

Formation of Organic Tracers for Isoprene SOA Under Acidic Conditions

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Abstract

The chemical compositions of a series of secondary organic aerosol (SOA) samples, formed by irradiating mixtures of isoprene and NO in a smog chamber in the absence or presence of acidic aerosols, were analyzed using derivatization-based GC-MS methods. In addition to the known isoprene photooxidation products 2-methylglyceric acid, 2-methylthreitol, and 2-methylerythritol, three other peaks of note were detected: one of these was consistent with a silylated-derivative of sulfuric acid, while the remaining two were other oxidized organic compounds detected only when acidic aerosol was present. These two oxidation products were also detected in field samples, and their presence was found to be dependent on both the apparent degree of aerosol acidity as well as the availability of isoprene aerosol. The average concentrations of the sum of these two compounds in the ambient PM_{2.5} samples ranged from below the GC-MS detection limit during periods when the isoprene emission rate or apparent acidity were low to approximately 200 ng m⁻³ (calibrations being based on a surrogate compound) during periods of high isoprene emissions. These compounds presently unidentified have the potential to serve as organic tracers of isoprene SOA formed exclusively in the presence of acidic aerosol and may also be useful in assessments in determining the importance and impact of aerosol acidity on ambient SOA formation.

Keywords: PM_{2.5}, secondary organic aerosol, isoprene, organic tracers, acidic sulfate, SO₂.

1. Introduction

Acidic aerosols are frequently found in the atmosphere (Zhang *et al.*, 2007) and have been shown to have significant impacts, including visibility reduction, climate forcing, cloud formation, and adverse health effects (Charlson *et al.*, 1992; Andreae and Crutzen, 1997; Schwartz *et al.*, 1996). Enhanced secondary organic aerosol (SOA) formation from isoprene and other hydrocarbon precursors has been suggested as one possible explanation for existing gaps between observed organic carbon concentrations and predicted values derived from global models (Heald *et al.*, 2005; Tsigaridis and Kanakidou, 2003; Pun *et al.*, 2002). However, recent field studies have indicated that increases in ambient SOC (secondary organic carbon) due to ambient acidity are likely subtle. Zhang *et al.* (2007), in an examination of increases of SOA species in the Pittsburgh area under acidic conditions, found at most a 25% increase in ambient SOA that could be attributed to acid catalyzed effects, although emissions of biogenic compounds or the fractions of biogenic SOA were not specified. In a recent study of the samples from the SEARCH network, Tanner *et al.* (2009) report low apparent impacts to aerosol acidity even at rural sites at Yorkville, GA and Centerville, AL where an effect due to aerosol acidity might be expected to have the greatest relative influence given low organic aerosol contributions from primary sources.

Notwithstanding these results, the effect of acidic aerosol on SOA formation is still not yet well understood. Particle-phase reactions involving oligomerization of reaction products (Tolocka *et al.*, 2004) or directly emitted precursor hydrocarbons (Liggio *et al.*, 2007) have been suggested as chemical processes leading to enhanced uptake of organic compounds by aerosols. Smog chamber studies on monoterpenes and isoprene photooxidation have shown that particle phase acidity can be linked to enhancement in SOA formation (Offenberg *et al.*, 2009a). However, at present, no specific organic markers for SOA attributed to particle acidity have been reported in these studies.

Isoprene, one of the most abundant non-methane hydrocarbons emitted into the troposphere, has been found to generate organic aerosol through the identification of three organic tracer compounds, 2-methylglyceric acid (2-MGA), 2-methylthreitol (2-MT), and 2-methylerythritol (2-ME), originally found in aerosol samples from the tropics (Claeys *et al.*, 2004). These compounds were subsequently detected in laboratory photooxidation of

isoprene in both the presence and absence of nitrogen oxides (Edney et al. 2005, Kleindienst et al., 2009). The presence of acidic aerosol was also found to substantially increase the isoprene SOA yield under laboratory conditions (Edney et al., 2005).

Kleindienst *et al.* (2007) adopted the use of 2-MGA, 2-MT, and 2-ME as tracer compounds for estimating isoprene SOA contributions to ambient SOA in the Southeastern U.S. According to the procedure, the mass fraction of tracer compounds in the SOA formed from the photooxidation of isoprene under laboratory conditions was measured using GC-MS analysis. Tracer concentrations were then measured in field samples using the same analytical techniques. Finally, the mass fraction from the laboratory studies was used to estimate the amount of ambient SOA derived from isoprene. Using this technique, they found that isoprene contributed substantially to ambient SOA in Research Triangle Park, NC, but only during the summer months. Note that isoprene is emitted primarily by deciduous trees and its emission was found to be high in the summer months in the U.S and increased by increasing temperature and light. The tracer technique was also used for monthly-composited samples collected in five Midwestern cities (Lewandowski *et al.*, 2008), again with strong summertime isoprene contributions identified at all five sampling sites.

Although the tracer technique as used appears to provide plausible estimates of SOA contributions from isoprene and other SOA precursors, considerable uncertainty remained as to the impact of acidic aerosol on the yield of both the isoprene tracer compounds and isoprene SOA as a whole. For example, a series of laboratory experiments conducted with varying levels of aerosol acidity (Surratt *et al.*, 2007a), 2-MGA concentrations were observed to be generally unaffected by changes in the aerosol acidity. The concentrations of the 2-methyltetrols, by contrast, increased at higher aerosol acidity levels, although both methyl tetrols have been observed under laboratory (Edney et al., 2005; Kleindienst et al., 2009) and field conditions (Claeys *et al.*, 2004) where aerosol acidity would be expected to be low.

More recent experiments conducted by Surratt *et al.* (2007b, 2008) have employed LC-MS analysis techniques to identify a series of organosulfate compounds, which were formed during the photooxidation of isoprene under laboratory conditions and only observed in the presence of acidic sulfate aerosols. The identification of compounds

formed exclusively in the presence of acidic aerosol is a significant first step towards evaluating the impact of acidity on ambient SOA concentrations, in that it suggests that acidic conditions can produce aerosol through distinct chemical pathways. However, the quantification of these organosulfate compounds via LC-MS has proven problematic, while, to date, these compounds have not been detectable by the derivatization-based GC-MS techniques (e.g., Jaoui *et al.*, 2004). Thus, a need remains for quantifiable tracer compounds formed exclusively in the presence of acidic aerosol to aid in estimating the impact of aerosol acidity on the formation of SOA from isoprene.

In a further effort for assessing the contribution of particle acidity on ambient SOA formation from isoprene, we have conducted a series of smog chamber experiments to identify additional organic products, formed under acidic conditions, which could potentially serve as tracers for acidity-enhanced isoprene SOA. The laboratory portion of the study consisted of isoprene/NO_x photooxidation experiments conducted both in the presence and the absence of gas phase SO₂, followed by derivatization-based GC-MS analysis to identify organic compounds. The relevance of the newly-identified organic compounds formed in the laboratory systems is assessed through an examination of field samples collected in various Midwestern and Eastern locations in the United States. Two candidate compounds are found in both the laboratory and field samples that might serve as tracer compounds for isoprene SOA formed exclusively in the presence of acidic aerosols.

2. Experimental Methods

Two laboratory experiments were conducted in a 14.5 m³ Teflon-coated smog chamber operated as a batch reactor to investigate the impact of particle-phase acidity on SOA formation from isoprene in the absence and presence of gas-phase SO₂. The details of the chamber and its operation have been previously described by Kleindienst *et al.* (2006) and will only be summarized here. The first experiment was conducted by irradiating isoprene in the presence of NO_x (ER296). In a second experiment (ER297), approximately 250 ppb of SO₂ was added to the chamber, while isoprene and NO_x concentrations were identical to the previous experiment. Isoprene, NO, and SO₂ were added to the chamber from high-pressure cylinders. Both experiments employed an

ammonium sulfate seed aerosol at an initial concentration of $\sim 1 \mu\text{g m}^{-3}$, which was generated by atomization of a 0.5 mg L^{-1} aqueous solution. The relative humidity in the chamber was 30%. Isoprene concentrations were measured by GC using flame ionization detection. NO and NO_x were monitored with a TECO oxides of nitrogen analyzer (Model 42C, Franklin, MA). SOA samples were collected using a carbon-strip denuder (URG, Inc., Chapel Hill, NC) followed by a 47-mm Teflon-impregnated glass-fiber filter (Pall Gelman Laboratory, Ann Arbor, MI). Table 1 summarizes the initial conditions for these experiments; Table 1 also provides the conditions for two previous experiments (ER299a, b), conducted in the absence and presence of acidic seed aerosol, which have been reexamined for this study (Surratt *et al.*, 2007a).

In addition to the laboratory experiments, PM_{2.5} filters from two sets of field samples from a number of locations were examined: (a) Samples collected in five Midwestern US cities (East St. Louis, IL; Detroit, MI; Cincinnati, OH; Bondville, IL; and Northbrook, IL) during 2004-2005 (Lewandowski *et al.*, 2008), and (b) samples collected between March and December of 2006 in Research Triangle Park, NC, at a site described by Offenberg *et al.* (2009b). Detailed descriptions of these field campaigns, filter sampling techniques, and sample extraction have already been reported (Lewandowski *et al.*, 2008; Offenberg *et al.* 2009b).

Filters were extracted for one hour with 1:1 dichloromethane/methanol mixture using sonication. Twenty micrograms of *cis*-ketopinic acid was added to each sample prior to extraction as an internal standard. The resultant extracts were dried and derivatized with *bis*(trimethylsilyl)trifluoroaccedimide (BSTFA) containing 1% trimethylchlorosilane (Jaoui *et al.*, 2004). Neat organic chemicals required for the analyses were purchased from Aldrich Chemical Co. (Milwaukee, WI) at the highest purity available and were used without further purification. Solvents (GC² quality) were from Burdick and Jackson (Muskegon, MI).

All derivatized extracts were analyzed by GC-MS using a ThermoQuest (Austin, TX) GC coupled with an ion trap mass spectrometer. The injector, heated to 270 °C, was operated in splitless mode. Compounds were separated on a 60-m-long, 0.25-mm-i.d. RTx-5MS column (Restek, Inc., Bellefonte, PA) with a 0.25- μm film thickness. The GC oven temperature program for the analysis started isothermally at 84 °C for 1 min,

followed by a temperature ramp of 8 °C min⁻¹ to 200 °C, then a 2-min hold, followed by a further ramp of 10 °C min⁻¹ to 300 °C, and then a final 15-min hold. The ion source, ion trap, and interface temperatures were 200, 200, and 300 °C, respectively. Mass spectra were collected in the chemical (methane as the chemical reagent) and (for some samples) electron ionization modes.

3. Results and Discussion

The GC-MS analysis of the laboratory-generated filter samples shows 2-MGA, 2-MT, and 2-ME, both in the absence and the presence of SO₂. A comparative analysis of the chromatograms reveals three peaks that have been found to be dependent on the presence of acidic aerosol. Extracted ion chromatograms (*m/z* 165, 238, 298, 321, 389, and 409) of the two experimental systems are presented in Figure 1a and Figure 1b. The earliest eluting peak, designated S1, is consistent with a BSTFA derivative of sulfuric acid, based on comparison to a standard. The CI mass spectra of the BSTFA derivative from a sulfuric acid standard is shown in Figure 2a. (Although this peak appears to serve as an effective marker of aerosol acidity, it does not provide a quantitative measure of acidic sulfate in ambient samples, and is thus expressed here in arbitrary concentration units, acu).

The remaining two peaks could not be readily identified, and have been designated N1 and N2. The CI mass spectra associated with peaks N1 and N2 are shown in Figure 2b and Figure 2c, respectively. The dominant ions include *m/z* 182, 238 ($M^+ - 15$; base ion), and 254 ($M^+ + 1$) for peak N1, and *m/z* 147, and 298 ($M^+ - 15$; base ion) for peak N2. The weak ions detected include *m/z* 73, ($M^+ + 29$), ($M^+ + 41$), and ($M^+ + 73$). These fragmentation patterns are consistent with compounds having one or more $-\text{OSi}(\text{CH}_3)_3$ groups present in the derivatized molecule, indicating the presence of acidic and/or alcoholic (-OH) groups (Jaoui *et al.*, 2004). Further EI mass spectra analysis is consistent with the CI analysis and supports BSTFA derivatives with apparent molecular weights 253 and 313 Da for peaks N1 and N2, respectively. Odd molecular masses for N1 and N2 are supported by fragments at *m/z* ($M^+ - 45$), which is consistent with loss of NO₂ group and indicates the presence of a nitrogenous moiety. Based on the above results, both N1 and N2 are tentatively identified as organic species bearing a nitrogenous moiety and at least

one acidic and/or alcoholic functional group, with derivative molecular weights of 253 and 313 Da, respectively. The presence of a sulfur moiety in the parent compounds cannot be excluded, since the BSTFA agent has been found to react with an active hydrogen that is bonded to the sulfur (Little, 1999), potentially eliminating a sulfate moiety. Further, given the relatively low molecular weights of the BSTFA derivatives, it is possible that N1 and N2 represent decomposition products of larger compounds or oligomers that are produced under acidic conditions (Tolocka et al., 2004), but subsequently broken down during the derivatization and analysis of the samples.

Figure 3a presents the estimated concentrations of both the isoprene SOA tracer compounds and the newly identified markers N1 and N2 in the laboratory experiments conducted in the presence of SO₂. Since standards are not available, all concentrations are estimated using the response factor of ketopinic acid (KPA). The detection limit of a series of organic compounds including ketopinic acid was determined previously by Jaoui et al., 2004. Figure 3b presents the same comparison for laboratory experiments from Surratt *et al.* (2007a). In this pair of experiments, acidic aerosol is generated through the nebulization of a solution containing both ammonium sulfate and sulfuric acid, rather than through the oxidation of SO₂, while the non-acidic experiment employed only ammonium sulfate in the nebulizer solution. Similar to the experiments in this study, N1 and N2 are only observed when acidic aerosol is present, although the relative abundance of N1 is significantly lower in the sample from Surratt *et al.* (2007a).

Next, the utility of N1 and N2 as markers for isoprene SOA formed in the presence of acidic aerosol is evaluated through an examination of PM_{2.5} samples collected at multiple field sites. The first set of samples were collected in several Midwest cities during 2004 (Lewandowski *et al.*, 2008). In contrast to the laboratory experiments discussed above, where isoprene SOA was present in all cases, isoprene emissions in the ambient environment are known to be affected by environmental factors and isoprene SOA is detected primarily during the spring and summer in the field samples from the Midwest cities. This creates a further precondition for evaluating the usefulness of peaks N1 and N2 as tracer compounds: N1 and N2 should only be detected when both (a) peak S1 is observed indicating acidic aerosol is present, and (b) the isoprene tracer compounds (2-

MGA, 2-MT, and 2-ME) are present indicating isoprene SOA formation is occurring. In the absence of either acidic aerosol or isoprene, peaks N1 and N2 should not be detected.

Figure 4 shows extracted ion chromatograms obtained from Midwest cities composited ambient samples showing three different sets of circumstances. Figure 4a shows a selected ion chromatogram of a derivatized filter extract from Northbrook, IL during the month of September. As in the laboratory experiments, the three isoprene tracer compounds are observed, indicating the presence of isoprene SOA on these sampling day. Further, an S1 peak is found in the chromatogram, indicating acidic aerosol was present during at least part of the sampling period. Finally, peaks N1 and N2 are observed, suggesting that isoprene SOA collected on the filter was formed in the presence of the acidic aerosol. In Figure 4b, samples collected during September in East St. Louis, IL, show isoprene emission lead to the formation of the tracer compounds, but the lack of an S1 peak suggests the absence of acidic sulfate in the ambient aerosol. Here, peaks N1 and N2 are not detected in the chromatogram. In Figure 4c, a composite sample collected in Detroit, MI, during October, acidic ambient aerosol results in an S1 peak but the absence of 2-MGA, 2-MT, and 2-ME peaks suggests minimal isoprene emissions and no isoprene SOA formation. Again, Peaks N1 and N2 are not observed under these conditions. The results taken together suggests a direct link between the availability of isoprene for SOA formation, the presence of aerosol acidity, and the formation of certain condensed-phase isoprene reaction products, including N1 and N2.

Figure 5 shows the sum of 2-MGA, 2-MT, and 2-ME; the sum of markers N1 and N2; and the S1 level; for 37 field samples collected on a 1 day in 6 sampling schedule between April and December, 2006 in Research Triangle Park, NC (Offenberg *et al.*, 2009b). As seen in the figure, the formation of N1 and N2 is dependent on both the degree of aerosol acidity and the amount of isoprene emitted as indicated by 2-MGA, 2-MT, and 2-ME. Markers N1 and N2 were detected mainly in the warmer months (April – August) when isoprene emissions are high, and when the ambient aerosol is most likely to be acidic. In no cases were N1 and N2 detected in the absence of either S1 or the isoprene tracers.

Figure 6 presents linear regressions for the estimated concentrations of N1 and N2 (in ng m^{-3} , measured as KPA) measured in the 2006 field samples as a function of three

different parameters: S1 levels only (a), isoprene tracer sum only (b), and the product of S1 and the isoprene tracer (c) concentrationFs. This allows an examination of the composite influence of both isoprene and ambient acidity on the concentrations of the N1 and N2 markers. Figure 6a presents the N1 and N2 concentrations as a function of the corresponding S1 level estimated in each sample. Many of the points near the origin, where [S1] is below 100 acu and [N1 + N2] is negligible, occur during early spring or winter. The seven points representing elevated N1 and N2 concentrations occur predominantly during the summer on days with elevated S1 levels. However, there are several sampling days, predominantly during the fall, which produce elevated S1 levels without corresponding observations of N1 and N2. A linear regression of [N1 + N2] as a function of [S1] produces a modest correlation (R^2 of 0.70) with a strongly negative intercept (-22.1 ng m^{-3}) which is likely strongly driven by the occurrence of high [S1] – low [N1 + N2] sampling days.

Figure 6b presents a comparison of N1 and N2 concentrations as a function of isoprene tracer concentrations. Virtually all of the sampling days showing elevated isoprene tracer concentrations ($>25 \text{ ng m}^{-3}$) occur between May 24th and August 27th. Seven of these sampling days correspond with elevated N1 and N2 concentrations. However, several days sampling days with elevated tracer concentrations (one each in June, July, and August) do not lead elevated N1 and N2 concentrations. The linear regression of [N1 + N2] versus isoprene tracer concentrations also produces a modest correlation (R^2 of 0.74) with a negative intercept (-5.6 ng m^{-3}), though the smaller number of high tracer – low [N1 + N2] days leads to a less negative intercept than the previous regression analysis.

Finally, Figure 6c plots the concentration of N1 and N2 as a function of the product of S1 and the isoprene tracer concentration. In this comparison, days with either low isoprene tracer concentrations or low S1 levels cluster near the origin, while the seven sampling days displaying both elevated S1 levels and high isoprene tracer concentrations are all observed to be correlated with higher concentrations of N1 and N2. A linear regression of this comparison produces a strong correlation (R^2 of 0.94) with an intercept near zero (-0.71 ng m^{-3}). This observation is consistent with the laboratory experiments showing the presence of N1 and N2 only under acidic conditions, as shown in Figure 3,

and reinforces the notion that these compounds are also strongly associated with isoprene emissions.

4. Conclusion

In the present study, two oxygenated compounds bearing nitrogenous moieties (N1 and N2) have been measured at substantial levels in chamber aerosol from the photooxidation of isoprene under acidic conditions. In the ambient samples, their presence was found to be dependent on both the aerosol acidity and on isoprene levels (as measured by the sum of 2-MGA, 2-MT, and 2-ME) with an excellent correlation (R^2 0.94) for the product of the two factors. While the correlation coefficient is high, the factors upon which correlation is based are at best surrogates for atmospheric parameters that represent the isoprene emissions and the aerosol acidity. For a more robust analysis, the isoprene tracers would need to be replaced with a metric that is a better measure of the isoprene emissions and S1 would need to be replaced with a metric that is a better measure of the aerosol acidity (such as $[H^+]_{\text{air}}$ (Surratt et al., 2007a)). This would allow a formal statistical analysis of the formation of N1 and N2 to be conducted as a function of the prevailing conditions.

The derivatization for the parent compounds of N1 and N2 appears to be more complex than for oxygenates not having heteroatoms due to the potential conversion of a sulfur-based moiety to a TMS group. As a result, the derivative molecular weights (N1: 253 Da; N2: 313 Da) represent parent compounds still having considerable uncertainty in their structure. However, as tracer compounds, this limitation should not be an inherent problem. Moreover, the high consistency of the formation of these compounds in both laboratory and field samples together with their absence without acidity or isoprene oxidation products indicates that N1 and N2 are unlikely to represent sampling or analysis artifacts.

Based on these results, it appears that N1 and N2 could serve as isoprene tracers specific to acidic conditions, although their chemical structures remain to be elucidated. Nonetheless, this work must be considered only an initial step in evaluating role of acidity on increased organic masses in the atmospheres where broad changes in OC are difficult to detect by statistical methods already reported (Tanner et al. 2009; Zhang et al., 2007).

Although neither the structure nor the overall contribution of these new markers to ambient organic PM_{2.5} have yet been obtained, the data presented in this study raise the possibility that separate contribution estimates may ultimately be obtained for isoprene SOA formed under acidic or neutral conditions. Such an estimates would allow for a more detailed assessment of the impact of acidity on ambient isoprene SOA which would be crucial for the further development of regional and global models, especially for regions where isoprene emission rates are high.

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Figure 1: Extracted ion gas chromatograms in CI mode of organic extracts as BSTFA derivatives from an irradiated isoprene/NO_x experiment (top) and an isoprene/NO_x/SO₂ experiment (bottom). Extracted ions are 165, 238, 298, 321, 389, and 409.

Figure 2: CI mass spectra associated with peak S1 (a), peak N1 (b), and peak N2 (c).

Figure 3: Concentrations (in $\mu\text{g m}^{-3}$ as ketopinic acid) of 2-methylglyceric acid, 2-methylthreitol, 2-methylerythreitol, N1, and N2 measured in SOA collected from chamber experiments ER296/ER297 (a), and ER299 (b).

Figure 4: Extracted ion gas chromatograms in CI mode of organic extracts as BSTFA derivatives from ambient PM_{2.5} sample at (a) Northbrook, IL, during September, 2004 (b) East St Lewis, IL, during September, 2004 and (c) Detroit, MI, during October, 2004. Extracted ions for the chromatograms are *m/z* 165, 238, 298, 321, 389, and 409.

Figure 5: Concentrations of (•) N1 + N2 (ng m^{-3} as KPA, left axis); (◊) sum of 2-MGA, 2-MT, 2-ME (ng m^{-3} as KPA, left axis); and (■) S1 (acu, right axis); measured in Research Triangle Park, NC, for April through December of 2006.

Figure 6: Correlation plot of N1 + N2 (ng m^{-3}) with (a) S1 (acu); (b) isoprene tracers (ng m^{-3}); and (c) the product of isoprene tracers with S1.

Table 1. Initial chamber conditions for experiments conducted in this study as well as ER299 experiment conducted by Surratt et al. (2007a).

Experiment ID	Isoprene (ppmC)	NO _x (ppb)	SO ₂ (ppb)
EP296	10.0	250	0
EP297	10.0	250	250
ER299a	15.4	300	0
ER299b	16.3	300	0 *

* acidic sulfate seed aerosol used

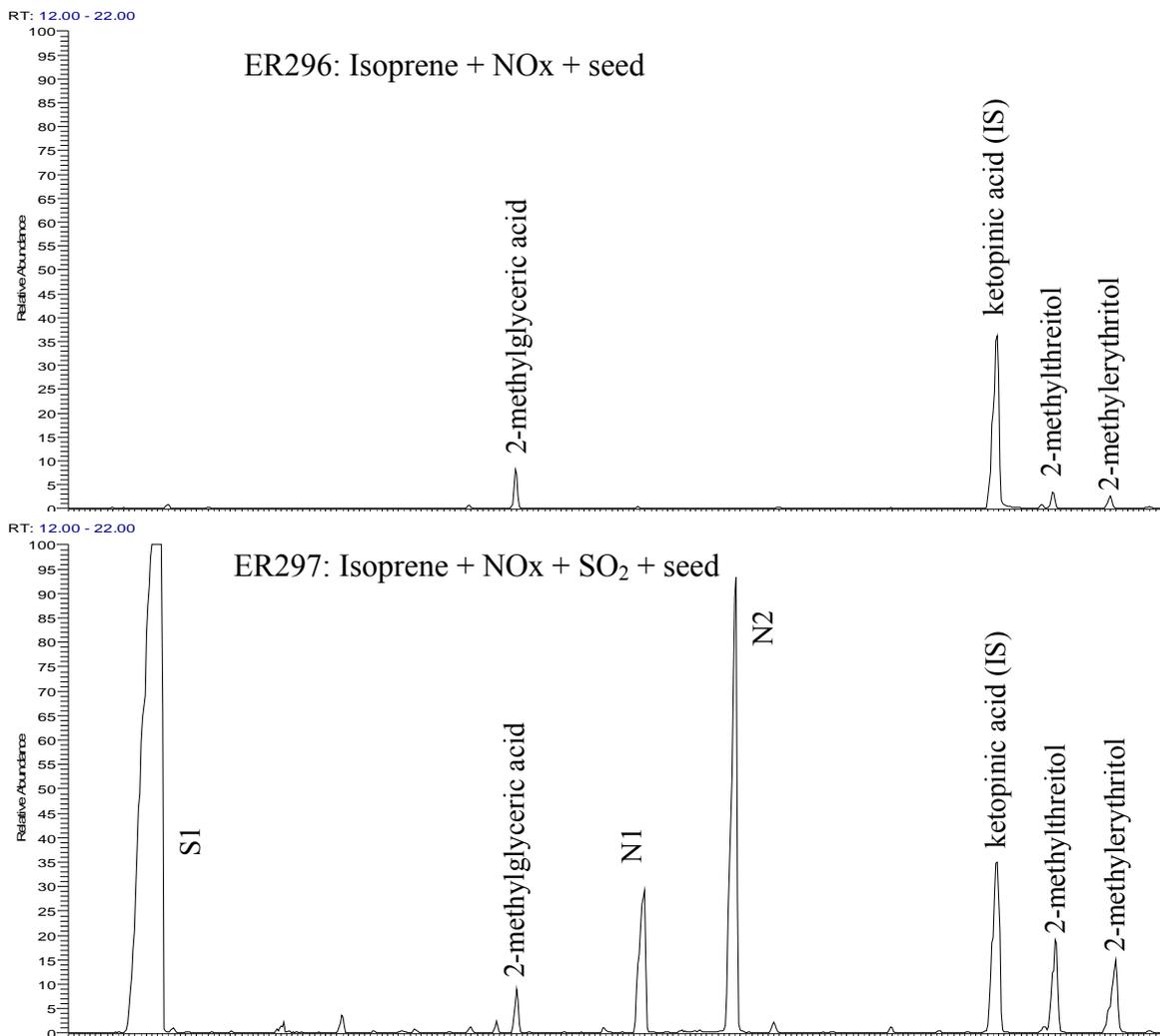


Figure 1

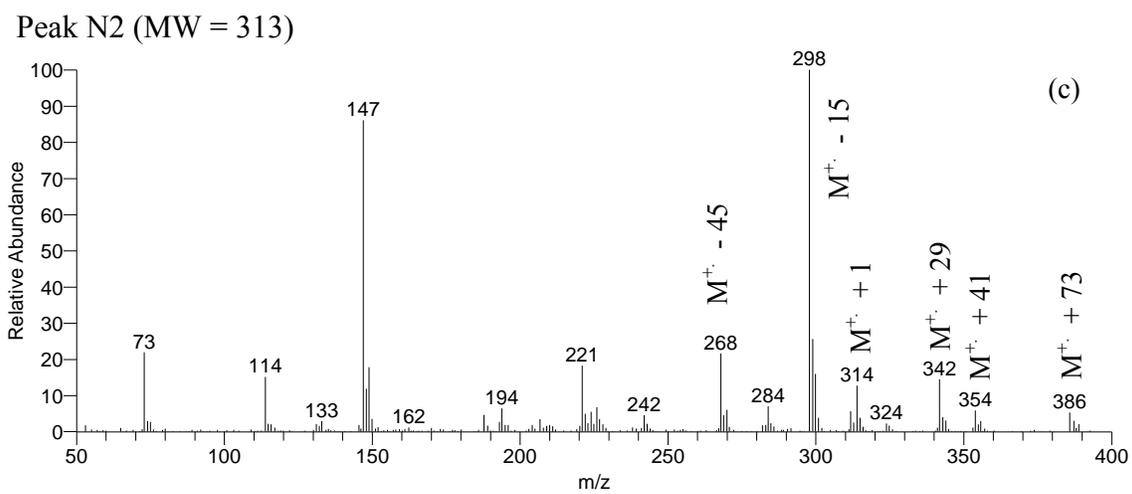
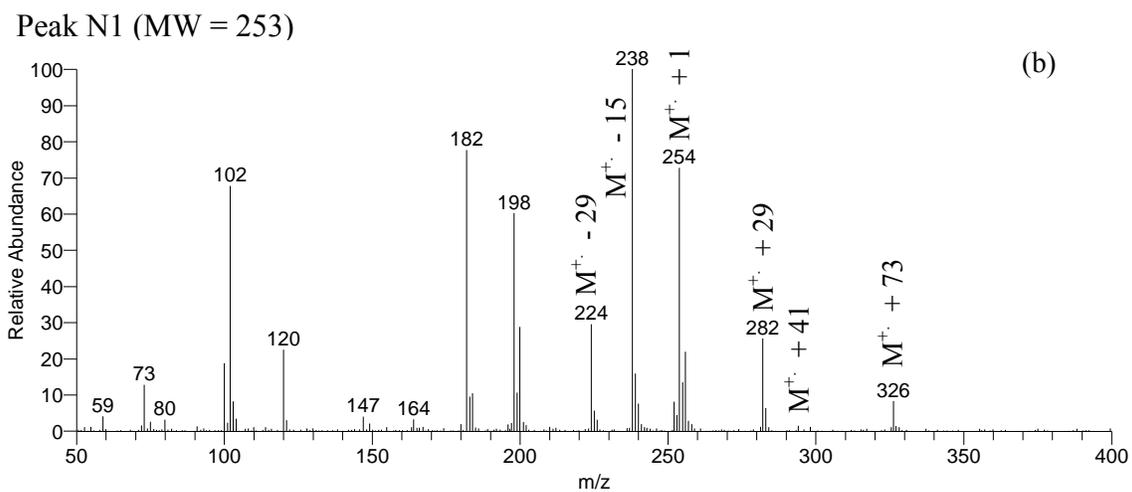
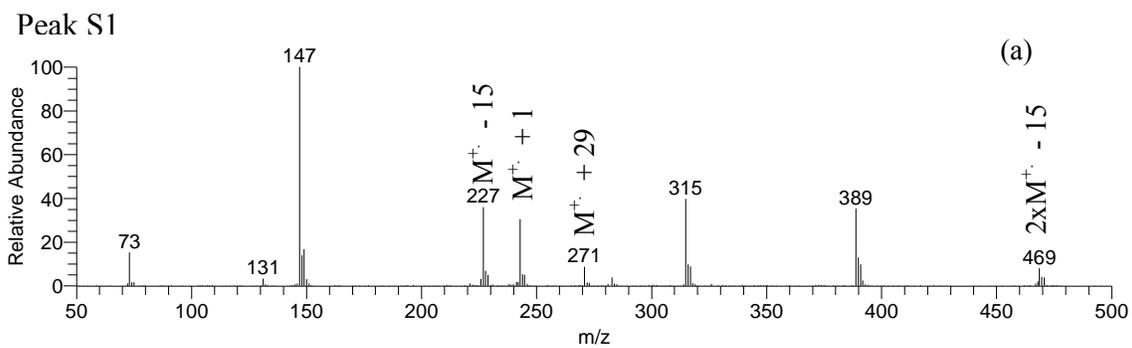


Figure 2

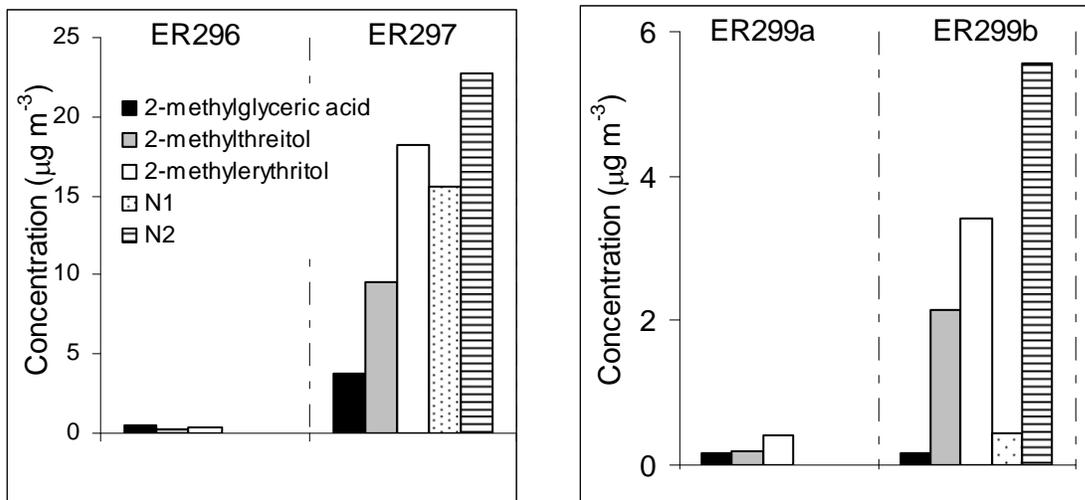


Figure 3

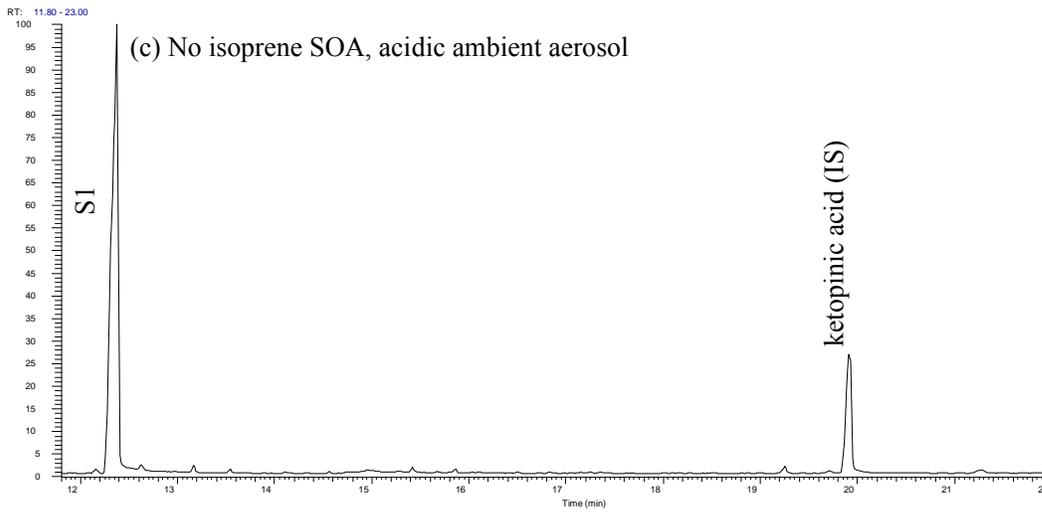
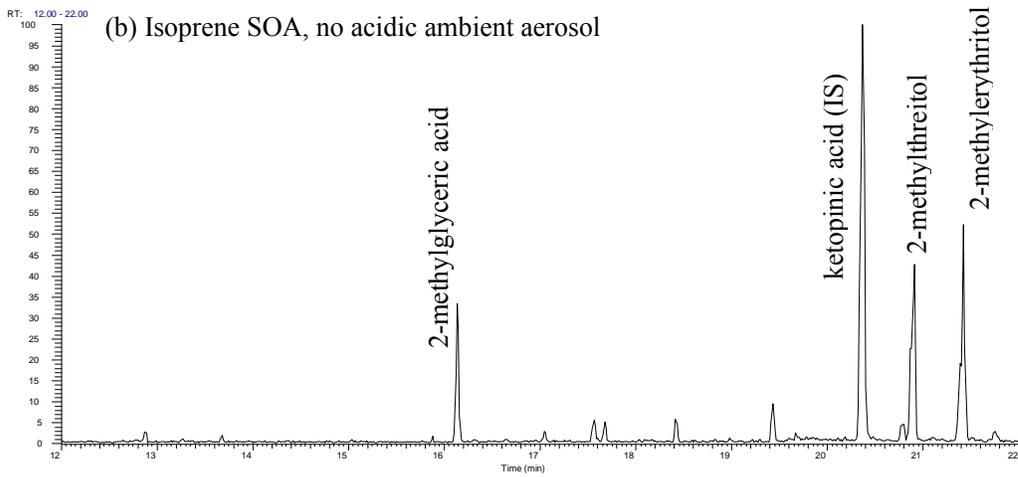
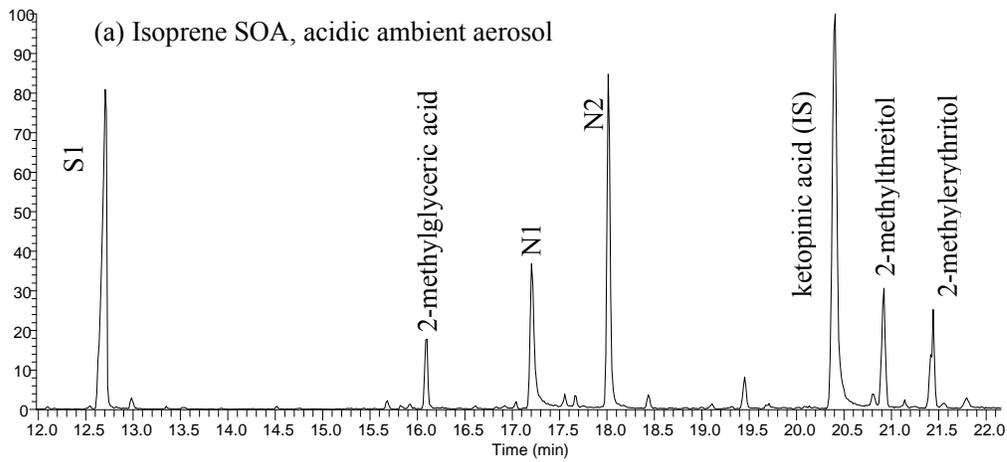


Figure 4

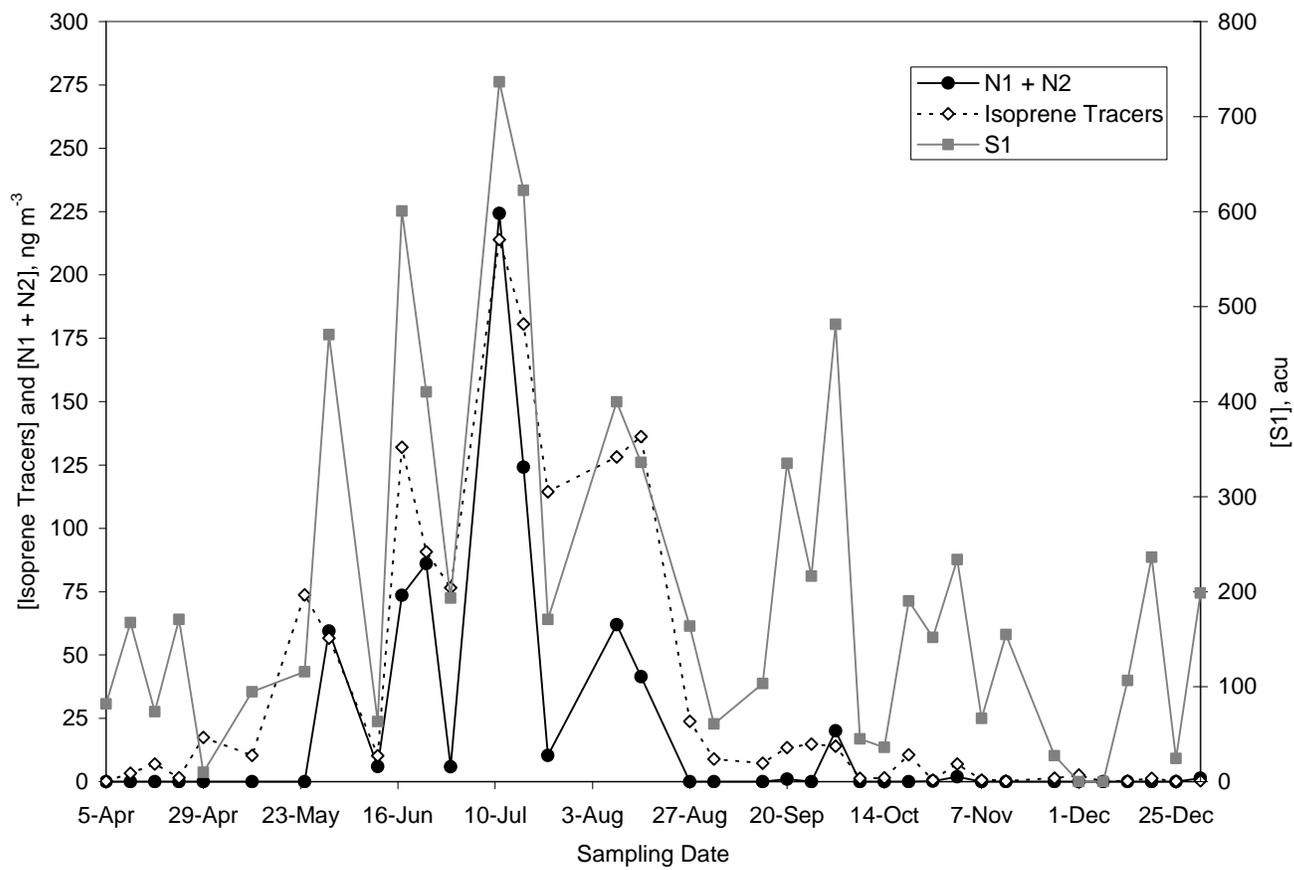


Figure 5

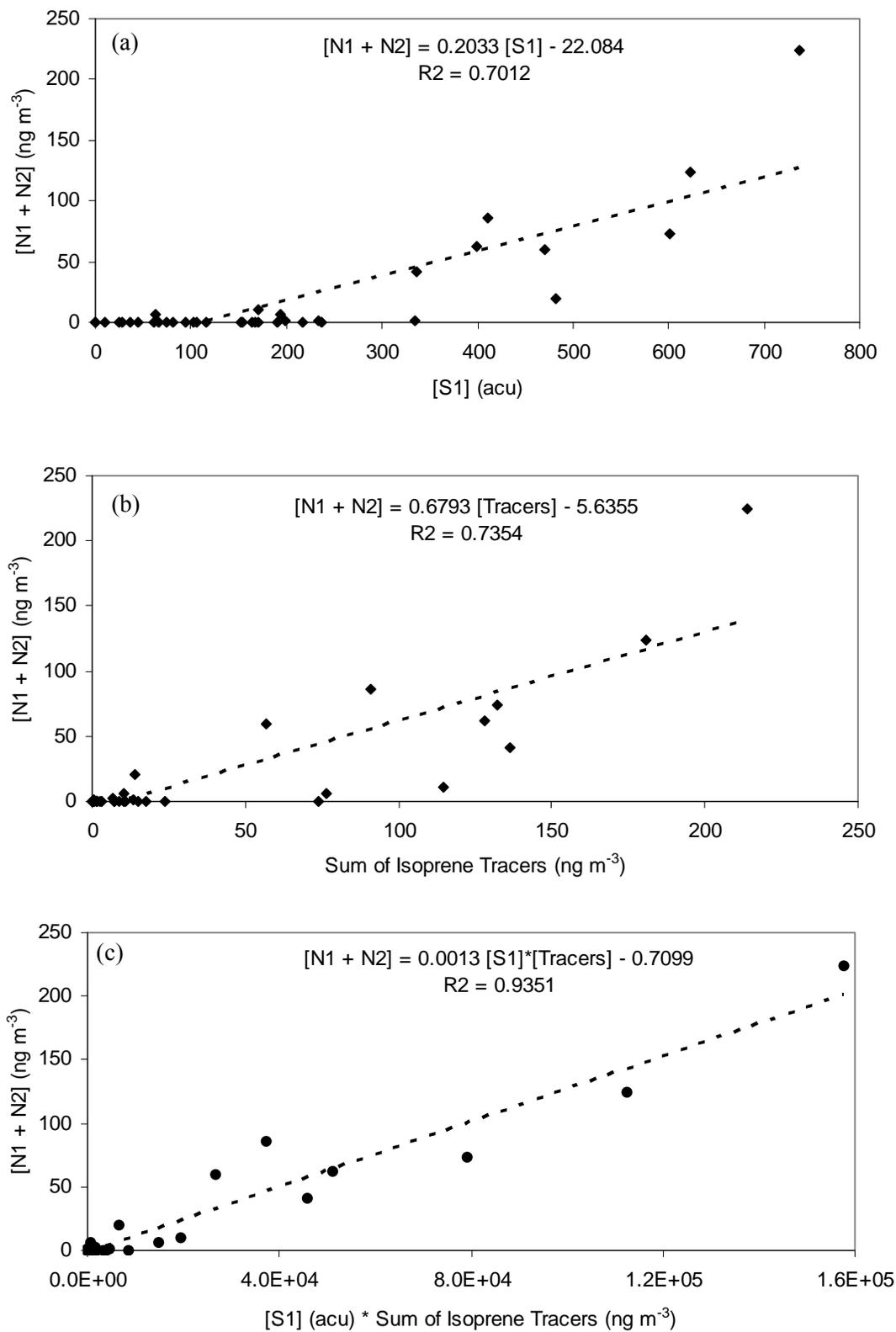


Figure 6