Table of Contents

Exit

VOC Measurements During the Southern Ontario Particulate Study '99

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ABSTRACT

In the summer of 1999, an atmospheric field study was carried out in Hamilton, Ontario by members of the Centre for Atmospheric Chemistry at York University. The goal of this study was to study secondary organic aerosol formation processes and the chemistry of oxidant episodes that are characteristic of this region during the summer. As part of that study, gas phase measurements of oxygenated and aromatic hydrocarbons were made at a suburban site that was intended to be "upwind" of the urban area. We report gas phase concentrations of 24 oxygenated and aromatic VOC species measured at that site during the period of July 10-27, 1999. The measurements include glyoxal and methylglyoxal, which were positively identified by their unique hydrazone spectra. The field study period was highlighted by a multiday regional ozone and particulates episode. Afternoon concentrations of aldehydes and ketones were enhanced during the main ozone episode period, particularly glyoxal. Total carbonyl mixing ratios determined by the sum of 11 aldehyde and ketone species had a maximum of ~20 ppbO. A linear relationship was found between total oxidant (O_3 + NO_2) and total carbonyls, as would be expected from the simple model of $OH^{\cdot}$ initiated hydrocarbon oxidation in the presence of NO_x. An oxidant/carbonyl slope of 6.1 ±1.3 ppb(O_3+NO_2)/ppbO was found during the study. Ozone sensitivity indicators, HCHO/NO_y and NO_y are presented, with afternoon thresholds as suggested by Sillman. The results suggest that the sensitivity of ozone formation at the upwind site was NO_x limited during most of the study period, especially during the main episode. The sensitivity indicators implied VOC sensitive ozone formation on days when ozone was lowest and when there was direct impact at the site from the downtown urban plume. We present a relative aromatic oxidation indicator consisting of afternoon ratios of the gas-phase secondary aromatic oxidation product concentration (ppbC) to aromatic hydrocarbons concentration (ppbC). This ratio was very low during the periods of direct influence from the urban plume and was significantly higher at other times, suggesting that there was significant oxidation of aromatics in the air mass, and the potential to contribute to secondary organic aerosols during the study.

INTRODUCTION

During periods of significant photochemical activity, it has been shown that up to 50% of the particulate organic matter can be secondary in nature[1], either biogenic or anthropogenic in origin. Of the anthropogenic pollutants, aromatic hydrocarbons are know to play an important role in regional atmospheric chemistry and are also known to have high aerosol yields[2]. Smog chamber studies have shown that oxidation of aromatic hydrocarbons can result in a multitude of secondary oxygenated hydrocarbons partitioning to the aerosol phase[3].

The purpose of the Southern Ontario Particulate Study (July, 1999) was to initiate measurements in an urban area of Southern Ontario during periods of summer photochemical activity that would aid in our understanding of oxidant formation processes as well as processes leading to the formation of secondary organic aerosols (SOA). These measurements are also intended to support modelling studies of the formation of SOA. The field study took place in Hamilton, Ontario. The city is part of the 'Windsor to Quebec corridor', one of the three problem areas identified in Canada for tropospheric ozone in the CCME NOx/VOC Management Plan[4]. The field study included measurements of total suspended particulates (TSP), particle size distributions, inorganic speciation of particulates, gas phase VOC and routine station measurements of O_3, NO_x, SO_2, CO and $PM_{2.5}$. The goal of the measurement of gaseous VOC's was to characterise the gas phase atmospheric chemistry as well as to measure potential organic precursors to SOA. VOC measurements included canister sampling for non-methane hydrocarbons, a semi-automated method for organic carbonyls using derivatization with 2,4-dinitrophenylhydrazine (DNPH) and solid-phase microextraction-gas chromatography (SPME/GC) for a variety of oxygenated hydrocarbons. In this paper, we present just the measurements of oxygenated and aromatic hydrocarbons during this field study using the DNPH and SPME techniques. The modified DNPH method is reported here for the first time and is therefore described in some detail. It is based upon the well known trapping of carbonyls using DNPH reagent followed by HPLC separation of the product carbonyls[5]. New to this system is the in-situ measurement with DNPH using a single cartridge with direct injection. The use of SPME for sampling and preconcentration of analytes has been well documented for liquid, headspace and indoor air analysis[6]. We apply the technique to ambient measurements of VOC using 1 hour integrated sample as we have reported previously[7].

EXPERIMENTAL

Field Study Overview

The Southern Ontario Particulate Study took place during July, 1999 in Hamilton, Ontario, a large urban area southwest of Toronto on the western tip of Lake Ontario. The city contains a significant amount of industrial activity, and is impacted by particulates of both primary and secondary origin during the summer months. In this study measurements were made at two different sites, Figure 1, both Ontario Ministry of the Environment and Energy monitoring stations. One station (Kelly) was located in the downtown area and is expected to be impacted by a variety of urban sources. The second station was located on top of an escarpment in a suburban area in the southern end of the city. This station is not expected to be heavily impacted by industrial or road-way sources. Being on the outskirts of the city, this site was selected in order to characterize the airmass entering the city during periods of south-southwesterly flow that dominates southern Ontario during the summer. Incidences of high levels of ozone are also experienced more frequently during flow from the south to southwest[4]. The region southwest of Hamilton is largely rural and agricultural with no major anthropogenic sources. Impacts from the city of Hamilton would only be felt at this upwind site during periods of flow from the north where the main urban area of Hamilton is.

DNPH Method

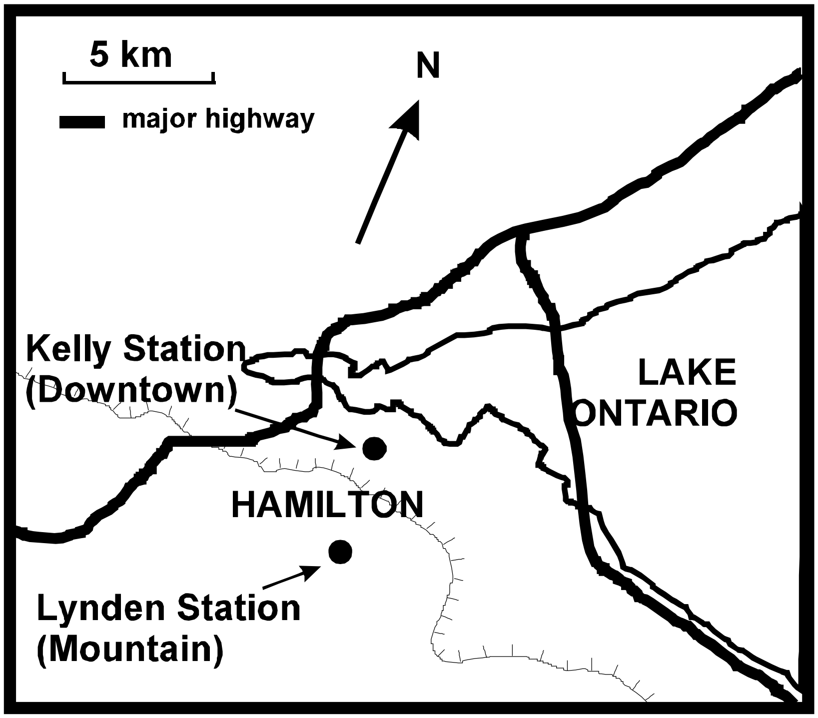

Figure 1. Study area for Southern Ontario Particulates Study.

Carbonyls were measured in-situ using a modified DNPH derivatization method. The method is still in the research stage and was not fully automated at the time of this study, a fact that only limited the cycle time for individual measurements. The premise for the development of this modified method is that measurements of carbonyls using DNPH trapping techniques are limited to a large extent by blank variability[8]. A large source of this variability is believed to be the result of cartridge to cartridge variability. Both the silica packing material and the polymers used to make these cartridges can be a source of carbonyls. With close attention to detail, the blank levels can be reduced if the cartridges are carefully prepared just prior to the measurement step[9]. In the system used in this study, a single custom built stainless steel cartridge was used for sampling the gas phase. Additionally, direct injection of the contents of the cartridge onto the HPLC system was used, allowing the elimination of intermediate elution steps that can contribute to variability, and allowing the use of low sampling flow rates. A measurement cycle includes the following steps: loading of the silica cartridge with DNPH, drying of the cartridge, active sampling of air through the cartridge, pausing to allow the derivatization reaction to come to completion, loading the cartridge with water, placement of cartridge in the injection loop of the HPLC system, and starting the elution program which sweeps the analyte hydrazones onto the chromatographic column. A micro-HPLC system was used for separations. A mutichannel detector allowed the collection of absorbance spectra for each chromatographic peak, giving additional confidence in identification of analytes when combined with the retention time information.

The measurement system is shown in Figure 2. The cartridge was made from stainless steel, 27mm in length with a 1mm ID, and was packed with 40/60 mesh silica gel. The coating solution was made by adding 0.3g of recrystallized DNPH and 10µl of concentrated H_2SO_4 to a 50mL volumetric flask, and filling with 95% acetonitrile (ACN)/5% water. This solution was used throughout the field study, and was constantly maintained under ultra high-purity helium at 50psi to protect it from exposure to gas-phase carbonyls. Immediately before sampling, the cartridge was loaded with 50µl of coating solution, and blown out with UHP helium for about 5 min, to remove excess solution. The cartridge was then transferred to the active sampling line, which included an ozone scrubber made from a 0.6 cm section of ¼” OD Teflon tubing packed with crystalline potassium iodide and a 0.2µm stainless steel screen at the inlet of the sampling line to prevent course particulates from entering the lines. The scrubber is meant to eliminate ozone because of known positive and negative artifacts when using DNPH in the presence of ozone[10;11] Samples were collected at a flow rate of 50 mL/min, using a pump (not shown) and calibrated mass flow controller (Tylan). In a separate series of experiments, this flow rate was found to be sufficiently low for quantitative trapping of a range of C1-C5 gas phase carbonyls. Samples were generally collected for one hour. After sampling, the cartridge was capped and allowed to sit for one hour to ensure complete conversion of the carbonyls to hydrazones. The kinetics of the derivatization reaction were measured on the same cartridge in a separate set of experiments. In those experiments, a 1-hour time period at room temperature was sufficient for completion of the reaction for all the carbonyls studied. The cartridge was then filled with pure water and installed as the sample loop in the HPLC injection valve (Rheodyne 8125). The contents of the loop were transferred to the separation column by switching the valve to inject, allowing the column effluent to flow through the cartridge for the duration of the run. Low water content of mobile phase early in the separation allows peak compression during the transfer.

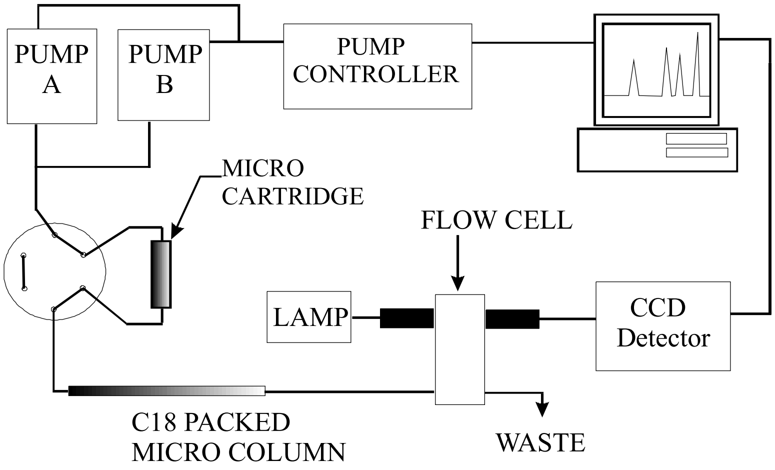

Figure 2. Experimental system for on-line measurement of gas-phase carbonyls

The HPLC system consisted of 2 micro-pumps, mixer and controller (Micro-Tech Scientific), a 1.0 x 250 mm C-18 column (3.5 µm Zorbax). Total flow rates were 50 µL/min. The two solvents were: A -100% H_2O; B - 75% ACN, 25% THF. The solvent program was: 60% A/40% B from 0 to 40min, increased linearly to 100% B at 80min. The nano flow-cell was custom built from stainless steel with a pathlength of 12mm and internal volume of only 30nL. Light from a deuterium lamp (Oriel) was delivered to, and collected from the flow cell using 400µm fiber optics. The transmitted light was coupled into a miniature fiber-optic spectrometer (Ocean Optics, S2000) with a 2048 element CCD detector. The operational resolution of the spectrometer was 3nm based upon a grouping of 10 CCD elements. Software was written to store the light intensity in the region of 294 - 476nm and to display chromatographic results.

Two types of calibrations were used; liquid and gas-phase. For liquid calibrations, pure solid carbonyl hydrazones synthesized in our lab were used to prepare liquid standards dissolved in ACN.. Injections were done with a 5µL injection loop in place. The total integrated absorbance (calculated separately for every 3nm grouping and then averaged across the whole wavelength range of elements) vs. concentration was linear up to 1.0×10^{-4}M (500 pmoles). These calibrations were used to determine the total moles sampled onto the cartridge. Separate gas-phase calibrations were done for a range of C1-C5 carbonyls not necessarily reported in this study. (formaldehyde, acetaldehyde, propanal, acetone, butanal, butanone, methylethylketone, methylvinylketone, pentanal, benzaldehyde), in which known amounts of gas phase carbonyls generated using a system similar to that in Figure 2 were sampled onto the cartridge from this study. The total recovery (moles of hydrazone observed/moles of carbonyl sampled on cartridge) was found to be equal to 100% within error, for all the above listed species for the conditions used in the field. Further experiments are being performed to verify this for other species.

SPME Method

Oxygenated and aromatic hydrocarbons were measured using solid-phase microextraction (SPME) passive sampling followed by analysis in the laboratory using gas chromatography with flame ionization detection. The methodology for ambient sampling of hydrocarbons using SPME has been described previously[12]. A brief description follows. Two Carboxen/PDMS fibers (Supelco) were calibrated for the range of humidity, temperatures and concentrations expected in the study. Gas phase calibrations were based upon a 1-hour sampling time using the system shown in Figure 3. A liquid standard containing 50-200 µL of twenty-six compounds, all soluble in each other, were mixed together to form a pure solution with a total volume of 4 mL. This solution was injected at flow rates of 0.02-0.08 µL/min using a syringe pump (Harvard Apparatus) into a stream of clean air (AADCO) flowing at 20 L/min controlled by a mass flow controller. The analytes are volatilized and carried into the mixing chamber. A second mass flow controller allows 1-5 mL/min to pass to the measurement region while the majority of the

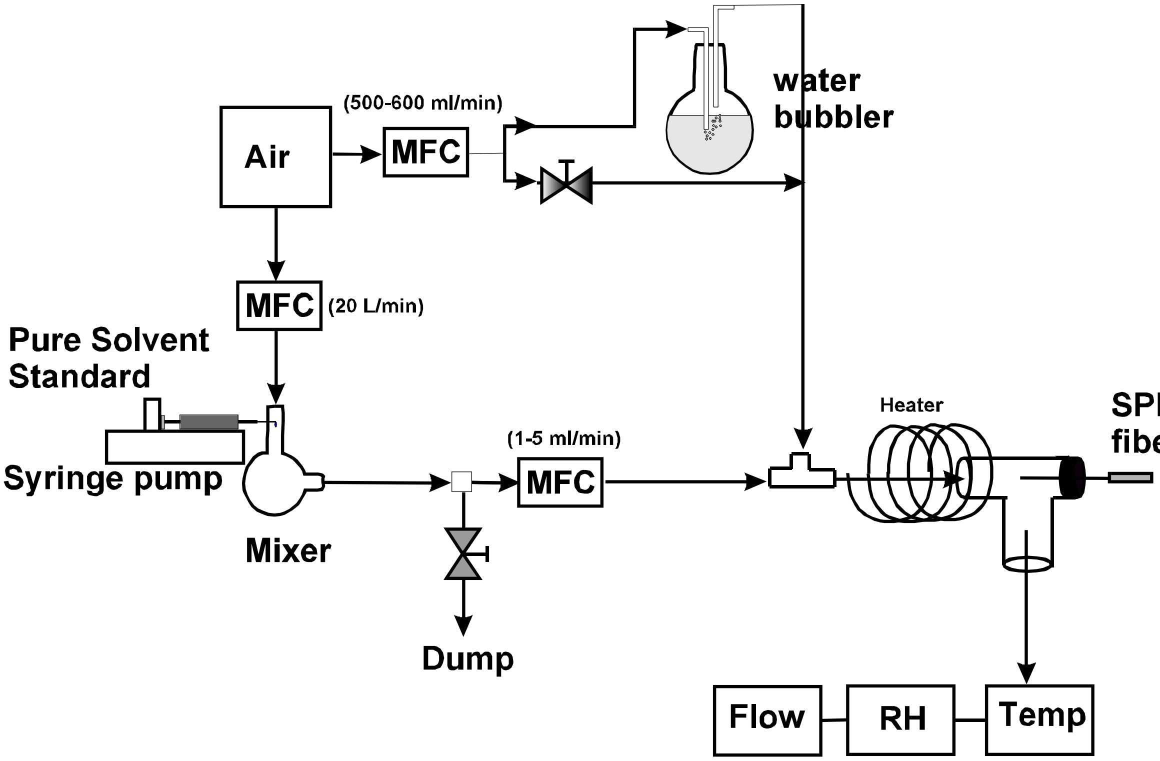

Figure 3. Gas phase calibration system for DNPH and SPME methods.

flow is released through the dump. This flow of 1-5 mL/min is diluted by a third controlled flow of 500-600 ml/min. A sufficient length of tubing is used after this step to ensure proper mixing before this final flow is passed over the SPME fiber for a given time. The final gas phase concentration is calculated based upon the liquid concentration, the liquid flow rate and the flow rate of the three gases. The system can be used to generate standard gases at ppb and ppt levels. The humidity of the air passing over the fiber is controlled by flowing the air through water, prior to the final dilution step. The temperature is controlled by heating a small length of the tubing before the sampling port. Monitoring of all parameters is accomplished through the outlet of the sampling port.

Fibers were cleaned in a flow of He at 300°C prior to storage in a clean vial with activated charcoal. The vial was kept on dry-ice for transport of the fiber to and from the field. Once in the field, the fibers were exposed to the air through an inverted glass cone covered with opaque material to shelter the fiber from direct sunlight and wind. The temperature and relative humidity were recorded to facilitate small corrections to each individual measurement due to the temperature and humidity dependence of the fiber response. A HP 5890 Series II GC with flame ionization detection was used to analyze VOC's absorbed onto the fibers. The VOC's were thermally desorbed from the fiber in the GC injector (300°C) for 0.5min to ensure complete mass transfer. The desorption was >95% for all species in the 0.5 min time. A polar polyethylene glycol column (60m, 0.25mm i.d., 0.5 µm film, J&W DB-WAX) was used for separations using the following program; 30°C for 1 minute, increased to 150°C at 14°C/min and hold at 150°C for 10 min. The carrier gas was ultrahigh purity He. The calibrated signal was the integrated peak area of the corresponding FID signal. The systems described above were used to calibrate the response for 26 different VOC species. Due to chromatographic interferences, we only report the concentrations of 17 species using the SPME method, including several aldehydes, ketones, acetates and aromatic hydrocarbons as identified in Table 1. This reduction in number is largely due to chromatographic interferences from impurities desorbed from the fiber or from chromatographic overlap of peaks. In a previous study[7], we were able to report more species and eliminate these interference through the use of a mass selective detector. We have confidence in the species that are reported based upon identification by retention time and the response of the FID detector used in this study.

A full list of oxygenated and aromatic hydrocarbons measured by the DNPH and SPME methods is given in Table 1. Note that the chromatographic separation using the DNPH method was optimized in order to allow separation of late eluting peaks that are of interest in aromatic hydrocarbon oxidation (glyoxal, methylglyoxal, benzaldehyde and tolualdehydes). This elution program allows the separation of some light carbonyls as well, but does not allow the separation of C4-C6 carbonyl-hydrazones. In this sense, the DNPH and SPME technique were complementary in this study. As a minimum, an attempt was made to make 1 measurement of each type during the afternoon period at the upwind station (Lynden) to help characterize the air mass. During episode periods, more frequent measurements were taken by the DNPH method, and occasionally, two SPME fiber samples were taken on these days. In total, 25 measurements were made with the DNPH method, and 19 measurements with the SPME method.

Table 1. List of species, method and afternoon median mixing ratios at Lynden site.

#	Name	Method	Median(ppb)	#	Name	Method	Median(ppb)
1	propanol	SPME	0.037	13	acetone	**DNPH**	2.28
2	butanol	SPME	0.039	14	2-butanone	SPME	0.436
3	pentanol	SPME	0.008	15	3-pentanone	SPME	0.090
4	formaldehyde	**DNPH**	4.11	16	ethyl-acetate	SPME	0.027
5	acetaldehyde	**DNPH**	4.27	17	propyl-acetate	SPME	0.055
6	propanal	**DNPH**	0.144	18	butyl-acetate	SPME	0.033
7	butanal	SPME	0.146	19	benzene	SPME	0.313
8	hexanal	SPME	0.293	20	toluene	SPME	0.742
9	benzaldehyde	**DNPH**	0.262	21	ethyl-benzene	SPME	0.082
10	glyoxal	**DNPH**	0.054	22	o-xylene	SPME	0.106
11	methylglyoxal	**DNPH**	0.180	23	m-xylene	SPME	0.127
12	methacrolein	SPME	0.118	24	p-xylene	SPME	0.086

RESULTS AND DISCUSSION

Station Measurements

The study period was marked by a major regional smog episode in the period July 14-17 that affected much of the northeastern regions of North America. Ozone levels in the Hamilton area reached a maximum 1-hour average of 93 ppb on July 16. Levels of $PM_{2.5}$ were also high during this period, reaching a maximum 1-hour average of 64 $\mu g/m^3$. A shorter and less intense episode occurred on July 22, with maximum O_3 and $PM_{2.5}$ of 86ppb and 51 $\mu g/m^3$ respectively. Ozone, $PM_{2.5}$ and NO_x recorded at the upwind station are show in Figure 4, along with the temperature measured at a nearby meteorological station. The four day smog episode was characterized by strong southwesterly flows, warm temperatures approaching 35° C, humid conditions and poor visibility due to haze. Because of the southwesterly flow throughout most of the study, especially during the main smog episode, we expect minimal impact from urban emissions on measurements taken at the upwind station. On two days, July 19 and 21, the upwind station did receive flow directly from the urban of Hamilton to the north.

VOC Measurements

The median distribution of all oxygenated and aromatic hydrocarbons measured at this site during the study are shown in Figure 5, identified by compound # in Table 1. Also shown for comparison are measurements made at two other sites in southern Ontario in 1998[7]. All distributions shown are median afternoon (1:00pm-5:00pm) mixing ratios. The most abundant oxygenated species were acetaldehyde, formaldehyde and acetone. All three of these species

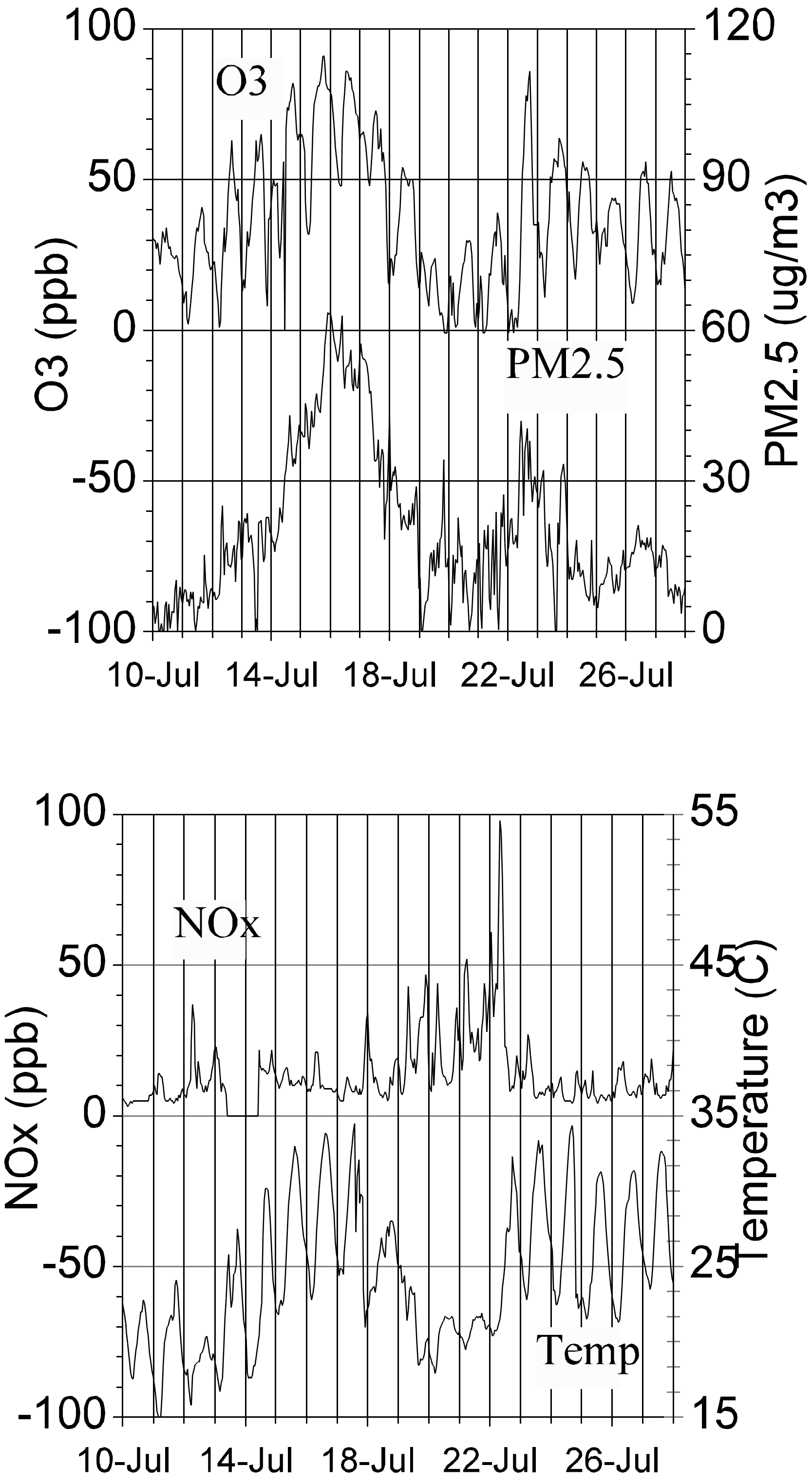

Figure 4. Ozone, $PM_{2.5}$, NOx and temperature at Lynden station.

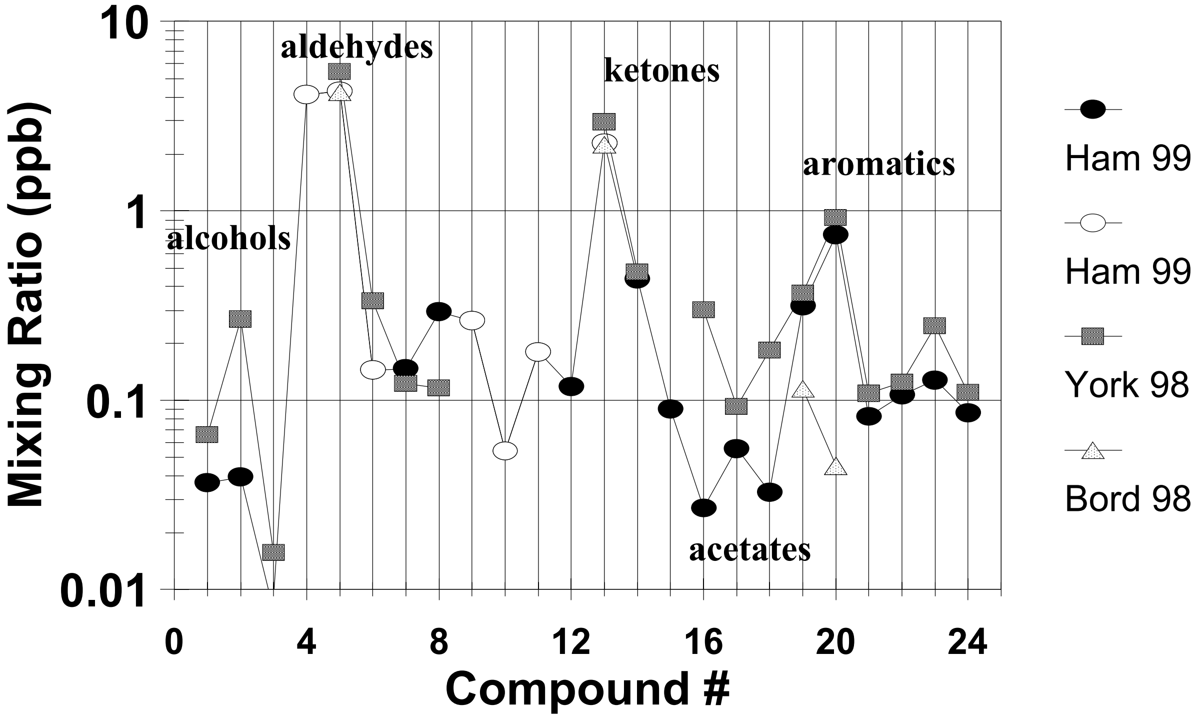

Figure 5. Distribution of median afternoon mixing ratios of oxygenated and aromatic hydrocarbons measured in Hamilton during this study (filled circles- SPME; open circles-DNPH), at York University in 1998 (squares) and at a forested site in Borden in 1998 (triangles).

have a variety of primary and secondary sources. Of note is the relatively high median value of acetaldehyde observed in this study, 4.3ppb using the DNPH method. In August-September of 1998, median afternoon values of acetaldehyde were 5.4ppb in an urban area (York University) and 4.2ppb in a rural forested area using the SPME/GC-MS method. The similarity of these three values using two different techniques in three very different environments (suburban, urban, rural-forested) implies that the main source of acetaldehyde in southern Ontario is not direct anthropogenic emission. Acetaldehyde is known to have significant secondary sources in the atmosphere through the oxidation of other hydrocarbons[13]. The same is true for formaldehyde and acetone. The median acetone observations are also relatively similar at the three sites; 2.3ppb in this study, 2.9ppb at York University and 2.2ppb in the rural forested area. All three of these species showed a typical secondary diurnal pattern on those days where multiple measurements were made, with maximum concentrations occurring in the afternoon (see Figure 7). This observation adds evidence to the belief that a significant fraction of the atmospheric burden of these species had a secondary source at the Lynden site and at other locations in Southern Ontario during the summer months. The most significant anthropogenic species observed in this study were toluene and methylethylketone (MEK). While MEK is know to have secondary sources through, for example, oxidation of butane by the hydroxyl radical, there appear to be significant primary sources of MEK at this site as well. The evidence for this is the strong correlation coefficient between concentrations of MEK and concentrations of other anthropogenic species that are indicative of impact by the urban plume of Hamilton (winds from the north); CO ($r^2 = 0.69$), toluene ($r^2 = 0.78$), the C8 aromatics ($r^2 = 0.87 - 0.95$) and NOx ($r^2 = 0.80$). In contrast, formaldehyde, acetaldehyde and acetone show either no significant correlation or a negative correlation with the same species.

DNPH Measurements

Samples were identified in the chromatograms by both retention time and by matching the absorbance spectra. Pure hydrazone absorbance spectra were obtained by injecting standard hydrazone solutions in the HPLC. The absorbance spectra from the middle of the appropriate chromatographic peak was then corrected by performing a background subtraction using the spectrum of the baseline adjacent to the peak. Sample spectra were obtained in this same way from the chromatograms of real air samples. The background sample and standard absorbance spectra of the hydrazones were found to match very well. While the absorbance spectra of carbonyl hydrazones in solution are broad and featureless, the difference between the spectra of each compound were clear both from the peak maximum and the shape. In particular, the wavelength of maximum absorbance was red shifted in the following progression: 355-365nm for the normal aldehydes, 370nm for acetone, 390 for benzaldehyde, and 400-440nm for the dicarbonyls, glyoxal and methylglyoxal. Under the conditions used, the derivatization reaction for the dicarbonyls proceeds to completeness for both carbonyl functionalities.

The time series of carbonyls measured by the DNPH technique are shown in Figure 6. Also shown is the total carbonyls in units of parts per billion of oxygen (ppbO), representing the mixing ratio of carbonyl groups (seven species only) measured by the DNPH technique. The diurnal pattern observed on July 16 is expanded in Figure 7. All species show a diurnal pattern indicative of secondary formation in the atmosphere with a peak concentration experienced in the afternoon. The only exception to this is glyoxal, which shows a minimum in the afternoon. This is somewhat perplexing but might be explained by the very rapid photolysis rate of glyoxal in the middle of the day. The other observation to be made is the significant enhancement of glyoxal during the main episode. Curiously, it does not peak during the second 1-day episode (July 22) as do most other species. The individual carbonyl species and the total carbonyls show a maximum concentration during the same periods as maximum ozone; July 14-16 and July 22. The total carbonyls was >15 ppbO during these periods. That carbonyl concentrations are correlated to ozone levels is expected when considering the chemistry. Consider the hydroxyl radical initiated oxidation of a generalized hydrocarbon, R-H. The following set of reactions describe the oxidation pathway including formation of peroxy radicals, conversion of NO to NO2, and the interconversion of NO_2 and O_3 through photolysis of the former.

Table of Contents

Exit

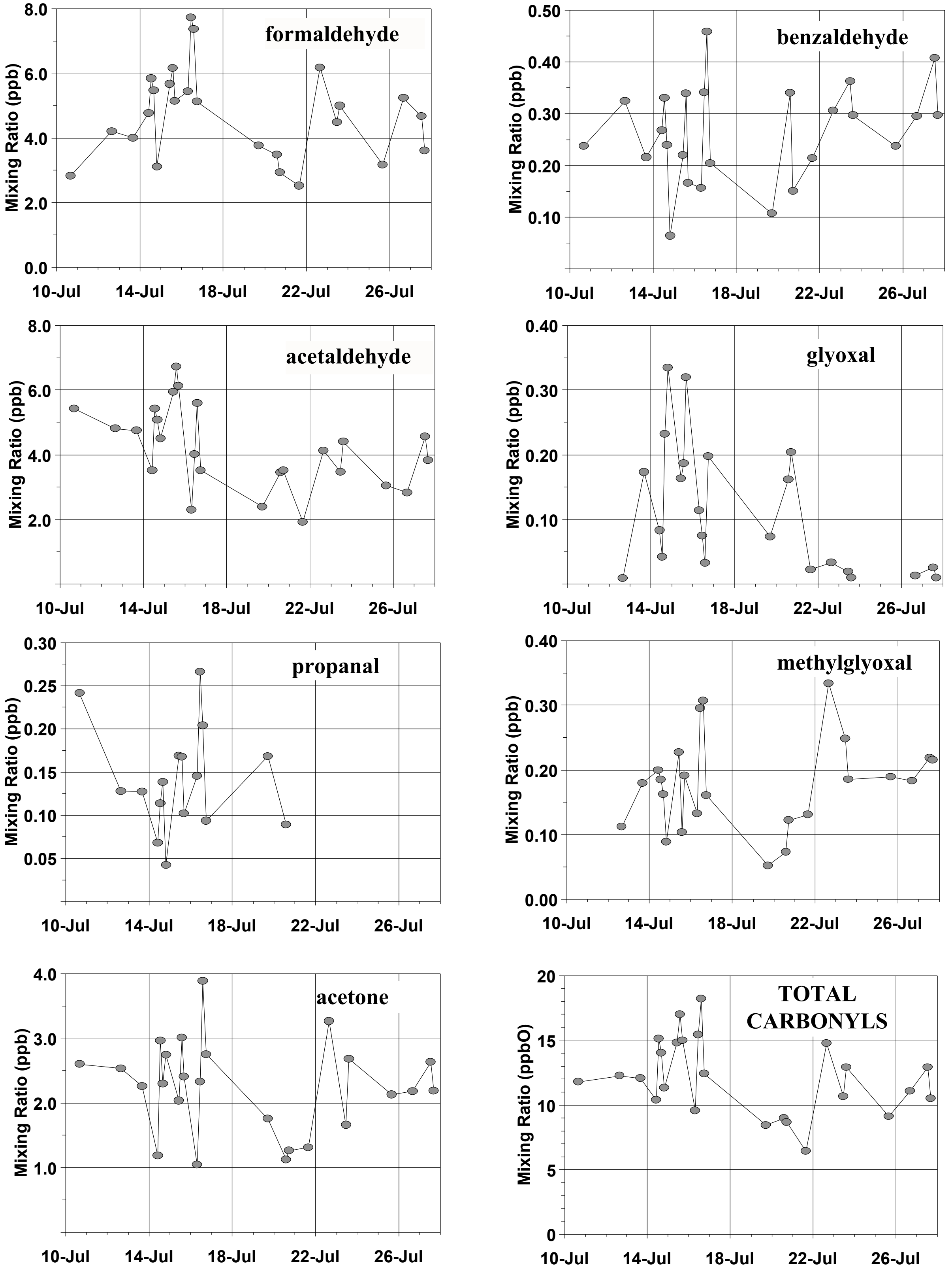

Figure 6. Time series of carbonyls measured by the DNPH method at the Lynden site.

$$R\text{-}H + OH^{\cdot} \qquad R^{\cdot} + H_2O \qquad \textbf{(R1)}$$

$$R^{\cdot} + O_2 \qquad ROO^{\cdot} \qquad \textbf{(R2)}$$

$$ROO^{\cdot} + NO \qquad RO^{\cdot} + NO_2 \qquad \textbf{(R3)}$$

$$RO^{\cdot} + O_2 \qquad R'{=}O + HO_2^{\cdot} \qquad \textbf{(R4)}$$

$$HO_2^{\cdot} + NO \qquad OH^{\cdot} + NO_2 \qquad \textbf{(R5)}$$

$$NO_2 + h\nu \qquad NO + O \qquad \textbf{(R6)}$$

$$O + O_2 \qquad O_3 \qquad \textbf{(R7)}$$

NET REACTION:

$$R\text{-}H + 2O_2 + 2NO + x\,h\nu \qquad R'{=}O + H_2O + (2\text{-}x)\,NO_2 + x\,O_3 \qquad \textbf{(R8)}$$

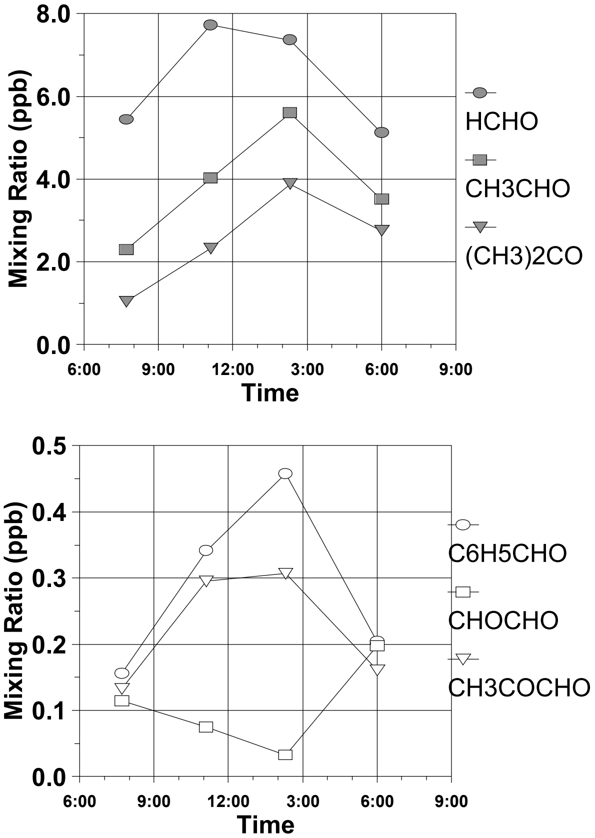

Figure 7. Carbonyl measurements at Lynden site on July 16, 6:00am-6:00pm

This mechanism and the net reaction, (R8), imply that for every carbonyl functional group produced (R'=O), a combination of two NO_2 or two O_3 molecules are produced, depending on the number of NO_2 molecules photolyzed. If all VOC oxidation followed this simple mechanism, then we would expect that the sum of the mixing ratios of O_3 + NO_2 would be twice the mixing ratio of total carbonyl functionalities (measured in ppbO). In reality, for each parent VOC molecule, a different number of NO to NO_2 conversions can occur. Furthermore, the oxidation of formaldehyde and CO can produce HO_2 without the production of a carbonyl. The simplified mechanism also ignores the subsequent losses of NO_2 to other NO_z species, the losses of O_3 to deposition and reactions with olefins, losses of peroxy radicals to self reactions when NO_x is low, direct emissions of both carbonyls and NO_2, and losses of carbonyls to deposition and partitioning to the particle phase. Despite all these uncertainties, during periods of significant oxidation in polluted air masses, we can expect a correlation between total oxidant; $O_3 + NO_2$, and total carbonyls. Figure 8 shows such a correlation for the total oxidant level as a function of the total subset of carbonyls measured by the DNPH method, using only afternoon samples (1:00pm-5:00pm) and excluding the two days when there were known direct impacts from the city (July 19 and July 21). The subset of species used in the measurement of total carbonyls is small (only 7 species) but can be expected to account for a significant fraction of total carbonyls. The slope was found to be 6.6 ±1.2 ppb(O_3+NO_2)/ppbO, while the x-intercept (2.6 ± 2.0 ppbO) could be interpreted as influence from direct emissions of anthropogenic or biogenic carbonyls. While other carbonyls were measured by the SPME method in this study, they were not always on the same time frame as the DNPH measurements. Using a separate analysis for four carbonyl species measured by SPME (butanal, hexanal, methacrolein and 3-pentanone), a similar linear fit was done, although their contributions to the total carbonyls is much less. Combining the results for all 11 aldehyde and ketone species, the total oxidant/total carbonyls slope was found to be:

6.1 ± 1.3 ppb(O_3+NO_2)/ppbO, where ppbO is the total mixing ratio of carbonyls groups represented by the eleven carbonyl species. The species, MEK, was excluded from this analysis since it was shown to have predominantly anthropogenic sources in this area (see SPME measurement discussion). It is difficult to interpret the meaning of the oxidant/carbonyl slope. The slope can only get lower if one were to include more organic carbonyl species in this analysis. At the same time, the oxidation of CO (1 NO to NO_2 conversion) and formaldehyde (2- NO to NO_2 conversions) can significantly increase the slope beyond the simple model ideal value of ~2.0 since they contribute to total oxidant formation without the production of a carbonyl species. The use of the total oxidant/carbonyl slope to ascertain the role of VOC's in oxidant formation would benefit from additional measurements in other environments as well as the development of a "total" carbonyl detector.

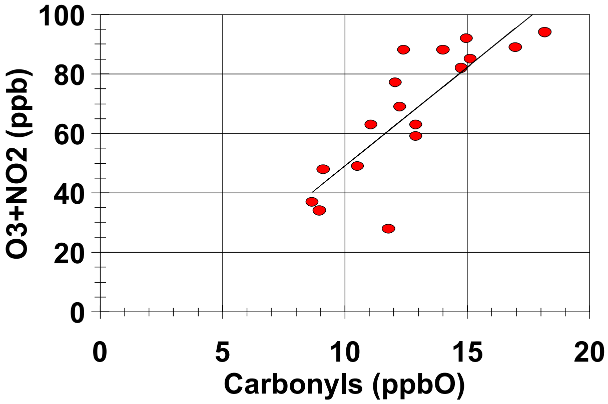

Figure 8. Total oxidant vs total carbonyls (7 species) for afternoon samples at Lynden site.

Ozone Sensitivity Indicators

Other information can be gathered about the air mass from the carbonyl data. There have been several reports on the use of indicator species to determine the sensitivity of ozone formation to VOC and NO_x in urban areas[14;15]. This issue has relevance to the proposed control of ozone through either NO_x or VOC or combined NO_x-VOC control. Sillman proposed the use of four "indicator species" to determine the NO_x or VOC sensitivity in a given area; NO_y, O_3/NO_z, $HCHO/NO_y$, and H_2O_2/HNO_3[15]. Of interest in this study is the proposal that NO_x sensitivity of ozone formation is indicated by afternoon NO_y < 20ppb and afternoon $HCHO/NO_y$ > 0.28 ppb/ppb. Although there was not a measure of NO_y in this study (NO_y = NO + NO_2 + PAN + HNO_3 + HONO + other reactive N species), the NO_x measurements made with the chemi-luminescent instruments used at the OMEE stations are actually a reasonable approximation to a NO_y measurement. This is because the reduction of NO_2 to NO achieved by the Mo catalyst is paralleled by a reasonable efficiency in reduction of some NO_z species to NO ($NO_z = NO_y - NO_x$). This is especially true in polluted environments where NO_x makes up a significant fraction of NO_y. For the purposes of the analysis presented here, we assume that the NO_x indicated by this instrument is at least >80% NO_y, as a conservative estimate. Using the available afternoon (1:00-5:00pm) formaldehyde and NO_x measurements at the Lynden site, the $HCHO/NO_x$ ratio (ppb/ppb) was determined for each day. Where two afternoon measurements were available, the ratios were averaged. The results are shown in Figure 9 along with the conservative estimate of $HCHO/NO_y$. Also shown is the recommended indicator of a transition from VOC to NOx limited ozone formation at a $HCHO/NO_y$ ratio of 0.28[15]. For the majority of the days during the study, the ratio is much greater than 0.28 indicating that ozone formation is NO_x limited, and hence that NO_x controls would benefit ozone reduction. The day with the maximum ratio (0.70) is July 16, the day of maximum O_3 at the peak of the episode. There were only three days that indicated that ozone was VOC limited, July 19-21. On all three of these days, the peak ozone was less than 40ppb. On two of the days (July 19 and 21), there was direct impact on this “upwind” site from the urban plume of the city. This would be in keeping with the expectation that urban plumes are at first VOC limited with respect to ozone formation because of the low VOC/NO$_x$ ratio. Also evident from the temperature data in Figure 4, is the very cool temperatures on these three VOC limited days and the lack of significant diurnal heating due to cloud cover. Figure 10 shows the related NO$_y$ indicator. Sillman has suggested that NO$_y$ > 20ppb is indicative of VOC limited ozone formation. The only two days that indicate VOC limited conditions are the urban plume days, July 19 & 21.

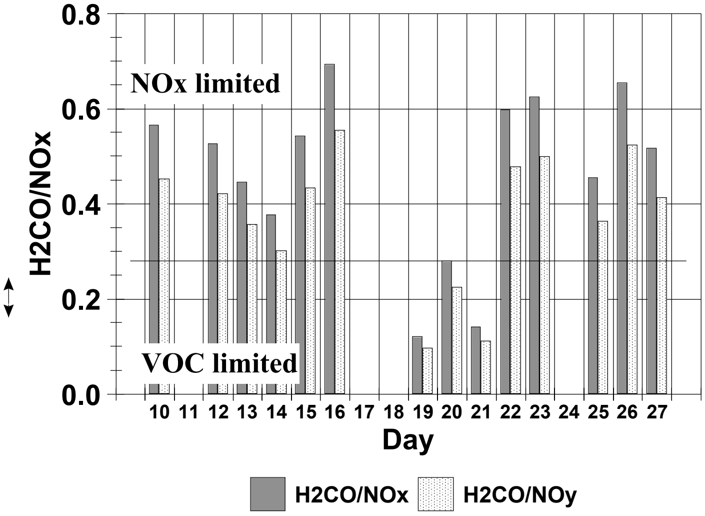

Figure 9. Sillman indicator of NOx/VOC sensitivity of ozone formation. H2CO/NOy is a lower limit assuming NOx/NOy = 0.80

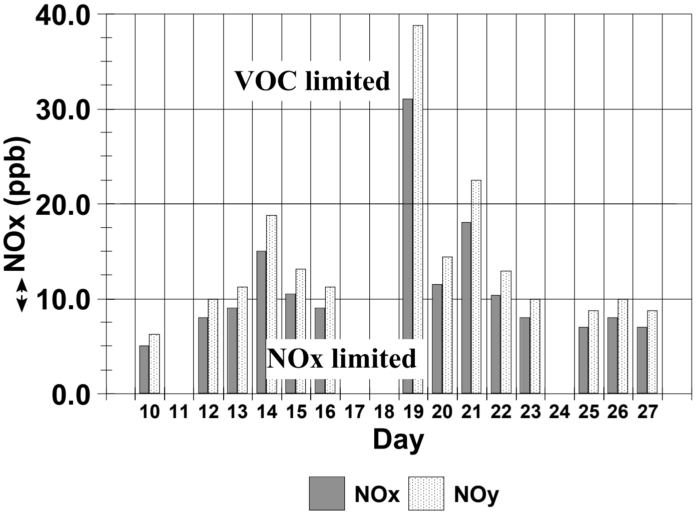

Figure 10. NOy as an indicator of NOx/VOC sensitivity to ozone formation. NOy is an assumed upper limit if measured NOx=0.8 NOy

SPME Measurements

The time series for mixing ratio of several species measured by the SPME method are presented in Figure 11. Many of the carbonyl species (butanal, hexanal, methacrolein and 3-pentanone) follow the same trend previously seen for other carbonyl species, in that peak concentrations are observed during the periods of maximum ozone, July 14-16 or July 22. The exception to this rule was 2-butanone (MEK). It’s maximum concentration is seen on the two days of urban plume impact, July 19 and 21. As mentioned previously, MEK had a strong correlation with other anthropogenic species such as toluene, ethylbenzene and the xylenes. MEK is a common solvent used in many industrial processes. In general, the 6 aromatic BTEX species had very good inter-correlations. The four C8 species had inter-correlations in the range of r^2 = 0.91-0.98 and toluene had intercorrelations with the C8 aromatics of r^2 = 0.77-0.91. Benzene was not as well correlated with the TEX species (r^2 = 0.29-0.45), likely due to it’s much longer lifetime in the atmosphere than the other components. Due to the high inter-correlations between the BTEX species and the

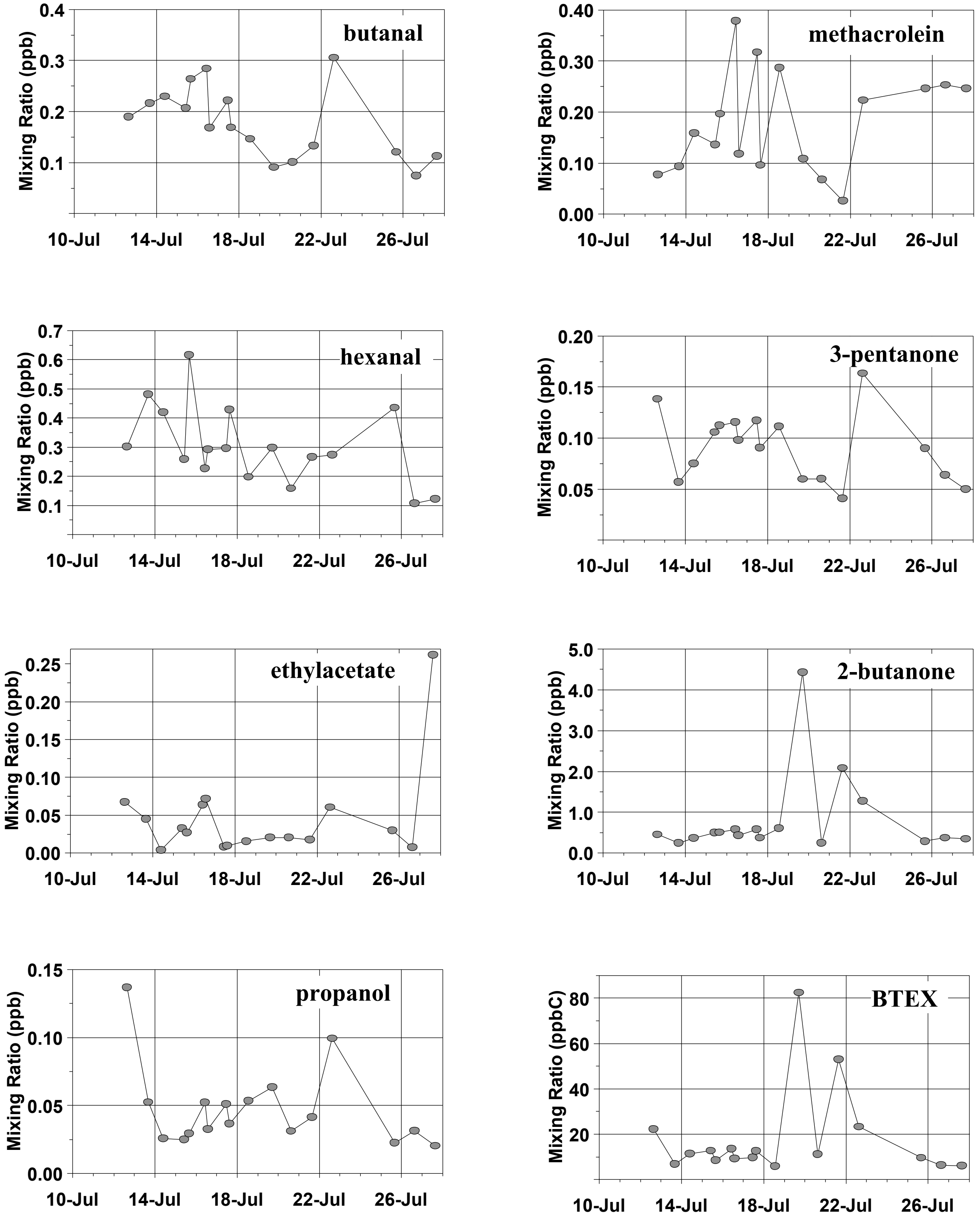

Figure 11. Time series of VOC measured at Lynden site by the SPME method.

similarity of their time series, the total BTEX concentration in ppbC is presented in Figure 11. It is evident that BTEX is not significantly enhanced during the main episode, July 14-17, compared to other times. There is a slight enhancement of BTEX during the one day episode on July 22. The alcohols and acetates were frequently close to detection limit and did not show striking patterns. The time series for ethyl acetate and propanol are shown as examples of these species in Figure 11.

Aromatic Oxidation

Aromatic hydrocarbons as well as biogenic hydrocarbons are believed to play a significant role in the formation of secondary organic aerosols[16]. In urban areas, toluene and higher substituted benzenes are expected to play a large role in this secondary process through their oxidation to form polar species that subsequently partition to the aerosol phase. It is thus of interest to look at the oxidation of aromatics in the air masses encountered in this study. Toluene is the most abundant aromatic in this study. It's oxidation by $OH^{\cdot}$ is known to proceed by both hydrogen atom abstraction to eventually yield benzaldehyde (12% yield), and by OH addition to the ring to obtain an adduct[17]. The ring adduct subsequently decays to give a variety of stable products, including methylglyoxal and glyoxal with yields of about 8-15% each[16]. Glyoxal and methylglyoxal are stable products produced in the gas-phase oxidation of many aromatics. With respect to benzene, toluene and the xylenes, the stable product yields of glyoxal and methylglyoxal initiated by hydroxyl radical oxidation range from 3-24% and 8-42% respectively. In the urban area, most of the emissions of BTEX are related to the use of transportation fuels. The level of benzaldehyde in the exhaust of gasoline automobiles is small. The relative percent of benzaldehyde to toluene in exhaust is known to be about 2.8 ± 0.9% based upon test results of several fleet of vehicles using several different fuels[18]. In an aged air mass, this ratio would be higher due to the decay of toluene and subsequent formation of benzaldehyde. The presence of glyoxal and methylglyoxal in auto exhaust has not been reported to the best of our knowledge. Although the DNPH methodology was used for the measurement of carbonyls in exhaust gases in the Auto/Oil Air Quality Improvement Program[19], glyoxal and methylglyoxal were not measured.

If we call the total concentration of aromatic oxidation products ZXAL (benzaldehyde + glyoxal + methylglyoxal), in ppb of carbon, and we call the total concentration of primary aromatic hydrocarbons BTEX (benzene + toluene + ethylbenzene + o,m,p xylenes) also in ppbC, then we suggest that the ratio, ZXAL/(ZXAL + BTEX) would be a good indicator of the extent of aromatic oxidation in the air mass. This presumes that the majority secondary source of glyoxal and methylglyoxal is from aromatics. This indicator ratio has been plotted in Figure 12. The lowest values of the ratio, indicating the least amount of aromatic oxidation are seen on the days when there was direct winds from the urban area, 0.013 and 0.035 for July 19 and 21, indicating that only 1.3% and 3.5% of the aromatic carbon is in the oxidized form (including only those species identified). This indicates that there is little glyoxal or methylglyoxal directly emitted from the urban area. The highest indicator ratios were about 0.3 on July 26-27 indicating that ~30% of the carbon was in the identified oxidized form. Considering the small subset of carbonyl species used, and the small yield of these species from direct parent species oxidation, the actual amount of BTEX that has been oxidized in the air mass is much higher that the indicated percentage. For example, considering the rates constants of reaction with OH as suggested by Atkinson, a daytime concentration of [OH] = $2*10^6$ molecules/cm^3, and a reaction time of 12 hours per day, then a two day air mass would have the following depletions of the original aromatics originating at the source: 20% for benzene, 66% for toluene, and 72-98% for the C8 aromatics. During the main oxidant episode (July 14-17), the indicator ratios were ~ 0.25. During the 1-day episode on July 22, the ratio was only 0.12, indicating that the aromatic oxidation in the air mass impacting the site was less than that encountered on July 16. Consistent with this observation is the higher level of BTEX observed on July 22 compared to that observed on July 16.

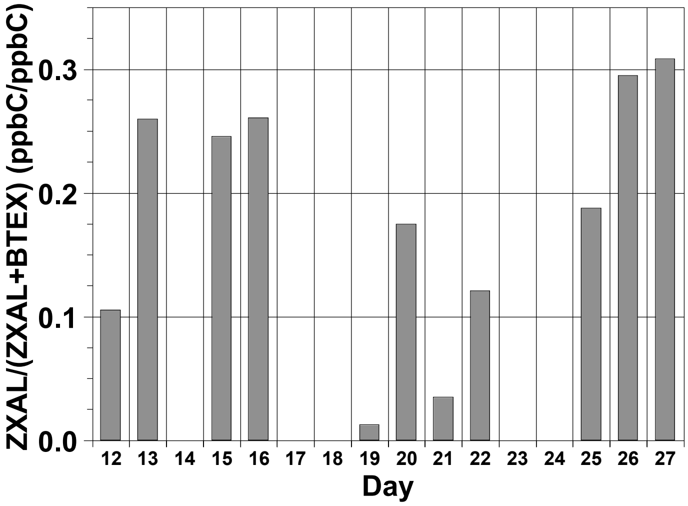

Figure 12. Relative indicator of aromatic hydrocarbon oxidation. ZXAL = benzaldehyde + glyoxal + methylglyoxal.

CONCLUSIONS

We report the gas phase concentrations of 24 VOC species, exclusively oxygenated and aromatic hydrocarbons, measured during a field study in Southern Ontario. The field study period was highlighted by a 3-4 day regional ozone and particulates episode. Concentrations of most aldehydes and ketones were enhanced during the episode. In particular, we report levels of the seldom reported species, glyoxal and methylglyoxal. Glyoxal levels were significantly enhanced during the regional episode to levels approaching 350 ppt. It also showed unusual behavior with a minimum in concentration in the afternoon, different than most other species that showed a typical maximum in the afternoon. Total carbonyl mixing ratios as determined by the sum of 11 aldehyde and ketone species approached 20 ppbO. A linear relationship was found between total oxidant (O_3 + NO_2) and total carbonyls, as would be expected from the simple model of $OH^{\cdot}$ initiated hydrocarbon oxidation in the presence of NO_x. The slope obtained from this correlation, 6.1 ±1.3 ppb(O_3+NO_2)/ppbO is more difficult to interpret and may reflect the roles of formaldehyde and CO oxidation as well as more complex processes. We have presented ozone sensitivity indicators, HCHO/NO_y and NO_y. Using afternoon thresholds as suggested by Sillman, the sensitivity of ozone formation at the "upwind" site was found to be NO_x limited during most of the study period, especially during the periods of maximum ozone. The sensitivity indicators implied VOC sensitive ozone formation during the days when ozone was lowest, and when there was direct impact at the site from the downtown urban plume. In order to address the potential for oxidation products of aromatic hydrocarbons to contribute to secondary organic aerosols, we present a relative aromatic oxidation indicator consisting of the ratio of secondary aromatic oxidation products to aromatic hydrocarbons. This ratio was found to be very low during the periods of direct influence at the site from the urban plume and was significantly higher during other times. Further interpretations of this oxygenated VOC dataset will incorporate the measurements made by other groups during this field study.

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