**Atmospheric
Chemistry
and Physics
Discussions**

Diurnally resolved particulate and VOC measurements at a rural site: indication of significant biogenic secondary organic aerosol formation

S. J. Sjostedt[1,2], J. G. Slowik[1], J. R. Brook[2], R.Y.-W. Chang[1], C. Mihele[2], C. A. Stroud[2], A. Vlasenko[1,2], and J. P. D. Abbatt[1]

[1]Department of Chemistry, University of Toronto, Toronto, ON, M5S 3H6, Canada
[2]Environment Canada, Science and Technology Branch, Toronto, ON, M3H 5T4, Canada

Correspondence to: S. Sjostedt (steve.sjostedt@ec.gc.ca)

ACPD

10, 27321–27359, 2010

Diurnally resolved particulate and VOC measurements at a rural site

S. J. Sjostedt et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀◀ | ▶▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

We report simultaneous measurements of volatile organic compound (VOC) mixing ratios including C_6 to C_8 aromatics, isoprene, monoterpenes, acetone and organic aerosol mass loadings at a rural location in Southwestern Ontario, Canada by Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) and Aerosol Mass Spectrometry (AMS), respectively. During the three-week-long Border Air Quality and Meteorology Study in June–July 2007, air was sampled from a range of sources, including aged air from the polluted US Midwest, direct outflow from Detroit 50 km away, and clean air with higher biogenic input. After normalization to the diurnal profile of CO, a long-lived tracer, diurnal analyses show clear photochemical loss of reactive aromatics and production of oxygenated VOCs and secondary organic aerosol (SOA) during the daytime. Biogenic VOC mixing ratios increase during the daytime in accord with their light- and temperature-dependent sources. Long-lived species, such as hydrocarbon-like organic aerosol and benzene show little to no photochemical reactivity on this timescale. From the normalized diurnal profiles of VOCs, an estimate of OH concentrations during the daytime, measured O_3 concentrations, and laboratory SOA yields, we calculate integrated organic aerosol production amounts associated with each measured SOA precursor. Depending on whether the SOA formation is occurring in a low- or high- NO_x regime, we estimate that the biogenic gases contribute between 10 to 36 times as much SOA as do the aromatic precursors, making this a highly biogenically dominated region for SOA formation. The conclusion that biogenic SOA formation is of significance to air quality in this region is supported by detailed air quality modeling during this period (Stroud et al., 2010).

1 Introduction

Although ozone and particulate matter have been historically viewed as two independent criteria for characterizing air quality, it is now recognized that there is a tight

relationship between the two. In particular, it is well known that oxidation of volatile organic compounds (VOCs) leads to tropospheric ozone production. Under close scrutiny of late is the coupled role that photochemistry and VOCs play in the production of secondary organic aerosol (SOA) (De Gouw and Jimenez, 2009; Hallquist et al., 2009; Kroll and Seinfeld, 2008; Seinfeld and Pankow, 2003).

The oxidation of VOCs is initiated by reaction with atmospheric radicals, and by ozone in the case of olefins (Atkinson and Arey, 2003). During the day the primary oxidant is the hydroxyl radical (OH) and, in the presence of sunlight and NO_x the products go on to form ozone and oxygenated volatile organic compounds (OVOCs). OVOCs can be further oxidized to form multi-functional-group species, including carboxylic acids. Thus, the oxidation of VOCs can lead to a reduction of vapor pressure relative to the precursor molecule due to the addition of polar functional groups. The decrease in vapor pressure can be offset by a reduction in the length of the carbon backbone by carbon-carbon bond breakage, since the vapor pressure of larger compounds is less than that of smaller ones. However, should the oxidation of the parent VOC ultimately lead to a substantial decrease in the vapor pressure and decomposition does not occur to a sizable degree, the products can then go into the condensed phase to form secondary organic aerosol (SOA) (Pankow, 1994). Formation of an OVOC product of sufficiently low vapor pressure may require multiple generations of oxidation products. Whether the oxidation products ultimately end up as an aerosol depends on several factors such as the structure of the parent compound, the composition of the aerosol and the NO_x concentration. Low NO_x environments are expected to be more conducive to SOA production due to the formation of low vapor pressure organic peroxides from reaction with HO_2 (De Gouw and Jimenez, 2009; Hallquist et al., 2009; Kroll and Seinfeld, 2008). Also, note that SOA formation may occur in the aqueous phase via condensed-phase processes, such as those driven by carbonyl uptake.

To assess the degree of SOA formation via gas phase oxidation and subsequent condensation that might have occurred over a specific region a standard approach is

to incorporate organic aerosol laboratory yields, i.e. the amount of SOA formed from a specific VOC precursor under a prescribed set of conditions in a large reaction chamber, into a chemical transport model that includes spatially resolved VOC emission fluxes, gas-phase chemistry, horizontal and vertical air transport, gas and particle de-
5 position, etc. (Chen et al., 2006; Kleeman et al., 2007; Murphy and Pandis, 2009). This approach is taken in the paper by (Stroud et al., 2010) that is part of this special issue, using Environment Canada's AURAMS chemical transport model (Gong et al., 2003; Makar et al., 2009; Stroud et al., 2008).

Here, we present a measurement-based approach where we match the degree of
10 chemical loss of diurnally averaged SOA precursors to the simultaneous measurement of oxygenated organic aerosol formation. This allows us to assess the degree to which the measured VOCs contribute to the total SOA formed. Carbon monoxide is used to normalize for dynamical effects, particularly associated with the changing height of the boundary layer (de Gouw et al., 2009). The advantage of this method is that both
15 the VOC precursor and oxygenated aerosol amounts are directly measured, without the need for an emissions model. The only external information required is the yield of SOA from specific VOC precursors and the rate constants for radical-driven loss of the VOCs, both of which can be taken from laboratory experiments described in the literature. Uncertainties to this approach are also important to point out, the most
20 significant of which is that the measurements are from only one location whereas SOA formation occurs over a wider geographic extent.

To illustrate this analysis approach we use measurements taken during the Boundary Air Quality and Meteorology Study (BAQS-Met), an air quality study during the summer of 2007 involving Environment Canada, academic researchers, and the Ontario
25 Ministry of the Environment. The overall goal of BAQS-Met was to evaluate the degree to which pollution in Southwestern Ontario is influenced by long-range transport or formed locally, and by complex meteorology that prevails across many areas due to the high frequency of lake breezes associated with the Great Lakes.

For this paper, a specific goal was to assess the relative degree to which different VOC precursors contributed to SOA formation at a rural location -1- Harrow, Ontario – using the analysis approach outlined above. Although VOCs of both biogenic and anthropogenic origin are known to be important in the formation of SOA, the magnitude of each contribution remains an open question (de Gouw et al., 2008, 2005; Heald et al., 2005; Kleinman et al., 2007; Volkamer et al., 2006). Past studies in polluted environments have had difficulty obtaining closure between the amount of SOA formed and that predicted by models. Agreement in biogenic regimes has been better of late (Capes et al., 2009; Slowik et al., 2010a). Harrow provides a locale that is influenced by both local and regional biogenic sources and anthropogenically impacted air that is photochemically fresh (when from Detroit) and aged (when from the Ohio Valley). As such, we focus on the relative degree to which biogenic sources contribute to SOA formation relative to aromatic (i.e. anthropogenic) precursors for this location. Finally, we perform an initial comparison of our results to those from the AURAMS chemical transport model.

2 Experimental

2.1 BAQS-Met field campaign

Measurements were conducted from mid June through early July at the Agriculture Canada field site at Harrow. See Fig. 1. Harrow is a small farming community in southwestern Ontario that can be influenced by air flow from Detroit ($\sim$50 km NW), the Ohio Valley ($\sim$400 km SW) as well as by local biogenic sources. The shores of Lake Erie are 8 km to the south. The measurement site was in a field, about 100 m from a two-lane rural highway, i.e. removed from major local particle sources. A major four-lane highway was located about 30 km to the north. For the most part the three week study was conducted under dry conditions, with three notable exceptions. There was measurable rainfall during the afternoon of 27 June, the pre-dawn hours of 4 July and

Diurnally resolved particulate and VOC measurements at a rural site

S. J. Sjostedt et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

◄◄   ►►

◄   ►

Back   Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

the afternoon and evening of 5 July. None of these periods was greater than eight hours in length.

2.2 Measurements

Volatile organic compounds (VOCs) levels were measured using a proton-transfer reaction mass spectrometer (PTR-MS) (de Gouw and Warneke, 2007; Lindinger et al., 1998) (Ionicon Analytik). In the PTR-MS, H_3O^+ ions generated by a discharge in water vapor ionize trace gases that have a higher proton affinity than water. The resulting ions are detected with a quadrupole mass spectrometer. Because this soft ionization technique causes relatively little fragmentation, measured mass-to-charge ratios can frequently be directly related to the parent ion, and so VOCs can be identified to some degree. Species with the same molecular weight, such as the xylenes and ethylbenzene cannot be distinguished. The same is true with all the monoterpenes, and with methyl vinyl ketone and methacrolein, that yield signal at the same mass-to-charge ratio.

The PTR-MS was calibrated with a custom standard that contained, amongst other species: acetone, isoprene, methyl vinyl ketone, benzene, toluene, and α-pinene in the 500 ppbv range (Apel-Riemer Environmental Inc., USA). Species-dependent calibration factors and detection limits, along with the activated charcoal backgrounding method and sample line details, are described in detail elsewhere (Vlasenko et al., 2009). For this study the sample line inlet was at 3 m a.g.l. The mass spectrometer was operated in full scan mode with data points collected across the full mass range (m/z 21–160) every 140 s.

Please refer to (Levy et al., 2010), which is part of this special issue, for details on the measurements of CO, O_3, and SO_2.

A time-of-flight aerosol mass spectrometer (C-ToF AMS, Aerodyne Inc., USA) measured the composition of the non-refractory component of submicron aerosol. The non-refractory component is empirically defined as species that are vaporizable at 870 K and 10^{-7} Torr. AMS operating principles are described elsewhere (Drewnick

et al., 2005; Jayne et al., 2000; Jimenez et al., 2003) while operation and analysis procedures during the present study are described in a paper in this special issue (Slowik et al., 2010b).

2.3 PMF analysis of the organic aerosol mass spectra

Positive Matrix Factorization (Paatero, 1997; Paatero and Tapper, 1994) was applied to the organic aerosol mass spectral data using the PMF2 software package (P. Paatero, Univ. of Helsinki, Finland) in robust mode, together with the CU AMS PMF Tool (Ulbrich et al., 2009). Details of the PMF are given in (Slowik et al., 2010b). As described in that paper, the best PMF solution consisted of four factors, which we label HOA (hydrocarbon-like organic aerosol), OOA-1, OOA-2 (oxygenated organic aerosol, types 1 and 2) and Factor 4. Briefly, the HOA factor is thought to arise from primary anthropogenic emissions and has a mass spectrum characteristic of aliphatic hydrocarbons. The OOA-1 and OOA-2 factors are more oxygenated; using the empirical relationship between the fraction of organic signal occurring at m/z 44 (CO_2^+ ion) and the molecular O:C ratio derived by (Aiken et al., 2008), we estimate O:C values of $\sim$0.96 and $\sim$0.50 for OOA-1 and OOA-2, respectively. The OOA-1 and OOA-2 mass spectra are similar to those of low-volatility OOA (LV-OOA) and semivolatile OOA (SV-OOA), respectively (Jimenez et al., 2009). It is likely that OOA-1 represents the less volatile and more aged SOA fraction. Factor 4 (also referred to as the UNKN factor in Slowik et al., 2010b), was only a minor component of the organic aerosol except at the end of the study, when winds shifted to a moderate, steady south/southwest flow. The CO_2^+ ion (m/z 44) intensity constitutes only 0.01 of its spectrum, suggesting a low O:C ratio consistent with fresh emissions. This factor coincides with a period of high isoprene and low aromatics, suggesting a biogenic influence, and a sulfate plume from Midwestern US locations. Taken together, these observations suggest the Factor 4 may be due to uptake of fresh biogenic VOCs onto preexisting sulfate aerosol (see also Slowik et al., 2010b; Stroud et al., 2010).

2.4 AURAMS model

AURAMS is an off-line chemical transport model that is driven by the Canadian operational weather forecast model, GEM. AURAMS was run in a one way nested configuration with a continental scale outer domain at 42 km grid spacing, an inner regional domain at 15 km grid spacing, and a high-resolution domain at 2.5 km grid spacing. Hourly anthropogenic emission files were prepared for AURAMS using the 2005 Canadian and 2005 US emissions inventories. Further details about the biogenic emission algorithms (BEIS v3.09) and the organic chemistry mechanism in AURAMS can be found in (Slowik et al., 2010a) and (Stroud et al., 2010).

3 Results and discussion

3.1 Diurnal profiles for the full campaign

The full gas-phase data set has been broken down into three specific groups for analysis. Aromatics, which consists of benzene, toluene, and C_8 aromatics (xylenes + ethyl benzene), are species of anthropogenic origin with variable chemical lifetimes. Biogenics are comprised of relatively short-lived (i.e. lifetimes less than a day) chemicals directly emitted from foliage, such as the monoterpenes and isoprene as well as the 1st generation oxidation products of isoprene, methacrolein (MACR) and methyl vinyl ketone (MVK). The final group is comprised of acetone and ozone, which are relatively longer-lived oxygenates primarily produced photochemically from the processing of both biogenic and anthropogenic VOC precursors. To this group we add carbon monoxide (CO) as a tracer species that is longer lived than the above species and sulfur dioxide (SO_2) as a primary pollutant from industrial fossil fuel combustion. Time series of the mixing ratios of these species are in Figs. 2, 3 and 4.

The aerosol data have been divided into two subsets. The first delineates the submicron aerosol mass arising from organics and the inorganic species, sulfate (SO_4^{2-}),

27328

nitrate (NO_3^-) and ammonium (NH_4^+). The second shows the organic aerosol factors that have been derived from the PMF analysis. There are four factors that arise, as described in the previous section. These time series are in Fig. 5.

The measurements exhibit consistent diurnal profiles for both the gas phase species and aerosol composition. As is commonly recognized, such diurnal changes in observed values can be attributed to both chemistry and dynamical effects, such as changes in the boundary layer height that occur over the course of a 24 h day. To account as best as possible for these dynamical effects, the diurnally averaged signals for each species are normalized to CO, given that it is a long-lived chemical tracer. This technique is used widely, for example by (de Gouw et al., 2009) where it was applied to both gas and aerosol data from the MILAGRO campaign in Mexico City. In our case, a background concentration of 80 ppbv was assumed for the Northern Hemisphere around the summer solstice (Li et al., 2004; Parrish et al., 2004). We assume the background is pervasive throughout the atmosphere, and so we normalize to the mixing ratios of CO less this background value.

The diurnal profile of CO at Harrow during the study is shown in Fig. 6, where it is seen that mixing ratios rise throughout the night, indicative of relatively local emissions occurring into an increasingly shallow boundary layer. During the time of afternoon heating the mixing ratios are smallest due to mixing within a deeper boundary layer. (Note that for this diurnal profile, and for all others in the paper, we do a 21 running point average of all data.) We acknowledge that CO could be impacted by short episodes of high anthropogenic input and/or a diurnal profile in the rate of local CO production that can be of biogenic or anthropogenic origin. However, these effects are minimized by our location, which is largely removed from major local sources of pollution, and by averaging data across the full campaign period.

After CO normalization, the aromatics (Fig. 7) exhibit a consistent pre-dawn peak and, for toluene and the C_8 species, an afternoon minimum that extends from about 12:00 to 19:00 EDT. Such a pattern is consistent with chemical species whose source is direct emission and whose primary oxidant is the hydroxyl radical. After normalization,

benzene mixing ratios remain constant throughout the day, consistent with the relatively long chemical lifetime of this species. Note that the flat diurnal profile for benzene provides added support that the normalization to the CO diurnal variation is a justifiable approach for decoupling boundary layer mixing from chemical loss processes, for the primary anthropogenic VOCs at least.

Conversely, secondary chemical species that are formed from photochemistry such as acetone, ozone and PTR-MS formaldehyde (not shown) display an enhancement during the afternoon hours (see Fig. 6). The peak, with normalization to the boundary layer, is around 18:00 EDT. The diurnal profiles of acetone and ozone are quite similar to each other, indicating that both are photochemically produced and that both have relatively long chemical lifetimes. The biogenic species (isoprene and MVK/MACR) also peak in the late afternoon (Fig. 7). Qualitatively, the profiles of both are consistent with enhanced isoprene emissions during the day and with subsequent loss via reaction with OH, although the isoprene signals likely arise from more local emissions than those of the longer-lived oxidation products. The release of monoterpenes is dependent on temperature and thus the early evening maximum is likely due to local emissions and decreasing OH as the sun sets.

The concentrations of the aerosol species also displayed prominent diurnal profiles (Fig. 8). Over the entire campaign organic matter constituted the largest fraction (~50%) of the sub-micron aerosol mass, as is common with a large number of sites worldwide (Zhang et al., 2007). Of the remaining half of the particulate matter, the majority was contributed by sulfate followed by ammonium and nitrate. The organics, sulfate and ammonium displayed a prominent daytime enhancement, similar to that of O_3 and acetone, indicative of photochemical formation of each species, whereas the nitrate profile was enhanced early in the morning and reached a minimum in the afternoon. The nitrate profile is likely affected by a variety of factors, such as accumulation of HNO_3 at night arising from N_2O_5 hydrolysis and by low temperatures of night that preferentially partition nitrate to particulates and the warm daytime temperatures which do not allow nitrate to persist. The sulfate afternoon maximum will be driven by

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

photochemistry, arising from gas-phase oxidation of SO_2 to form H_2SO_4, which either partitions to pre-existing particles or participates in new particle formation.

As described above, the organic aerosol fraction was broken down into four factors by Positive Matrix Factorization. Briefly, HOA is representative of primary, hydrocarbon-like emissions, whereas OOA-1 and OOA-2 both represent oxidized organic aerosol, with the former more oxygenated than the latter. Factor 4, also oxygenated, is associated with a significant fraction of the total organic mass only during the last three days of the campaign.

With diurnal analysis (Fig. 8), the normalized profiles show that the amounts of aerosol mass attributed to the two oxygenated factors and to Factor 4 rise in the afternoon when photochemistry is most active. OOA-1 reaches its peak value somewhat later than OOA-2, consistent with it arising from oxidation of OOA-2 components and being more oxidized. Both factors rise in value at the same time just before 12:00 EDT. Conversely, HOA remains relatively unchanged throughout the 24-h day, much like the long-lived aromatic species, benzene. We interpret this to indicate that the timescale for heterogeneous or photochemical oxidation of HOA chemical components into volatile products or into a more oxygenated factor is longer than a few hours.

3.2 Campaign episodes

Although this paper focuses primarily on the overall behavior observed during the BAQS campaign at Harrow, a variety of air mass types were prevalent during the full campaign. To demonstrate this, we illustrate three distinct periods. Please refer to (Slowik et al., 2010b) for an analysis of the nature and transformation of the organic aerosol during specific campaign periods.

The first period is from 06:00 EDT on 24 June until 16:00 EDT on 27 June, during which the acetone levels are especially high while the C_8 aromatics are not. Winds were generally out of the southwest. Furthermore, the toluene-to-benzene ratio, a marker of photochemical aging (Roberts et al., 1984), is also low (mean value = 1.4), indicative of photochemically processed air. In the aerosol phase, sulfate was the

dominant species by mass, although substantial organics were present. This period is referred to as *Processed Air*, which we believe arrived from the US Midwest by passing over Lake Erie without recent significant anthropogenic VOC input. In particular, the fetch from the north shore of Lake Erie is quite short, only a few km, to the observation site over farmland. Temperatures were also elevated with air flow from the south. During the *Processed Air* period OOA1 was the largest organic PMF component, generally consistent with the view that OOA1 is indicative of highly aged, oxidatively processed air.

The second period, from midnight on 5 July until 12:00 EDT on 7 July, was dominated by winds out of the northwest, in the direction of Detroit. As such, this period is referred to as *Detroit Air*. In contrast to the *Processed Air* the aromatic mixing ratios reached their highest mixing ratios during this period. Also, the toluene to benzene ratio (mean = 2.4) was higher indicating that Harrow was influenced by fresher anthropogenic emissions. In the aerosol phase the highest organic mass loading occurred at this time and there was little sulfate. This period is referred to as *Detroit Air*. During the Detroit Air plume, the OOA2 factor, less oxygenated than OOA1, is more dominant, consistent with new SOA formation.

The final period, from 05:00 EDT on 8 July until the end of the campaign, looks similar to the processed air in that the toluene-to-benzene ratio is diminished (mean = 1.4). This period is distinguished from the *Processed Air* period by the extremely low aromatic signals and the enhanced mixing ratios of isoprene, which reached their peak values during this time. There is a steady wind flow from the southwest-west and the temperatures are high. As the sulfate levels are elevated at times, we refer to this period as *Sulfate and Biogenic Air*, and we believe it is characterized by aged air to which fresh biogenic emissions have been injected. PMF Factor 4 is attributed to the majority of the organic aerosol mass during this period.

We now examine diurnal profiles of the selected time periods. Whereas diurnal profiles for a full three week campaign are expected to give some average representation of the nature of the air at the site, we anticipate that average diurnal profiles over short

Diurnally resolved particulate and VOC measurements at a rural site

S. J. Sjostedt et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀ | ▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

time periods of a few days will not be as smooth due to more prominent interference by specific events. Nevertheless, qualitatively, the results are expected to provide valuable insight into the atmospheric processes involved.

In particular, in Fig. 9, the diurnal profiles of the OOA-1 factor during these different episodes are all roughly the same, with similar timing and amounts of organic aerosol formed during the day. During the *Processed Air* event, the increase in OOA-1 levels is more than a factor of two higher than that of OOA-2 formed, whereas the amount of OOA-2 formation is similar to the amount of OOA-1 formation during *Detroit Air*. It appears as though there are similar levels of OOA-1 precursors (and oxidants) present in all the sampled air masses suggesting that OOA-1 formation occurs in a highly regional manner, whereas the levels of OOA-2 precursors are significantly enhanced during the polluted episode of *Detroit Air*. This is consistent with the higher levels of aromatics measured at that time, and perhaps unmeasured, semivolatile VOCs (Robinson et al., 2007), that are likely to also form OOA-2.

3.3 Relationship of VOCs to SOA formation

The goal in this section is to assess the relative degree to which specific VOCs lead to SOA formation. The approach we take uses the data from Sect. 4i. where diurnal profiles were presented for the whole campaign. We attempt to quantitatively connect the integrated loss rate of VOCs to the total formation of the oxygenated organic PMF factors during the day (which we define as being the sum of OOA-1 and OOA-2), assumed to represent the total SOA formation rate at the site.

Specifically, the approach we take is to calculate the integrated production rate of SOA (Δ SOA) due to OH oxidation according to:

$$\Delta SOA = Y\, k_{VOC+OH} \int_0^T [VOC][OH]\, dt \qquad (1)$$

where Y is the yield of SOA from a specific VOC precursor, k_{VOC+OH} is the gas-phase rate constant for reaction of the VOC with OH, (OH) is the OH concentration at time

t, and (VOC) is the VOC concentration at time t. Appropriate unit conversions are performed so that Δ SOA is expressed in µg/m^3. In practice we approximate the integral of E1 as a summation, with time steps of 5 min. We recognize that the quantity Δ SOA represents the total production of SOA over a time period T under the assumption that the OH and VOC concentrations, and the SOA yield, are the same at locations upwind of the observation site, i.e. that the local production rate as calculated by E1 at Harrow is the constant over a spatial extent corresponding to the distance travelled by a gas-phase precursor during its chemical lifetime. We believe that uncertainties that may arise are diminished by the use of average diurnal behavior across the full campaign time period plus the fact that the environs close to Harrow are all similar, with small sections of forest interspersed amongst agricultural land.

We now discuss how each of the terms in E1 was obtained. First, the laboratory yields of SOA from a variety of VOC precursors have been studied extensively in numerous chamber experiments. For example, for the aromatics, studies (e.g. Hildebrandt et al., 2009; Hurley et al., 2001; Jang and Kamens, 2001; Ng et al., 2007b) have measured yields with many showing high NO$_x$ levels leading to lower SOA yields. Biogenic precursors have also been studied (e.g. Kleindienst et al., 2009; Kroll et al., 2006; Ng et al., 2007b) and a NO$_x$ dependence has also been observed in some cases. For use in E1, where we are interested in comparing the relative roles of aromatic and biogenic precursors, we choose to use yields recently measured by the same research group, to give us the greatest possibility of internal consistency. As a result, we have used the following studies and their NO$_x$ dependencies as measured using similar experimental approaches: isoprene (Kroll et al., 2006), aromatics and terpenes (Ng et al., 2007a, b). Note that we assume that α-pinene constitutes all the PTR-MS monoterpene signal. Yields from other research groups could equally well have been used. In our calculations, yields are assessed using the organic mass present at a specific time step in the summation, and yields are evaluated in both the high and low NO$_x$ limits.

Second, the gas-phase rate constant between OH and the VOC is taken directly from (Atkinson et al., 2006), calculated for the field temperature conditions. In the case

of the C8 aromatics, with the PTR-MS signal possibly arising from the three different xylenes and also from ethyl benzene, we weight the rate constants for the four individual species by the typical relative mixing ratios for these species measured in tunnel emission studies (Schauer et al., 1999, 2002).

5 Third, the VOC concentrations are taken directly from the time-resolved, diurnally averaged VOC mixing ratios measured at Harrow.

Finally, given that OH concentrations were not measured at Harrow, we estimate the amount of OH present near the observation site by following the approach published by (de Gouw et al., 2009) who evaluated the average amount of OH present in Mexico City 10 during the MILAGRO field campaign. We refer the reader to this paper for additional details. Briefly, noting that the loss of C_8 aromatics and toluene is due to OH chemistry, we use the following expression:

$$\frac{[\text{Aromatic}_0] - [\text{Aromatic}_T]}{[\text{Aromatic}_0]} = A(1 - \exp(-k_{\text{Aromatic+OH}}\overline{[\text{OH}]}_{\text{est}}\Delta t)) \qquad (2)$$

This expression is the integrated rate equation for loss of aromatics due to OH chem-15 istry over a time period Δt extending from an initial time 0 to time T. The factor A takes into account that aromatics may be emitted locally during the day and are not lost to reaction with OH, i.e. the value of A would be unity if there were no local daytime emissions. Its value can be determined empirically by noting that the most reactive C_8 aromatics, i.e. the xylenes and ethyl benzene, reach a steady minimum value early in 20 the afternoon that extends through to early evening.

For this work, we estimate the average OH concentration, $\overline{(\text{OH})}_{\text{est}}$, that extends from 06:00 EDT to 18:00 EDT, corresponding to the total time over which there is loss of aromatics observed, i.e. the aromatic mixing ratios rise after 18:00 EDT due to decreasing OH and continued aromatic emissions. Thus, we set $T = 12$ h. We choose the A factor 25 from the C_8 aromatic time series, i.e. the most reactive aromatics, as the minimum value within a five-h window about 15:00 EDT. At this time, the aromatic mixing ratio is 0.28 of its starting value (i.e. as a one-h average centered at 06:00 EDT), representing

27335

an A value of 0.72. The average OH concentration was then calculated from E2 for both the C_8 aromatic and the toluene data, yielding an average value of 3.6×10^6 molecules cm^{-3}. Specifically, this is a measure of the average OH concentration at the Harrow site over the 12 h window from 06:00 EDT to 18:00 EDT. We do not believe this value is accurate to more than a factor of two given the uncertainties involved in its calculation. As an example, if we choose, instead, the A factor from the value for the C_8 aromatics for a one-h window around 18:00 EDT, i.e. the end period of the minimum plateau reached by the aromatics, we arrive instead at a value for A = 0.61. In this case, the average OH concentration across the 12-h window is estimated to be 6.7×10^6 molecules cm^{-3}. On the other hand, we know that the A value is not unity. In particular, there certainly are local emissions of aromatics during the day because the C_8 aromatic signal reaches its minimum value so close to noon. If there were no local emissions, the PTR-MS signal for these species would continue to drop throughout the afternoon hours when OH concentrations are high.

To accurately implement E1, we require time resolved OH concentrations, whereas the above calculation yields only a 12-h average. To determine the average OH concentrations in each 5-min interval we scale the time-resolved OH concentrations calculated from the averaged results of the AURAMS model (Stroud et al., 2010) that was run for the Harrow study time period to give the average concentration from the 06:00 EDT to 18:00 EDT time period that was determined above. This scaling provides a midday maximum OH number density of 7.0×10^6 molecules cm^{-3}.

The results from the calculation of the integrated and CO normalized SOA formation amounts during the entire campaign are presented in Table 1, where we indicate estimates under both high and low NO$_x$ conditions. Also included in the table are the observed increases in the AMS oxygenated organic aerosol amount from the same time period, as deduced from Fig. 8. Finally, we include the contribution to the SOA that may arise from ozonolysis of monoterpenes calculated using E1 but with measured ozone concentrations, and the appropriate rate constant (Atkinson et al., 2006) and laboratory secondary aerosol yields for α-pinene (Lee et al., 2006).

From the table it is clear from the calculations that the biogenic sources of SOA during the BAQS-Met study at Harrow dominate over the aromatic sources, with 10 to 36 times more production of SOA via biogenic sources than from the aromatics. Southwestern Ontario is not widely recognized as a highly biogenically active region and it sits close to a number of pollution sources both in Ontario and in neighboring US Midwest states. Nevertheless, the dispersed forests amongst farmland that extends for hundreds of kilometers in Southwestern Ontario appear to provide sufficient biogenic emissions to be important as far as SOA formation occurs for the majority of air mass back trajectories arriving at Harrow over the 3-week study. One caveat is there may be unidentified anthropogenic VOCs that act as SOA precursors, such as primary alkanes associated with transportation emissions, so in this work we can only make the claim that biogenics dominate over the aromatics measured by the PTR-MS, in terms of SOA formation capability.

We recognize that there are uncertainties in the absolute values of the SOA production values. First, there are uncertainties in the OH values as described above. Second, the assumption being made in this work is that the VOC mixing ratios measured at Harrow are representative of those in the surrounding regions in which the daytime production of SOA is proceeding. With an average wind speed of 3.3 m/s during the campaign in the daytime time period, this region is roughly 70 km in extent. Overall, land usage close to the measurement site is typical of the surrounding terrain, i.e. mostly farmland with interspersed forests of mixed deciduous and coniferous trees, with the notable exception of Windsor/Detroit. Third, processes not addressed with this approach include aerosol deposition during the time interval under study. However, aerosol depositional loss we consider to be quite small given the flat diurnal profiles of the CO-normalized HOA PMF factor. The flat diurnal profile indicates that there are no substantial loss processes of particles containing HOA species, either chemical or depositional. Fourth, we have done the analyses using average values. If, instead, we use median values we find that the predicted SOA closure (i.e. comparison between modeled and measured values) is decreased by roughly a factor of two, i.e. roughly

Diurnally resolved particulate and VOC measurements at a rural site

S. J. Sjostedt et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

50% less SOA is generated. Finally, we are only using the SOA yields from processes studied in traditional chamber experiments and we assume instantaneous formation of SOA after VOC loss. We are not accounting for SOA that might arise from aqueous phase processes such as carbonyl uptake processes that might occur on acidic particles.

To gain a better sense of the absolute accuracy of this SOA-formation calculation method, we also report the calculated and observed integrated formation rates of the sulfate aerosol species. We assume that the formation of sulfate in the afternoon proceeds via OH chemistry, specifically via the rate-limiting gas-phase reaction of SO_2 with the OH radical. Indeed, the formation rate of sulfate in the afternoon resembles that of organics which are presumably also forming via OH-driven processes. We are not addressing processing that may occur via clouds, which would not have the same diurnal profile. Once ultimately formed from this chemistry, gas-phase sulfuric acid condenses to form aerosol sulfate. This is clearly seen in Fig. 8 where the diurnal analysis indicates a large amount of sulfate production during the photochemically active daytime. Contrary to the organics where the VOC precursors are more uniform both spatially and temporally, SO_2 mixing ratios are temporally variable due primarily to passage of sporadic pollution plumes arising from power plants nearby, both in Ontario and the US Midwest. Part of the morning enhancement in SO_2 levels may be due to mixing from aloft as the boundary layer breaks up in the morning.

Using the equivalent form of E1 but with the VOCs replaced by SO_2 and with the appropriate gas-phase rate constant (Sander, 2006), the calculated and observed sulfate integrated production rates are also included in Table 1. We assume that the yield, Y, is equal to unity, i.e. all sulfuric acid formed by SO_2 oxidation condenses to form AMS-measureable sulfate.

The agreement between the measured and observed sulfate amounts is roughly a factor of two. If the higher estimate of the OH concentration offered above were used, then the level of agreement would be close to 100%. We believe this level of agreement provides a level of validation for the general approach that we present in this paper.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Finally, with no HO_2 measurements at Harrow, it is difficult to determine whether SOA formation was proceeding in a high or low NO_x regime. Specifically, a key step in the reaction mechanism that leads to condensable organics is thought to be the loss of the RO_2 radical that is formed after initial OH attack on the VOC precursor and subsequent O_2 addition. The RO_2 species can react either with peroxy radicals, principally HO_2, or with NO. Without HO_2 measurements, we include in Table 1 SOA formation by OH oxidation under conditions of both high and low NO_x, as specified by the different yields measured in laboratory experiments. Under both limits, it is noteworthy that the calculated SOA production amounts match the observed levels quite closely, to a factor of two. This level of agreement is similar to that between the calculated and observed sulfate production amounts and to our rough estimates in the uncertainty of the average OH concentration.

3.4 Comparison to predictions from an air quality model

The approach we have presented for the calculation of SOA production amounts is empirically based, relying on simultaneous measurements of VOCs and organic aerosol amounts, and literature values for VOC/oxidant rate constants and SOA yields. It is conceptually and computationally simple. By contrast, commonly used chemical transport models are highly complex, relying on coupled chemical, emissions and dynamics modules. Although such models are clearly the first choice for modeling organic aerosol formation across a regional domain, it is important that their output can be validated through detailed diagnostic evaluations, i.e. they need to be able to match observations and evaluations of relevant processes at a fixed site as we have done here.

To that end we compare diurnal profiles of AURAMS model predictions and the PTR-MS and AMS measurements at Harrow during BAQS. It is seen in Fig. 10 that the comparison for the gas-phase aromatics is good, especially for the reactive species toluene and the C_8 aromatics. On the other hand, the comparison with the biogenic SOA precursors is poor, with substantial levels of isoprene and monoterpenes observed during

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►◄

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

the day whereas the AURAMS model predicts low levels, likely due to a combination of (1) excessive OH levels within the model, (2) too low local biogenic emissions and/or (3) not enough vertical mixing at dusk and dawn in the model. Finally, the predicted levels of SOA formation during the day are somewhat lower than those observed at
5 Harrow, likely because of insufficient biogenic SOA contributions (Fig. 11). While we point these differences out, detailed analysis of the source of these inconsistencies within the model are well outside the scope of this paper.

4 Summary

In this paper we have applied a diurnal analysis approach to assess the role of different
10 VOC precursors to SOA formation, where the VOCs are measured by PTR-MS. Measurements were conducted at a rural site in southwestern Ontario subject to a wide variety of air masses during a three-week campaign near summer solstice in 2007. A long-lived tracer, CO, is used to normalize for dynamical effects associated primarily with changing boundary layer height during the day. Integrated production rates of
15 SOA are compared to observed values, as measured by the formation of oxygenated organic aerosol components measured with an AMS. The major conclusion we reach is that biogenic precursors dominate SOA production over aromatic source gases at this site during the campaign, consistent with continental observations that indicate a large contribution from fresh (versus fossil fuel) carbon to SOA (De Gouw and Jimenez,
20 2009). The one possible exception being when there is direct pollution plume transport from Detroit.

We have more confidence in our prediction of the relative role of different precursors given that absolute comparisons of predicted to measured SOA diurnal enhancements are made somewhat uncertain through the lack of OH measurements at this site. Nev-
25 ertheless, using diurnal loss of aromatics to estimate the average OH present during the day allows us to estimate that the biogenics (isoprene, monoterpenes) and aromatics (benzene, toluene, C_8 species) together account for roughly 52% to 97% of

the total SOA production, depending on whether production is proceeding via the high or low NO$_x$ regimes. This level of closure is quite high given recent reports of large disagreements between measured and modeled levels of organic aerosol (De Gouw and Jimenez, 2009). In particular, agreement between models and measurements in

5 biogenically dominated regimes, as we believe this is, is comparably good (Capes et al., 2009; Slowik et al., 2010a). We note that this approach also predicts the observed production of aerosol sulfate to within a factor of two to three, a rough measure of the inherent uncertainties in the approach.

We propose that measurements of this type, that are now relatively standard (such as

10 those by PTR-MS and AMS, and increasingly OH), could be performed at multiple sites across a region to determine the generality of diurnal profiles observed at any one site. If similar, this straightforward approach for estimating secondary aerosol production rates would be validated and would provide a valuable method for assessing chemical transport model predictions of SOA formation across the same region.

References

Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich,
20 I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry, Environ. Sci. Technol., 42, 4478–4485, 2008.
25 Atkinson, R. and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: A review, Atmos. Environ., 37, S197–S219, 2003.
Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and IUPAC Subcommittee: Evaluated kinetic and photochemical

data for atmospheric chemistry: Volume II gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625–4055, doi:10.5194/acp-6-3625-2006, 2006.

Capes, G., Murphy, J. G., Reeves, C. E., McQuaid, J. B., Hamilton, J. F., Hopkins, J. R., Crosier, J., Williams, P. I., and Coe, H.: Secondary organic aerosol from biogenic VOCs over West Africa during AMMA, Atmos. Chem. Phys., 9, 3841–3850, doi:10.5194/acp-9-3841-2009, 2009.

Chen, J., Mao, H., Talbot, R. W., and Griffin, R. J.: Application of the CACM and MPMPO modules using the CMAQ model for the eastern United States, J. Geophys. Res., 111, D23S25, doi:10.1029/2006JD007603, 2006.

de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P. D., Kuster, W. C., Roberts, J. M., Fehsenfeld, F. C., Worsnop, D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W. C., Marchewka, M., Bertman, S. B., and Bates, T. S.: Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, J. Geophys. Res., 110, D16305, doi:10.1029/2004JD005623, 2005.

de Gouw, J. and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry, Mass. Spectrom. Rev., 26, 223–257, 2007.

de Gouw, J. A., Brock, C. A., Atlas, E. L., Bates, T. S., Fehsenfeld, F. C., Goldan, P. D., Holloway, J. S., Kuster, W. C., Lerner, B. M., Matthew, B. M., Middlebrook, A. M., Onasch, T. B., Peltier, R. E., Quinn, P. K., Senff, C. J., Stohl, A., Sullivan, A. P., Trainer, M., Warneke, C., Weber, R. J., and Williams, E. J.: Sources of particulate matter in the northeastern United States in summer: 1. Direct emissions and secondary formation of organic matter in urban plumes, J. Geophys. Res., 113, D08301, doi:10.1029/2007JD009243, 2008.

de Gouw, J. A., Welsh-Bon, D., Warneke, C., Kuster, W. C., Alexander, L., Baker, A. K., Beyersdorf, A. J., Blake, D. R., Canagaratna, M., Celada, A. T., Huey, L. G., Junkermann, W., Onasch, T. B., Salcido, A., Sjostedt, S. J., Sullivan, A. P., Tanner, D. J., Vargas, O., Weber, R. J., Worsnop, D. R., Yu, X. Y., and Zaveri, R.: Emission and chemistry of organic carbon in the gas and aerosol phase at a sub-urban site near Mexico City in March 2006 during the MILAGRO study, Atmos. Chem. Phys., 9, 3425–3442, doi:10.5194/acp-9-3425-2009, 2009.

de Gouw, J., and Jimenez, J. L.: Organic aerosols in the earth's atmosphere, Environ. Sci. Technol., 43, 7614–7618, 2009.

Drewnick, F., Hings S.S., DeCarlo P., Jayne J.T., Gonin M., Fuhrer K., Weimer S., Jimenez J.L., Demerjian K.L., Borrmann S., and Worsnop D.R., A new time-of-flight aerosol mass

Diurnally resolved particulate and VOC measurements at a rural site

S. J. Sjostedt et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

spectrometer (TOF-AMS) – Instrument description and first field deployment, Aerosol Sci. Tech., 39(7), 637–658, 2005.

Gong, S. L., Barrie, L. A., Blanchet, J. P., von Salzen, K., Lohmann, U., Lesins, G., Spacek, L., Zhang, L. M., Girard, E., Lin, H., Leaitch, R., Leighton, H., Chylek, P., and Huang, P.: Canadian Aerosol Module: A size-segregated simulation of atmospheric aerosol processes for climate and air quality models 1. Module development, J. Geophys. Res., 108, D1(4007), doi:10.1029/2001JD002002, 2003.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5236, doi:10.5194/acp-9-5155-2009, 2009.

Heald, C. L., Jacob, D. J., Park, R. J., Russell, L. M., Huebert, B. J., Seinfeld, J. H., Liao, H., and Weber, R. J.: A large organic aerosol source in the free troposphere missing from current models, Geophys. Res. Lett., 32, L18809, doi:10.1029/2005GL023831, 2005.

Hildebrandt, L., Donahue, N. M., and Pandis, S. N.: High formation of secondary organic aerosol from the photo-oxidation of toluene, Atmos. Chem. Phys., 9, 2973–2986, doi:10.5194/acp-9-2973-2009, 2009.

Hurley, M. D.: Organic aerosol formation during the atmospheric degradation of toluene, Environ. Sci. Technol., 35, 1358–1366, 2001.

Jang, M., and Kamens, R. M.: Characterization of secondary aerosol from the photooxidation of toluene in the presence of NO_x and 1-propene, Environ. Sci. Technol., 35, 3626–3639, 2001.

Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., and Worsnop, D. R.: Development of an aerosol mass spectrometer for size and composition analysis of submicron particles, Aerosol Sci. Tech., 33, 49–70, 2000.

Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R. C., Zhang, X., Smith, K. A., Morris, J. W., and Davidovits, P.: Ambient aerosol sampling using the Aerodyne aerosol mass spectrometer, J. Geophys. Res., 108(D7), 8425, doi:10.1029/2001JD001213, 2003.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H.,

Diurnally resolved particulate and VOC measurements at a rural site

S. J. Sjostedt et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, Science, 326, 1525–1529, 2009.

Kleeman, M. J., Ying, Q., Lu, J., Mysliwiec, M. J., Griffin, R. J., Chen, J., and Clegg, S.: Source apportionment of secondary organic aerosol during a severe photochemical smog episode, Atmos. Environ., 41, 576–591, 2007.

Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., Jaoui, M., and Edney, E. O.: The formation of secondary organic aerosol from the isoprene + OH reaction in the absence of NO_x, Atmos. Chem. Phys., 9, 6541–6558, doi:10.5194/acp-9-6541-2009, 2009.

Kleinman, L. I., Daum, P. H., Lee, Y. N., Senum, G. I., Springston, S. R., Wang, J., Berkowitz, C., Hubbe, J., Zaveri, R. A., Brechtel, F. J., Jayne, J., Onasch, T. B., and Worsnop, D.: Aircraft observations of aerosol composition and ageing in New England and Mid-Atlantic States during the summer 2002 New England Air Quality Study field campaign, J. Geophys. Res., 112, D09310, doi:10.1029/2006JD007786, 2007.

Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation, 40, 1869–1877, 2006.

Kroll, J. H. and Seinfeld, J. H.: Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, Atmos. Environ., 42, 3593–3624, 2008.

Lee, A., Goldstein, A. H., Keywood, M. D., Gao, S., Varutbangkul, V., Bahreini, R., Ng, N. L., Flagan, R. C., and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the ozonolysis of ten different terpenes, J. Geophys. Res., 111, D07302, doi:10.1029/2005JD006437, 2006.

Levy, I., Makar, P. A., Sills, D., Zhang, J., Hayden, K. L., Mihele, C., Narayan, J., Moran, M. D., Sjostedt, S., and Brook, J.: Unraveling the complex local-scale flows influencing ozone patterns in the southern Great Lakes of North America, Atmos. Chem. Phys. Discuss., 10, 19763–19810, doi:10.5194/acpd-10-19763-2010, 2010.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀ | ▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Li, Q., Jacob, D. J., Munger, J. W., Yantosca, R. M., and Parrish, D. D.: Export of NO_y from the North American boundary layer: Reconciling aircraft observations and global model budgets, J. Geophys. Res., 109, D02313, doi:10.1029/2003JD004086, 2004.

Lindinger, W., Hansel, A., and Jordan, A.: Proton-transfer-reaction mass spectrometry (PTR-MS): On-line monitoring of volatile organic compounds at pptv levels, Chem. Soc. Rev., 27, 347–354, 1998.

Makar, P. A., Moran, M. D., Zheng, Q., Cousineau, S., Sassi, M., Duhamel, A., Besner, M., Davignon, D., Crevier, L.-P., and Bouchet, V. S.: Modelling the impacts of ammonia emissions reductions on North American air quality, Atmos. Chem. Phys., 9, 7183–7212, doi:10.5194/acp-9-7183-2009, 2009.

Murphy, B. N. and Pandis, S. N.: Simulating the formation of semivolatile primary and secondary organic aerosol in a regional chemical transport model, Environ. Sci. Technol., 43, 4722–4728, 2009.

Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from m-xylene, toluene, and benzene, Atmos. Chem. Phys., 7, 3909–3922, doi:10.5194/acp-7-3909-2007, 2007.

Ng, N. L., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Kroll, J. H., Kwan, A. J., McCabe, D. C., Wennberg, P. O., Sorooshian, A., Murphy, S. M., Dalleska, N. F., Flagan, R. C., and Seinfeld, J. H.: Effect of NOx level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes, Atmos. Chem. Phys., 7, 5159–5174, doi:10.5194/acp-7-5159-2007, 2007.

Paatero, P. and Tapper, U.: Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values, Environmetrics, 5, 111–126, 1994.

Paatero, P.: Least squares formulation of robust non-negative factor analysis, Chemometr. Intell. Lab., 37, 23–35, 1997.

Pankow, J. F.: An absorption model of gas/particle partitioning of organic compounds in the atmosphere, Atmos. Environ., 28, 185–188, 1994.

Parrish, D. D., Ryerson, T. B., Holloway, J. S., Neuman, J. A., Roberts, J. M., Williams, J., Stroud, C. A., Frost, G. J., Trainer, M., Hübler, G., Fehsenfeld, F. C., Flocke, F., and Weinheimer, A. J.: Fraction and composition of NO_y transported in air masses lofted from the North American continental boundary layer, J. Geophys. Res., 109, D09302, doi:10.1029/2004JD004226, 2004.

Roberts, J. M., Fehsenfeld, F. C., and Liu, S. C.: Measurements of aromatic hydrocarbon ratios

Diurnally resolved particulate and VOC measurements at a rural site

S. J. Sjostedt et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

and NO(x) concentrations in the rural troposphere: Observations of air mass photochemical aging and NO(x) removal, Atmos. Environ., 18, 2421–2432, 1984.

Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking organic aerosols: Semivolatile emissions and photochemical aging, Science, 315, 1259–1262, 2007.

Sander, S.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 15, NASA, JPL, 2006.

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of emissions from air pollution sources. 2. C_1 through C_{30} organic compounds from medium duty diesel trucks, Environ. Sci. Technol., 33, 1578–1587, 1999.

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of emissions from air pollution sources. 5. C_1–C_{32} organic compounds from gasoline-powered motor vehicles, Environ. Sci. Technol., 36, 1169–1180, 2002.

Seinfeld, J. H. and Pankow J. F., Organic atmospheric particulate material, Annu. Rev. Phys. Chem., 54, 121–140, 2003.

Slowik, J. G., Stroud, C., Bottenheim, J. W., Brickell, P. C., Chang, R. Y.-W., Liggio, J., Makar, P. A., Martin, R. V., Moran, M. D., Shantz, N. C., Sjostedt, S. J., van Donkelaar, A., Vlasenko, A., Wiebe, H. A., Xia, A. G., Zhang, J., Leaitch, W. R., and Abbatt, J. P. D.: Characterization of a large biogenic secondary organic aerosol event from eastern Canadian forests, Atmos. Chem. Phys., 10, 2825–2845, doi:10.5194/acp-10-2825-2010, 2010.

Slowik, J. G., Brook, J., Chang, R. Y.-W., Evans, G. J., Hayden, K., Jeong, C.-H., Li, S.-M., Liggio, J., Liu, P. S. K., McGuire, M., Mihele, C., Sjostedt, S., Vlasenko, A., and Abbatt, J. P. D.: Photochemical processing of organic aerosol at nearby continental sites: contrast between urban plumes and regional aerosol, Atmos. Chem. Phys. Discuss., 10, 24993–25031, doi:10.5194/acpd-10-24993-2010, 2010.

Stroud, C. A., Morneau, G., Makar, P. A., Moran, M. D., Gong, W., Pabla, B., Zhang, J., Bouchet, V. S., Fox, D., Venkatesh, S., Wang, D., and Dann, T.: OH-reactivity of volatile organic compounds at urban and rural sites across Canada: Evaluation of air quality model predictions using speciated VOC measurements, Atmos. Environ., 42, 7746–7756, 2008.

Stroud, C., Makar P. A., Moran M. D., Gong W., Gong S., Zhang J., Mihele C., Brook J., Lu P. S. K., Abbatt J. P. D., Slowik J. G., Sills D., and Li Q. B., Biogenic and Anthropogenic Contributions to Organic Aerosol in Southern Ontario: Air Quality Modeling for the BAQS-Met Study, Atmos. Chem. Phys., to be submitted, 2010.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, Atmos. Chem. Phys., 9, 2891–2918, doi:10.5194/acp-9-2891-2009, 2009.

Vlasenko, A., Slowik, J. G., Bottenheim, J. W., Brickell, P. C., Chang, R. Y. W., Maedonald, A. M., Shantz, N. C., Sjostedt, S. J., Wiebe, H. A., Leaitch, W. R., and Abbatt, J. P. D.: Measurements of VOCs by proton transfer reaction mass spectrometry at a rural Ontario site: Sources and correlation to aerosol composition, J. Geophys. Res., 114, D21305, doi:10.1029/2009JD012025, 2009.

Volkamer, R., Jimenez, J. L., San Martini, F., Dzepina, K., Zhang, Q., Salcedo, D., Molina, L. T., Worsnop, D. R., and Molina, M. J.: Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected, Geophys. Res. Lett., 33, L17811, doi:10.1029/2006GL026899, 2006.

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.: Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, Geophys. Res. Lett., 34, L13801, doi:10.1029/2007GL029979, 2007.

Table 1. Calculated Contributions to Secondary Aerosol Formation (all normalized to CO). Units for secondary aerosol amounts are $\mu g\,m^{-3}\,ppbv^{-1}$.

	High NO$_x$		Low NO$_x$	
	Calculated ΔOrg ($\mu g\,m^{-3}\,ppbv^{-1}$)	Fraction of Observed (%)	Calculated ΔOrg ($\mu g\,m^{-3}\,ppbv^{-1}$)	Fraction of Observed (%)
Benzene-OH	8.4×10^{-5}	0.14	2.5×10^{-4}	0.42
Toluene-OH	3.7×10^{-4}	0.61	1.8×10^{-3}	3.0
C$_8$ Aromatic-OH	4.1×10^{-4}	0.69	3.0×10^{-3}	5.0
Calculated Total Anthropogenic ΔOrg	8.6×10^{-4}	1.4	5.0×10^{-3}	8.3
Isoprene-OH	6.0×10^{-3}	10	3.9×10^{-3}	6.5
Monoterpenes-OH	8.4×10^{-3}	14	3.3×10^{-2}	55
Monoterpenes-O$_3$	1.6×10^{-2}	27	1.6×10^{-2}	27
Calculated Total Biogenic ΔOrg	3.0×10^{-2}	51	5.3×10^{-2}	88
Calculated Total ΔOrg (i.e. Biogenic + Anthropogenic)	3.1×10^{-2}	52	5.8×10^{-2}	97
Observed ΔOrg	6.0×10^{-2}			
Calculated ΔSulfate	2.5×10^{-2}			
Observed ΔSulfate	6.2×10^{-2}			

Fig. 1. Harrow, ON and the surrounding area.
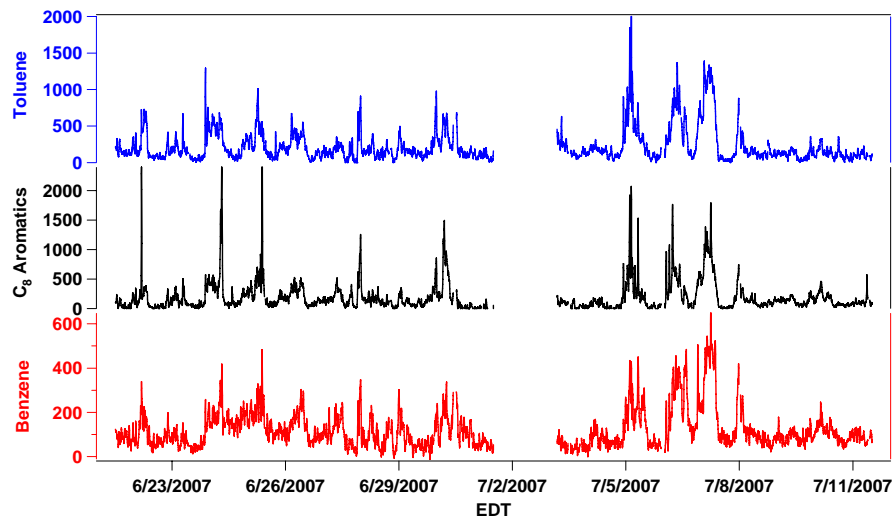
Fig. 2. Aromatic VOC time series, as measured by the PTR-MS. Units are in pptv.
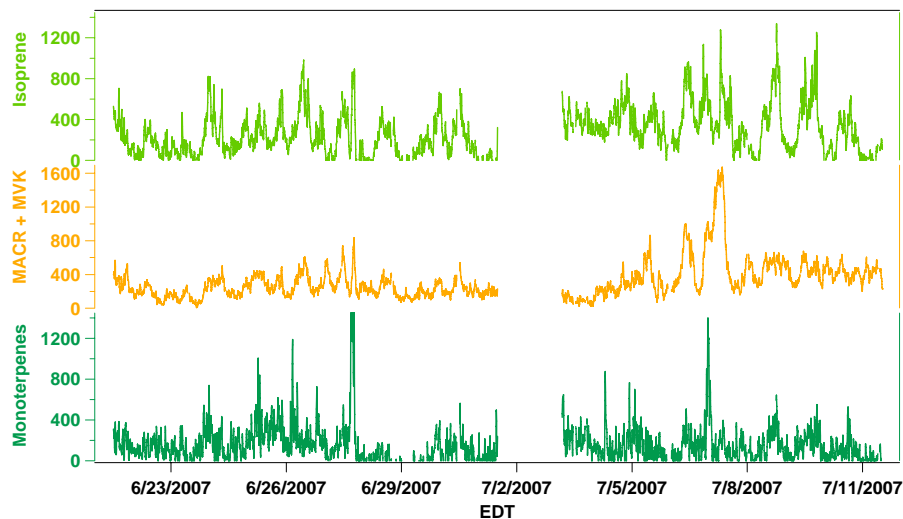
Fig. 3. Biogenic VOC time series, as measured by the PTR-MS. Units are in pptv.
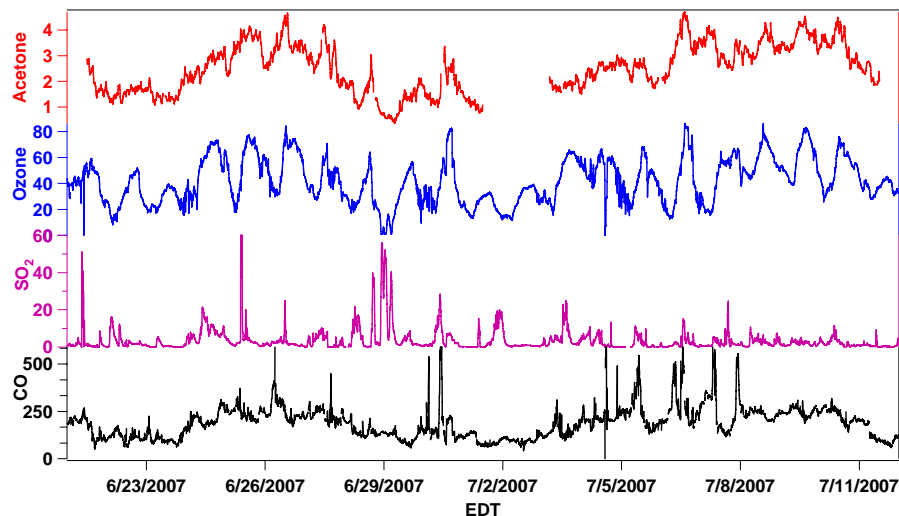
Fig. 4. Selected gas species time series. Acetone was measured by the PTR-MS, whereas the others by standard air quality measurement instruments. Units are in ppbv.
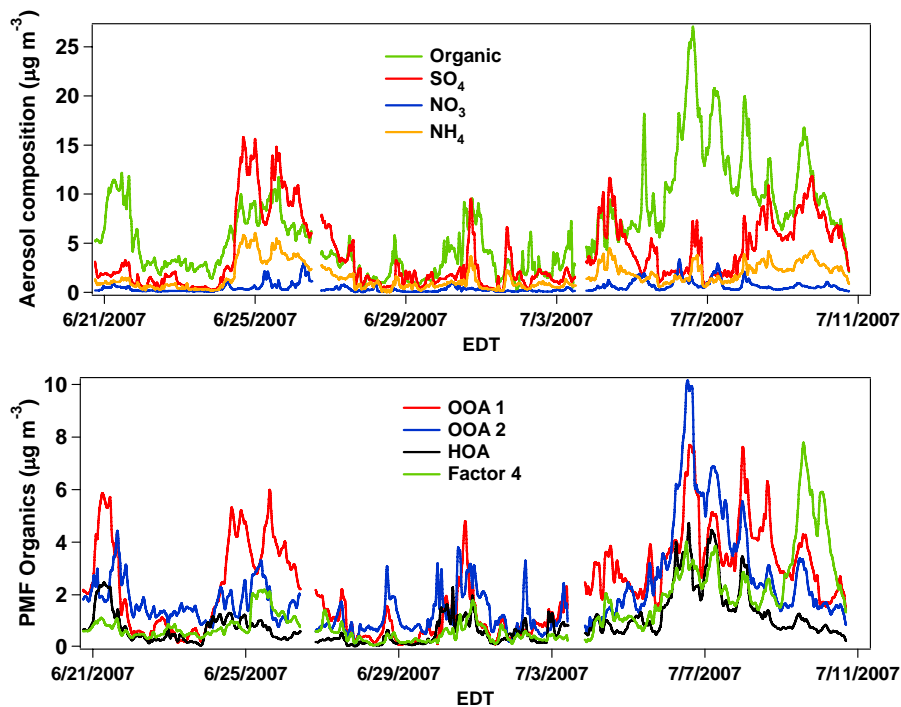
Fig. 5. Time Series of AMS species in the upper frame. Factors from the Positive Matrix Factorization of the AMS organics are shown in the lower frame.
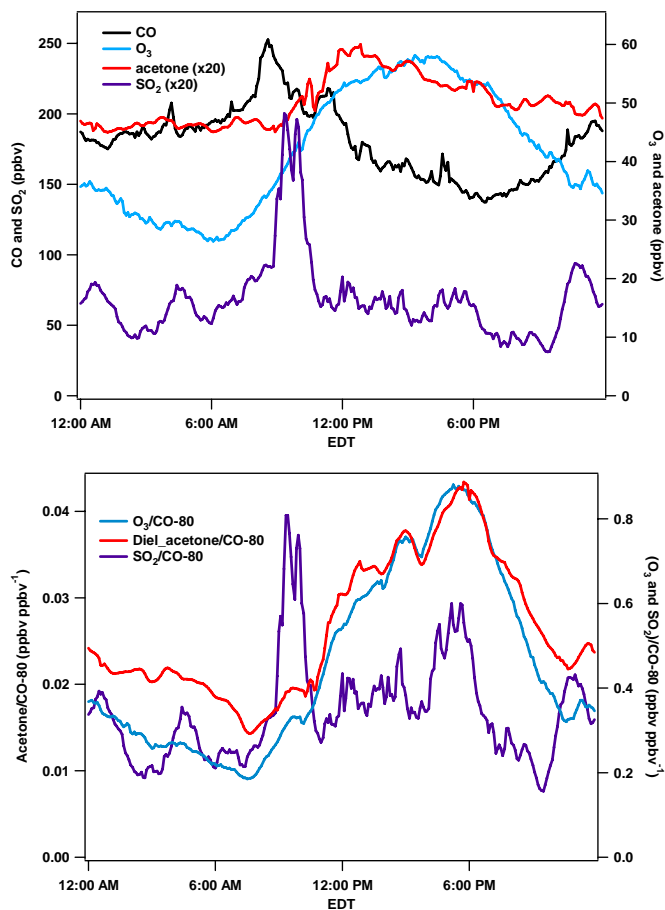
Fig. 6. Diurnal profiles of selected trace gases, with (lower frame) and without (upper frame) normalization to CO less its regional background value.
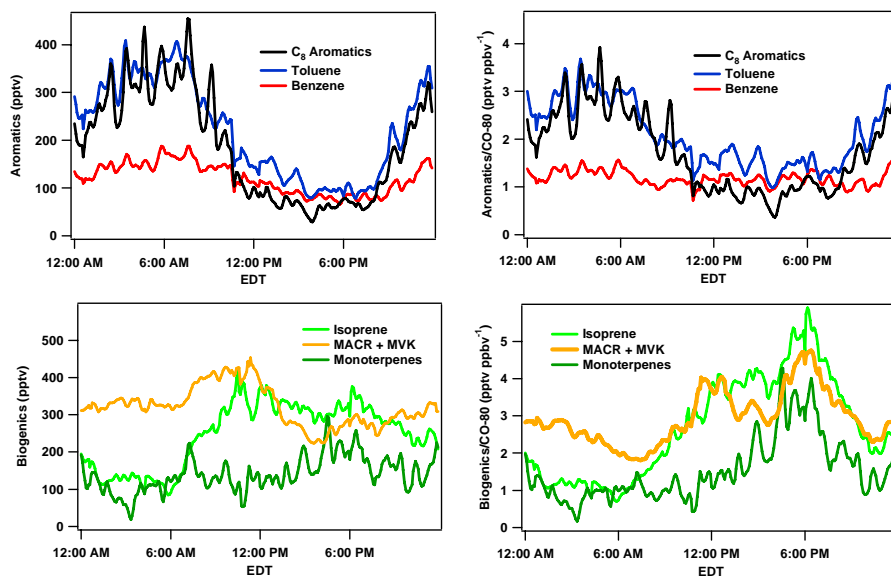
Fig. 7. Diurnal profiles of aromatics (upper frames) and biogenic species (lower frames), without normalization to CO less its regional background value (left frames) and with normalization (right frames).

Full Screen / Esc
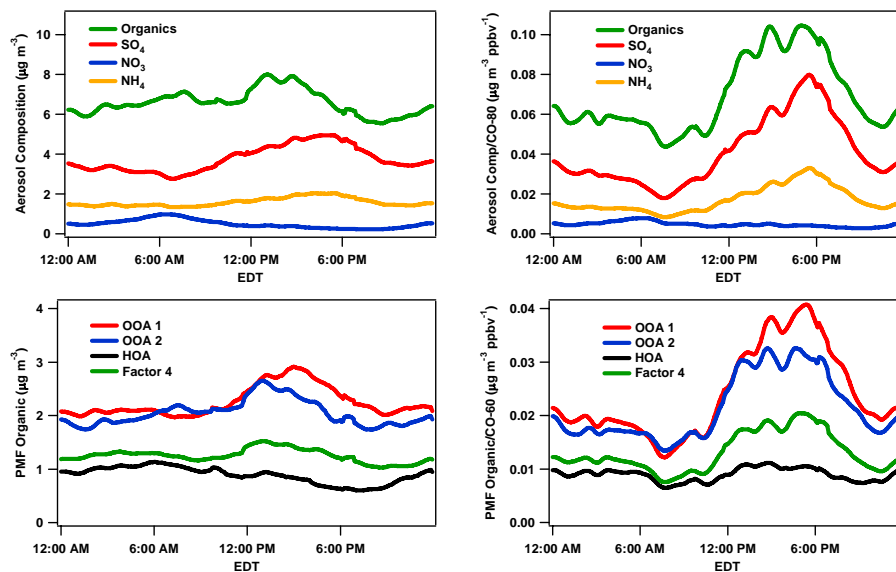
Fig. 8. Diurnal profiles of AMS species (upper frames) and AMS organic PMF factors (lower frames), without normalization to CO less its regional background value (left frames and with normalization (right frames).
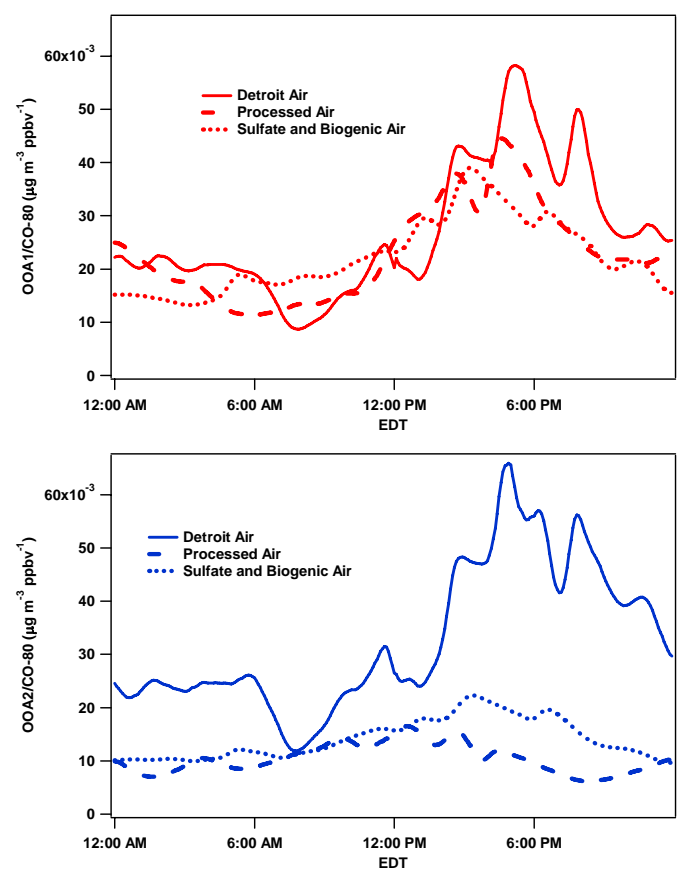
Fig. 9. Diurnal profiles of CO-normalized AMS PMF factors during selected episodes of the campaign: OOA1-upper frame, OO2-lower frame.

Diurnally resolved particulate and VOC measurements at a rural site

S. J. Sjostedt et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
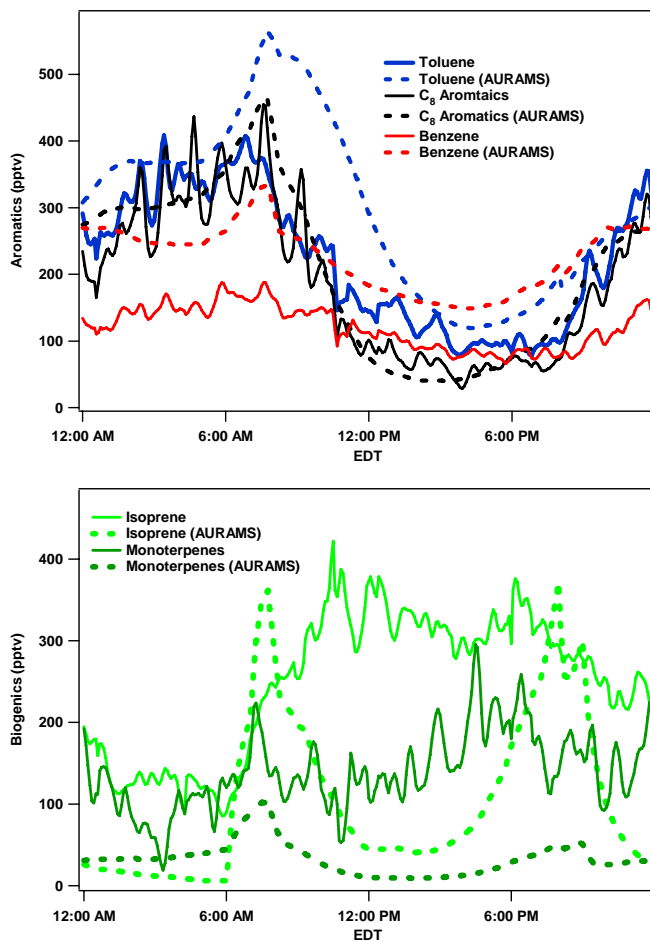
Fig. 10. Diurnal profiles of measured (solid lines) aromatic (upper frame) and biogenic species (lower frame) compared to those from the AURAMS photochemical model (dashed lines).

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close
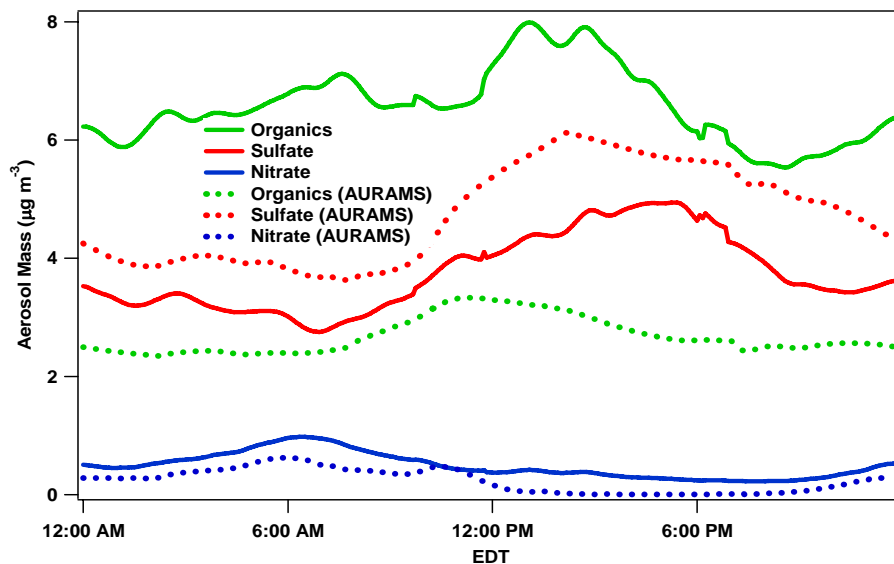
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Fig. 11. Comparison between diurnal profiles for AMS measurements (solid lines) and AU-RAMS predictions (dotted lines).