that span the ranges observed in the NEAQS 2002 study (Figure 4). In the Nash 99 data set, the highest PAN was dominated by AHC chemistry (with one notable BHC episode) because of the location of the site with the Nashville metropolitan area.

[19] The brings up the question of whether the systematically higher PAN/ethanal ratios shown in Figure 4 can be used to give a quantitative estimate of the isoprene source of PAN. If one assumes that the deviation is due solely to higher PAN and that this extra PAN is due to isoprene chemistry, an estimate of the excess PAN can be made by calculating the ratio of measured PAN to modeled PAN for each modeled time. The calculation was limited to the times between 0.5 and 4 hours, and resulted in a median ratio of

2.44 with the central two thirds of the data falling in the range 1.6 to 4. This factor can be compared to numerical modeling studies of the impact of isoprene chemistry on PAN. A regional modeling study was performed for North America by *Horowitz et al.* [1998] in which they found that PAN mixing ratios from isoprene chemistry alone resulted in roughly 3 times more PAN than anthropogenic hydrocarbon (AHC) chemistry alone in the northeastern U.S. summertime. This is in broad agreement with the high end of the PAN/ethanal ratios in Figure 4. The global modeling study of *Folberth et al.* [2005] included AHC and explicit isoprene chemistry and found that isoprene accounted for PAN increases of 75 to 750 pptv at the surface in the Northern Hemisphere summertime. These values would be in the range needed to cause the systematically higher PAN/ethanal ratios. *Von Kuhlmann et al.* [2004] observed a direct dependence of PAN on isoprene emissions, however their model did not include AHCs so a quantitative comparison is not possible.

5. Conclusions

[20] The measurements made during NEAQS 2002 show the obvious impact of isoprene on the VOC-NOx chemistry in the New England coastal environment. The agreement (±50%) of the measured points with the OH kinetic line confirms that isoprene chemistry is well represented by current branching ratios. The observations during NEAQS 2002 were systematically "older" than those from continental surface sites, consistent with the additional transport times in this study. The subset of measurements when the products could be quantified, but isoprene was below detection limit, were included in the analysis by assuming isoprene = half detection limit. These points showed even longer processing times and were systematically off the OH kinetic line in a direction that implied contributions from O_3 and perhaps NO_3 reactions. Ratios of PANs to their parent aldehydes showed systematic effects of the production of PAN from isoprene chemistry, that roughly confirms what is predicted from regional and global modeling studies. The production of PAN from isoprene can be as much as 4 times the source from anthropogenic hydrocarbons.

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