Stable Carbon Isotope Characterization of Nonmethane Hydrocarbons in Vancouver and Toronto Airsheds

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ABSTRACT

The focus of my research is to apply stable isotopes as a new tool to understand free radical chemistry in the troposphere. Stable carbon isotope ratios are used as indirect tracers of the reaction of nonmethane hydrocarbons (NMHC) with OH radicals in ambient air from Toronto and Vancouver air-sheds, Canada.

Compound-specific stable carbon isotope ratios of NMHC were determined in ambient air from urban, suburban, rural and source sites in the air-sheds using Gas Chromotograph-Isotope Ratio Mass Spectrometry (GC-IRMS). In the Greater Toronto Area, the average isotope ratio of all ambient measurements of NMHC, including halogenate NMHC was found to be –25.7 ± 3.4 ‰. Traffics related source sites in the Greater Toronto Area have an average isotope ratio of –25.7 ± 3.5 ‰, whereas the ratio for traffic related emissions in the Lower Fraser Valley are –25.9 ± 4.2 ‰.

The extent of chemical processing due to OH radical reactions that the individual NMHC has experienced since emission is quantitatively determined. It is shown that in combination with concentration measurements, isotope ratio measurements are an extremely valuable new approach to study the spatial and temporal differences in chemical removal mechanisms, mixing and dilution processes.

Examiners:

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1 Introduction

1.1 Background

Atmospheric volatile organic compounds (VOCs), including non-methane hydrocarbons (NMHC) and oxygen containing volatile organic compounds (OVOCs), are ubiquitous atmospheric trace gases that have important impacts on atmospheric chemistry in both the troposphere and the stratosphere. VOCs combine with oxides of nitrogen to produce O_3, contribute to aerosol growth, impact atmospheric radiative processes and visibility, substantially control the oxidative capacity of the troposphere in polluted and forested regions, and strongly influence OH radical cycling. Specifically, sources of NMHC can typically be classified as dominantly biogenic or dominantly anthropogenic. Terrestrial plants dominate biogenic NMHC emissions, with forested ecosystems being the largest source. In urban centres with little vegetation, the most commonly measured anthropogenic NMHC are C_2-C_{10} alkanes, alkenes, alkynes, and aromatics compounds (Goldstein and Shaw 2003). Major source categories for these NMHC are traffic related sources, including vehicle emissions, solvent evaporation, and fuel combustion. Biomass burning also emits substantial quantities of a wide range of NMHC. In rural and remote areas 30-50 different hydrocarbons are frequently observed at sub-ppbv concentrations, (Greenberg *et al.* 1999). In urban areas only a limited number of compounds are present at concentrations in the ppbv range. Relatively high urban concentrations, expressed as mixing ratios, of some ubiquitous aromatics, unsaturated and saturated nonmethane hydrocarbons are shown in Table 1.1.

Table 1.1: Typical NMHC urban mixing ratios measured in part per billion by volume (ppbV)

Compound	**Mixing Ratio, ppbv**
Propane	0.4-221
Propene	0.1-39
Isoprene	0.1-2
Benzene	0.9-26
Toluene	0.3-39
m,p-xylene	0.3-30
o-xylene	0.4-6

[d]*Finlayson-Pitts and Pitts [2000]*

Stable isotope ratios of carbon containing trace gases, particularly CO_2 and CH_4, are useful in providing additional constraints on atmospheric budgets and biogeochemistry (Brenninkmeijer et al., 1995; Conny and Currie, 1996). Until recently, analytical measurements of isotope ratios of atmospheric NMHC were not possible because their ambient atmospheric concentrations are too low. The coupling of a cryogenic unit for the concentration of VOCs from ambient air collected in stainless steel canisters, described by Greenberg *et al.* (1984), to the Gas Chromatograph - Combustion - Isotope Ratio Mass Spectrometer (GC-C-IRMS) was first applied to atmospheric VOCs by Rudolph *et al* (1997). Since the development of this method, few studies on the isotopic composition of atmospheric NMHC have been published. However, the advances in measurement techniques have stimulated research on the potential applications of this information for increasing our understanding of source identification, budget constraints, and the differentiation between mixing and chemical processing of VOCs in the atmosphere (Goldstein and Shaw 2003, Thompson *et al.* 2003, Tsunogai and Yoshida 1999).

The atmospheric oxidation process that provides the highest degree of chemical turnover involves reactions with OH radicals (Atkinson 1984). Atmospheric oxidation processes relating to OH-radical chemistry determine the removal rates of many important atmospheric pollutants (NMHC) and contribute to the formation of many secondary pollutants, such as O_3 and aldehydes, identified as harmful to human health and vegetation (Heddle et al., 1993; Temple and Taylor, 1983). The short lifetime of an OH-radical has made it both analytically difficult and costly to measure directly. To derive average tropospheric concentrations, chemical kinetics have been applied as an indirect method of measuring OH-radicals; however, a large degree of error has been associated with the method. By using stable carbon isotope kinetic analysis, additional constraints on the atmospheric hydroxyl radical concentration may be provided.

1.2 Objectives of Study

To assess the effectiveness of stable carbon isotope ratios analysis to study the oxidizing capacity of the ambient air in the troposphere, a spatial and temporal study of NMHC in ambient air in the Lower Fraser Valley (LFV) and Greater Toronto Area (GTA) was conducted. My research had the following objectives:

- Establish a Gas Chromatograph-Combustion-Isotope Ratio Mass Spectrometry (GC-C-IRMS) methodology appropriate for ambient tropospheric NMHC measurement at the Biogeochemistry Facility-School of Earth and Ocean Science, University of Victoria.

- Make stable carbon isotope ratio measurements for the most prominent NMHC sources in the Lower Fraser Valley (LFV) and Greater Toronto Area (GTA).
- Apply the isotope hydrocarbon clock method to obtain average photochemical ages of NMHC air parcels that are independent of parcel mixing (Rudolph *et al.* 2000).
- Develop tools to verify OH-radical chemistry in air pollution models.

1.3 The Hydrocarbon Clock

Given that the primary removal mechanism of NMHC are by reaction with photolytically generated OH radicals, the general chemical reaction can be described as follows:

Eq. 1.1
$$C_1 + \bullet OH \rightarrow \bullet C_1 + H_2O$$

In this study, C_1 is a NMHC, •OH is the hydroxyl radical and $\bullet C_1$ is a reaction product. The average rate of reaction, or the change in concentration of reactants and products over time, can be expressed as follows:

Eq 1.2
$$\mathrm{Rate} = -\frac{\Delta[\mathrm{C_1}]}{\Delta t} = -\frac{\Delta[\bullet\mathrm{OH}]}{\Delta t} = \frac{\Delta[\bullet\mathrm{C_1}]}{\Delta t} = \frac{\Delta[\mathrm{H_2O}]}{\Delta t}$$

Where Δ denotes change and t is the variable expressing time.

The average rate of reaction is often described in terms of a rate law (Equation 1.3) that expresses the relationship of the concentration of each reactant and a rate constant, k_{OH}, to the rate of reaction. The value of the rate constant differs for each NMHC as k_{OH} is dependant on the compounds reactivity with the hydroxyl-radical.

Eq 1.3
$$Rate = k_{OH}[C_1][OH]$$

Since they are related through the rate law, a concentration-time relationships can be derived. For a first order reaction, Equation 1.3 and be substituted in Equation 1.4 to derive a concentration-time relationship for compounds, c_1:

Eq 1.4
$$-\frac{d[c_1]}{dt} = k_{OH}[c_1][OH]$$

When Equation 1.4 is integrated from time, t_1 to time, t_2, the concentration of the compound can be expressed by the following first order reaction with respect to compound, c_1 (Kleinman et al., 2003).

Eq 1.5
$$-\int_{[c1]_{t1}}^{[c1]_{2t}} \frac{d[c_{1]}}{[c_1]} = \int_{t1}^{t2} k_{OH}[OH]dt$$

If the time integrated OH concentration (or photochemical age) of a compound is expressed as the amount of time passed multiplied by the average OH concentration ($[OH]_{av}$) as in Equation 1.6:

Eq 1.6
$$\int_{t1}^{t2} [OH]dt = t[OH]_{av}$$

By integrating Equation 1.5 and substituting the expression into Equation 1.6, the following equation relating the photochemical age of a NMHC to the concentration of NMHC can be derived:

Eq 1.7
$$\ln\left(\frac{[c_1]_{t2}}{[c_1]_{t1}}\right) = -k_{OH} \times (t[OH]_{av})$$

Where $[c_1]_{t1}$ and $[c_1]_{t2}$ are the concentrations of compound c_1 at time t_1 and t_2 and k_{OH} is the rate constant for the reaction of compound c_1 with OH radicals.

Experimentally, the average photochemical age of an air parcel is derived by measuring the change in ratio of different compounds over time in a method known as the hydrocarbon clock. The first order decay reaction, expressed in Equation 1.7, is modified to include the concentration of a second compound (c_2) and the differing reaction rates (${}^{c2}k_{OH}$) of c_2 with OH radicals:

Eq 1.8
$$\ln\left(\frac{[c_1]_{t2}}{[c_2]_{t2}}\right) = \ln\left(\frac{[c_1]_{t1}}{[c_2]_{t1}}\right) + ({}^{c1}k_{OH} - {}^{c2}k_{OH}) \times t \times [OH]_{av}$$

The units of the photochemical age are dependant on the units of k_{OH}. As the value of k_{OH} used in this study are cm^3 molecules^{-1} s^{-1}, the photochemical age is expressed in units of molecules s cm^{-3}.

If dilution of the air parcel occurs with an air mass that contains none of the compounds of interest, then the relative concentrations of compounds contained in the initial air mass remain unchanged. However, if mixing of air parcels containing the same compounds does occur, it is ambiguous as to whether or not the change in concentration ratios is from photochemical aging or dilution processes. For example, n-pentane and iso-pentane can be used to derive photochemical ages independent of air parcel mixing because the reaction rate for n-pentane with OH radicals differs from that of iso-pentane by only a few percent (see Table 1.2). If dilution processes occur, however, and a compound with a large residence time, such as benzene, is included in hydrocarbon clock analysis, Equation 1.8 deviates from linearity. The usefulness of the method is therefore restricted to compounds with atmospheric residence times differing by only a few percent.

1.4 Stable Carbon Isotope Analysis

The stable isotope ratio of a specific element in a given sample is measured as a ratio of the rare isotope to the abundant isotope. Because absolute abundances of individual isotopes are difficult to measure, two isotopes are measured as a ratio by

IRMS that is compared to that of a known standard. For carbon, $^{13}C/^{12}C$ ratios in natural abundances are commonly referenced to the internationally accepted standard Pee Dee Belemnite (PDB). The accepted $^{13}C/^{12}C$ ratio for PDB is 0.01124 (Craig 1957). Small differences in carbon isotope composition are conveniently expressed using delta (δ) notation as the per mil (‰) difference of the sample to a known standard:

Eq 1.9
$$\delta\,^{13}C(‰) = \frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample} - \left(\frac{^{13}C}{^{12}C}\right)_{standard}}{\left(\frac{^{13}C}{^{12}C}\right)_{standard}} \times 1000$$

Variations in isotope ratios occur due to differences in sample source material and/or the dependency of certain thermodynamic properties of a given sample on the mass of the atoms that compose the sample (Faure 1986). The latter causes isotope fractionation to occur through equilibrium and kinetic effects. Equilibrium effects occur because of differences in the translational, vibrational, and rotational energy of each isotope and is proportional to the relative mass difference between isotopes. Equilibrium fractionation can occur during the exchange of a molecule between two phases at equilibrium. This type of fractionation is not likely to be important for atmospheric NMHC because typically the rate of irreversible reaction of these compounds with OH radicals are short compared to equilibrium rates.

Fractionation effects of importance in atmospheric NMHC processes are caused by kinetic effects associated with heavier isotopes having stronger bonds and typically slower reaction rates. Although other sinks, for example O_3 exist, the atmospheric lifetimes of the compounds are mostly determined by their rate of irreversible reaction with OH radicals, with lifetimes covering a range of minutes to months (Table 1.2). The magnitude of kinetic fractionation is usually presented as the ratio of the reaction rate constant of the compound containing the heavy and light isotope as:

Eq. 1.10 $$\alpha = {}^{12}k_{OH} / {}^{13}k_{OH}$$

Here ${}^{12}k_{OH}$ is the rate constant for reaction of the NMHC containing only ${}^{12}C$ atoms with OH radicals and ${}^{13}k_{OH}$ is the rate constant for NMHC that contain a ${}^{13}C$ atom. Because α is generally close to unity, the resulting kinetic isotope effect (KIE_{OH}) associated with the primary NMHC loss process is defined using delta notation:

Eq. 1.11 $$KIE_{OH} = \left[\left({}^{12}k_{OH} \big/ {}^{13}k_{OH}\right) - 1\right] \times 1000$$

The value of KIE_{OH} can be derived experimentally from the slope of a plot of the following form:

Eq. 1.12 $$\ln({}^{12}c_{t_2} / {}^{12}c_{t_1}) = {}^{12}k_{OH} / {}^{13}k_{OH} / (1 - {}^{12}k_{OH} / {}^{13}k_{OH}) \ln[({}^{13}c_{t_2} / {}^{12}c_{t_2}) / ({}^{13}c_{t_1} / {}^{12}c_{t_1})]$$

where c_{t1} and c_{t2} refer to concentrations of isotopes at time t_1 and time t_2 respectively.

The KIE_{OH} is derived on the assumption that the heavy carbon atom is the atom being attacked. The attack of a carbon atom by the OH radical is sometimes preferential to location (i.e. the second carbon atom is preferentially attacked in a propane molecule, whereas for propene, attack is preferential at the first carbon atom in the molecule). When there is preferential abstraction to carbon atom location, a deviation in the linear function from which the KIE^{OH} values are experimentally derived occurs.

Experimentally derived KIE_{OH} values for the reaction of NMHC with OH radicals are positive indicating that molecules containing only ^{12}C react faster than the ^{13}C labelled molecules (see Table 1.2). The KIE_{OH} values for n-alkanes are quite small: between 2.84‰ and 3.26‰. The small values have been explained by the mass dependence on the collision frequency between n-alkanes and OH-radicals. The substantially higher KIE_{OH} for alkenes (propene 11.7‰) are attributed to the larger fractionation effects caused by the addition of OH-radicals across a double bond. NMHC with low reactivity towards OH-radicals, large atmospheric resident times, and large KIE_{OH} can be anticipated to undergo significant chemical processing caused by long atmospheric exposure to OH-radicals. Benzene and ethyne are included amongst these NMHC.

Table 1.2. Atmospheric lifetimes due to OH radicals, O_3, rate constants (k_{OH}) and fractionation factors (KIE_{OH}) for the reaction of selected NMHC with OH radicals.

Compound	[g]Lifetime due to OH·	[g]Lifetime due to O_3	[a]k_{OH} (x 10^{-12}) cm^3 molec^{-1} s^{-1}	KIE_{OH}, ‰	Ref, KIE_{OH}
Ethyne			0.91	15.84± 0.6	e
Benzene	9.4 day	>4 yr	1.23 ± 0.24	8.13 ± 0.5	b
Iso-Butane			2.35 ± 0.09	9.29 ± 1.12	f
n-Butane	4.7 day	>4500 yr	2.56 ± 0.02	2.84 ± 0.17	b
Iso-Pentane			3.90	2.91 ± 0.43	f
n-Pentane			3.97 ± 0.10	3.26 ± 0.64	f
Toluene	1.9 day	1.9 yr	5.96 ± 1.13	5.56 ± 0.28	c
Ethylbenzene			7.10 ± 1.75	4.34 ± 0.28	d
o-Xylene	19 h		1.4 ± 3.4	4.27 ± 0.05	d
p-Xylene	19 h		2.1 ± 3.6	4.83 ±0.81	d
Propene	5.3 h	4.9 day	2.60	11.70 ±0.19	b
Propane	10 days	>4500 yr	1.15 ± 0.04	3.44 ± 0.26	b
Isoprene	1.4 h	1.3 day		6.94 ± 0.80	b

Source

a. Atkinson, R., Gas Phase tropospheric chemistry of organic compounds, *J. Phys. Chem. Ref. Data, Monograph 2,* 1-216, 1994.
b. Rudolph, J., Czuba, E., Huang, L. The stable carbon isotope fractionation for reactions of selected hydrocarbons with OH-radicals and its relevance for atmospheric chemistry. *J. Geophysical Research* 105, 29,329-29,346 (2000).
c. Anderson, R., Czuba, E., Ernst, D., Huang, L., Thompson, A., Rudolph, J. Method for Measuring the Carbon Kinetic Isotope Effects of Gas-Phase Reactions of Light Hydrocarbons with the Hydroxyl Radical. *J. Phys. Chem.* 107, 6191-6199.
d. Anderson, R., Iannone, R., Thompson, A., Rudolph, J., Huang, L. Carbon kinetic isotope effects in the gas-phase reactions of aromatic hydrocarbons with the OH radical at 296 ± 4K Submitted.
e. Czuba, E. Development of a technique to study stable carbon isotope composition of NMHCs in ambient air, M.Sc. thesis, York University, Toronto, 1999.
f. Anderson, Rebecca. Personal communication
g. Atkinson, R. Atmospheric chemistry of VOCs and NO_x, Atmospheric Environment. 34, 2063-2101, 2000.

1.5 The Isotopic Hydrocarbon Clock

Assuming that no dilution or mixing processes have occured, it follows from Equation 1.7 that the preferential removal of NMHC containing light atoms from an air parcel obeys the Rayleigh fractionation curve described in the following equation:

Eq 1.13 $$\delta_{ct2} = -KIE_{OH} \times \ln\left(\frac{c_{t2}}{c_{t1}}\right) + \delta_{ct1}$$

where δ_{ct1} is the delta (‰) value of c_1 in the air mass at t_1 and δ_{ct2} is the delta value (‰) of c_1 at t_2. By substituting Eq 1.13 into Eq 1.7 the following equation for the photochemical age, ($t[OH]_{av}$) of the compound under investigation (c_1) is obtained:

Eq 1.14 $$t[OH]_{av} = (\delta_{ct2} - \delta_{ct1})/(KIE_{OH} \times k_{OH})$$

If we measure δ_{ct1} at the time of emission and δ_{ct2} in an aging air parcel and derive ^{OH}KIE and k_{OH} experimentally, it is possible to solve for the photochemical age in a method known as the isotopic hydrocarbon clock (Rudolph *et al.* 2000). Figure 1.1 depicts the photochemical age resulting from the change in isotope ratio from time t_1 to time t_2 for major NMHC under investigation. As predicted by Equation 1.14, the photochemical age of a compound is dependant on the magnitude of KIE_{OH} and k_{OH}. Because the difference between the rate constant for reaction of NMHC containing only ^{12}C atoms with OH radicals and the rate constant for NMHC that contain a ^{13}C atom is usually smaller than a percent, Rudolph and Czuba (2000) have shown that using stable isotope ratios of a compound removes many ambiguities associated with air parcel mixing using the conventional hydrocarbon clock method.

Although the hydrocarbon clock and the isotopic hydrocarbon clock are both applied to derive photochemical ages, it is important to note several differences between the two methods. Firstly, the isotopic hydrocarbon clock determines the photochemical age of the studied compound and not, as in the hydrocarbon clock method, the linearly weighted average of all NMHC measured in the investigated air parcel. Secondly, the use of isotope ratios gives a linearly weighted average photochemical age for an individual NMHC in the air parcels with non-uniform photochemical ages. Thirdly, the isotope hydrocarbon clock can be applied to air masses containing a mixture of air parcels of different ages to determine the mean photochemical age of a particular NMHC.

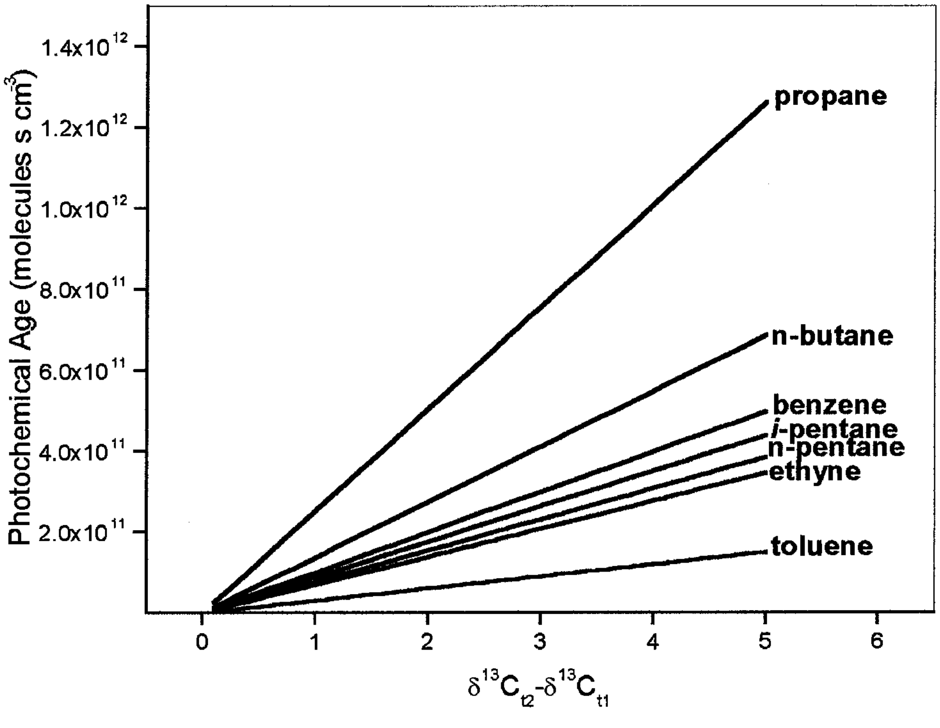

Figure 1.1: Model of NMHC photochemical ages derived from the change in isotope composition from time, t_1 to time, t_2 for some compounds under investigation.

2 Methods

2.1 Sampling Method

Air samples were collected in stainless steel 3 dm^3 SUMMA™ canisters using a battery powered Teflon membrane pump. The samples were collected by compressing ambient air in the canister to approximately 3 atm. Personnel from the Centre for Atmospheric Chemistry (CAC), York University, collected samples in the Greater Toronto Area. Personnel from the Biogeochemistry Facility-School of Earth and Ocean Science, University of Victoria, collected Lower Fraser Valley air samples.

2.2 Sample Sites

2.2.1 Traffic Related Source Study

On November 20, 2003 sample sets were collected at the Cassiar Tunnel in the Lower Fraser Valley (LFV) in British Columbia, Canada. A sample set consisting of sixteen canisters was taken during periods of high automotive activity in the tunnel (7:30-9:30, 15:30-17:30 local time). Tailpipe emissions from cars and trucks travelling at moderate speed dominate emissions at the tunnel site and are expected to give an average source composition from transport related fuels. On the same date and times, samples were taken in the Greater Toronto Area (GTA) at a railway overpass in the city's downtown area (Union Station Overpass). The samples taken at this location are a reasonable representation of the vehicle emission mix in Toronto, Canada (Rudolph 2002). Complete details of sampling conditions are given in Appendix 1.

2.2.2 Urban Ambient Air

Samples were collected in downtown Toronto at major intersections on June 17 & 18, July 15, and August 21, 2003. Sampling locations for urban ambient air are represented in Figure 2.1 by numbers 1-13. Complete details of sample conditions are given in Appendix 1. Samples were collected at hourly time intervals and represent hourly integrated samples. Within each hour, two five-minute samples were collected. In this text urban samples are abbreviated urban.

2.2.3 York University Ambient Air

Diurnal samples were collected at York University in suburban Toronto on May 22, June 24, July 29 and August 14, 2003. York University is located approximately 20 km northwest of downtown Toronto. As there are highways, airports, residential areas and gasoline storage facilities in the vicinity, the site is expected to be affected by all types of emissions. Complete details of sample conditions are given in Appendix 1. Samples were taken at hourly time intervals and represent integrated samples for that time duration. Two five-minute samples were taken within each hour sampled. Based on average wind speed and direction, air travelling across York University passed through downtown approximately Toronto two hours before hand. In this text York University samples are abbreviated YU.

2.2.4 Suburban/Rural Ambient Air

In the summer of 2003 intensive samples were collected in suburban/rural areas in the GTA on July 14, August 19 and August 20. Suburban/Rural sites were chosen to represent, based on most frequent wind directions, downwind conditions for the urban centre. Sampling locations for suburban/rural ambient air are represented by numerals

14-25 in Figure 2.1 Complete details of sampling conditions are given in Appendix 1. Samples were taken at hourly time intervals and represent integrated samples for that time duration. As in urban and suburban air studies, two five-minute samples were taken within the hour. In this text suburban/rural samples are abbreviated SR.

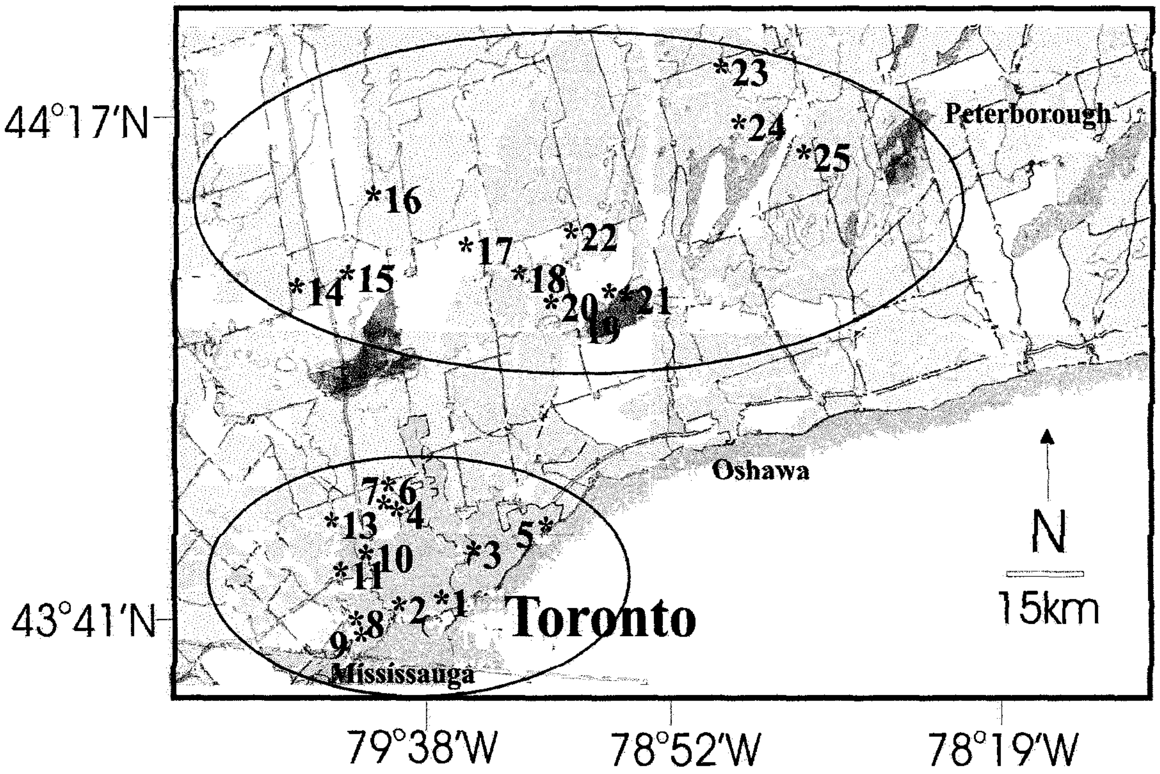

Figure 2.1: Site of ambient air collection in the GTA. Urban samples (bottom left) are represented by numbers 1-13. Suburban and rural locations (top left) are represented by numbers 14-25.

2.3 Analytical Method

Ambient levels of NMHC are low in urban air (ppb and sub-ppb). A sample enrichment unit similar to the one described by Rudolph et al. (1997) was built to concentrate samples to amounts detectable by instrumentation. Sample analysis consisted of a series of steps listed below that will be described in greater detail in the paragraph that follows:

(1) NMHC are absorbed onto a trap in a preconcentration step.

(2) NMHC are heated at a rapid rate and transferred in a cryofocussing step before injection onto a chromatographic column for analyte separation.

(3) NMHC are combusted online by a high temperature oxidation process.

(4) Compound specific isotopic measurements of NMHC are made by IRMS.

A general schematic of the experimental setup located at the Biogeochemistry Facility - School of Earth and Ocean Science (BF-SEOS), University of Victoria is shown in Figure 2.2. The CO_2 and H_2O traps together with the first six-port valve comprise the preconcentration unit. The second six port valve comprises the cryo-focusing unit.

The sample was first passed through stainless steel tubing (30 cm x ½") packed with Ascarite (8-20 mesh size) to remove CO_2 and then sample air was passed through a 30 cm x 1/2" length stainless steel silica lined tubing immersed in liquid ethanol cooled to –30°C to remove sample moisture. The analytes were then cryogenically trapped at liquid argon temperature (-186°C) on silica lined tubing (1/4"x 30 cm). Sample volumes were controlled using a mass flow controller and a manual timer. Depending on sample concentration, flow rates ranged from 50 to 90 ml min^{-1} in the pre-concentration unit. The analytes were flash heated to remobilize the NHMC, then transferred to a cryo-focussing trap submerged in liquid argon using He as a carrier gas. Cryogenic temperatures were high enough to allow N_2 and O_2 to vent from the sample. The He flow rate for transfer to the second focus loop was between 5-10 ml min^{-1}. All transfer lines were maintained at 80°C in the preconcentrator/cryofocus unit. Following sample enrichment, the sample was transferred to a Varian 3400 Gas Chromotograph (GC) by switching a six-port to the inject position. The GC was equipped with a GS-GasPro 0.32 mm i.d. x 30 m PLOT capillary column with a He carrier gas flow rate of 2 ml min^{-1}. The column was held at 30°C for 2 minutes before being heated to 230°C at a rate of 20°C/min. Final column hold time was 15 minutes at 230°C.

Following analyte partitioning, the effluent was passed through a combustion interface where hydrocarbons were oxidized to carbon dioxide and water in a method similar to that described by Matthews and Hayes (1978). The combustion oven consists of single copper, nickel and platinum wires held in a ceramic tube at 890°C. The nickel and copper in the combustion interface were reactivated by continuously passing oxygen through the ceramic tube. Following removal of H_2O produced by the combustion process by nafion permeable dryer, approximately 0.5ml/min of gas was transferred to a Finnegan MAT-252 Continuous Flow Isotope Ratio Mass Spectrometer via an open split. Here carbon isotope ratio measurements were made by simultaneously monitoring mass to charge ratio (*m/z*) 44($C^{12}O^{16}O^{16}$), 45($C^{13}O^{16}O^{16}$, $C^{12}O^{16}O^{17}$) and 46($C^{12}O^{16}O^{18}$). Details of the combustion interface, nafion dryer and open split are given by Merrit et al. (1995)

A reference gas inlet allowed the introduction of a flow of CO_2 of known $\delta^{13}C$ content relative to PBD for a defined period of time. Reference gas was injected four times during each sample run at times where no chromatographic peaks were observed. Peak integration was performed using the commercial software product

ISODAT™. The individual NMHC peak boundaries and baseline was manually defined three times and the average of the three was taken to be the isotope ratio in per mil (‰ PBD) units. Calculations for isotope ratio were made relative to the reference gas included in the same chromatogram.

An external gas standard was run daily to ensure system calibration and accuracy of the $\delta^{13}C$ determinations. The standard consisted of an air filled summa canister spiked with a commercial Scotty Standard containing a homologous series of n-alkanes (nC_1 to nC_6). Aromatic house standards and alkene Scotty standards were run less frequently to monitor measurement accuracy and precision. Preparation methods for gas standards account for variability from analytical and sampling uncertainty. Standard deviations of the mean were better than 0.5‰ for injections greater than 5ng of carbon, which corresponds to a concentration in the 0.1 ppbv C range in a pressurized 3L canister. Throughout analysis, the experimental uncertainty is equal to or less than 0.5‰ for all compounds. The variability in the values of atmospheric NMHC was much larger than the accuracy and precision of the measuring method. Identification of compounds was based on retention times obtained from a series of standard injections. A list of NMHC measured in this study and their abbreviations found GC-C-IRMS chromatograms is shown in Table 2.1.

Concentrations, also referred to in the text that follows as mixing ratios, of NMHC in samples were determined at the CAC, York University, by established GC-FID methods. Detection limits of the concentration measurements are in the ppt range. The average relative reproducibility is determined to be approximately 5% for these methods for mixing ratios exceeding 100ppt. Estimated relative accuracy is in the range of 10%.

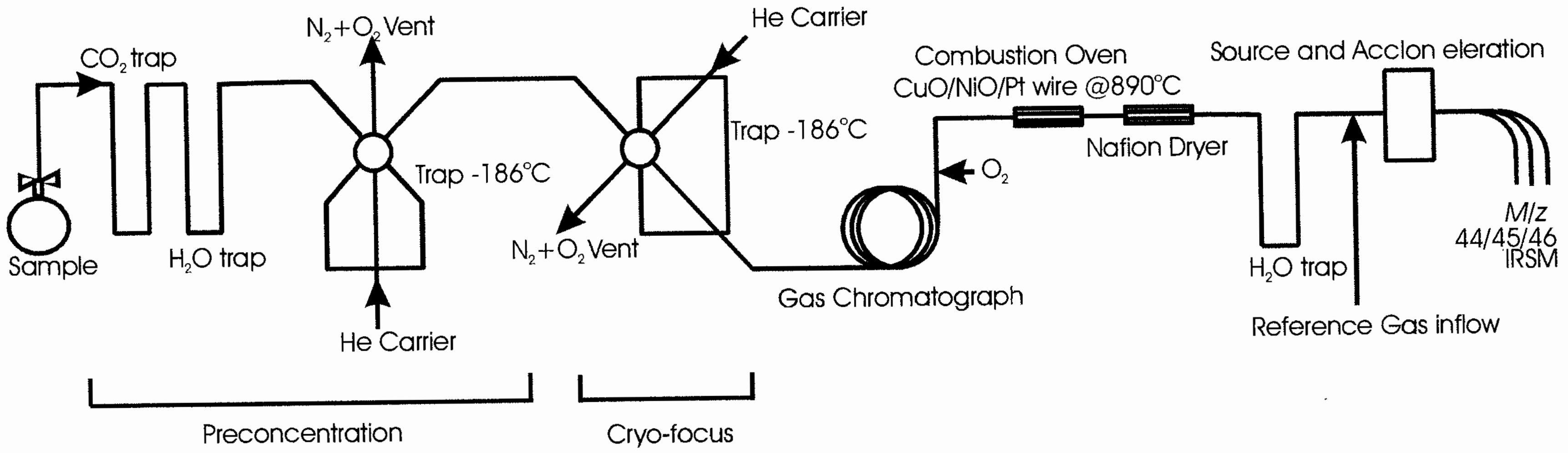

Figure 2.2: Schematic of instrumental unit for isotopic stable carbon isotope analysis located at BF-SEOS, UVic.

Table 2.1: List of measured NHMC compounds, abbreviations, experimental uncertainty and chromatogram peak number.

Abbreviation	Chemical name	Peak Number	Experimental Uncertainty	N
nC2	Ethane	1		
Ace	Ethyne	2	0.5	12
nC3	Propane	3	0.5	128
Propene	Propene	4		
iC4	iso-butane	5	0.5	
nC4	n-butane	6	0.4	128
1-butene	1-butene	7		
i-butene	iso-butene	8		
CH_3Cl	Methyl chloride	9		
iC5	iso-pentane	10	0.5	34
nC5	n-pentane	11	0.4	128
23DMC4	2,3-dimethylbutane	12		
2MC5	2-methylpentane	13		
3MC5	3-methylpentane	14		
Isoprene	2-methyl-1,3-butadiene	15		
MCYC5	cyclopentane	16		
nC6	n-hexane	17	0.4	128
MCYC5	methylcyclopentane	18		
Benz	Benzene	19	0.4	34
nC7	n-heptane	20	0.5	12
Tol	Toluene	21	0.4	34
nC8	n-octane	22	0.4	12
iC8	iso-octane	23		
C2Benz	ethylbenzene	24	0.5	34
xmXyl	x,m-xylene	25	0.4	34
oXyl	o-xylene	26	0.5	34

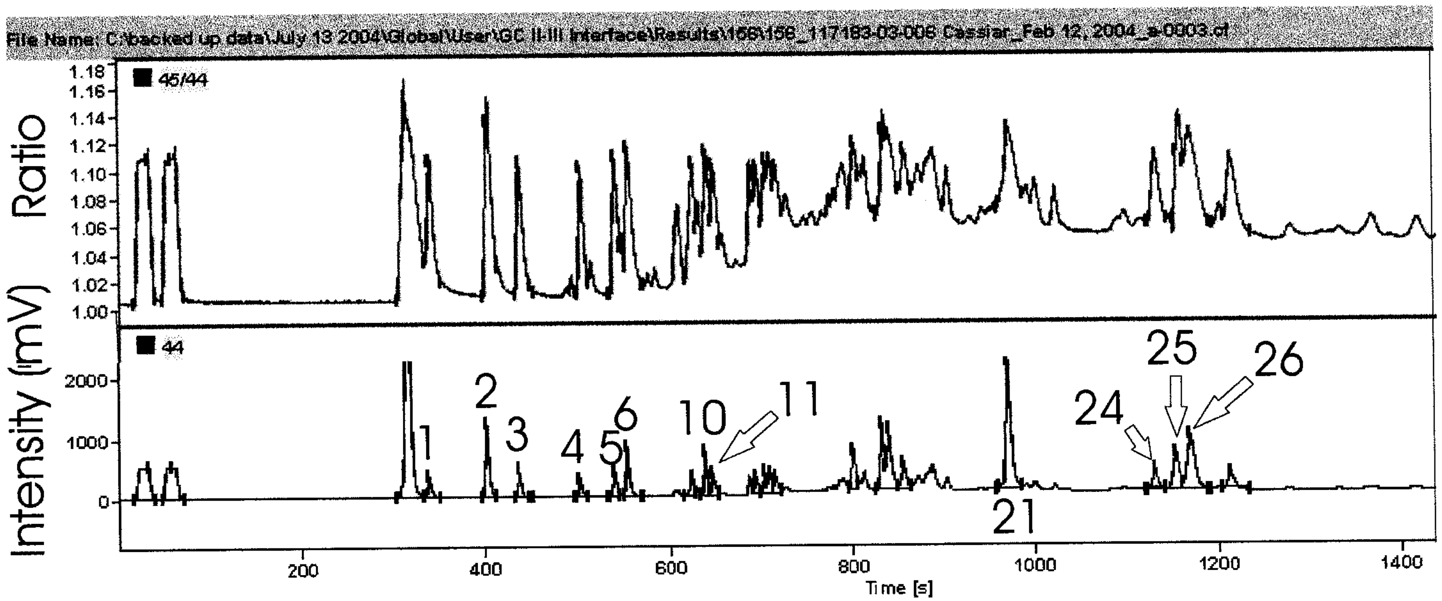

Figure 2.3: CF-IRMS chromatogram (lower frame) and mass to charge ratio (m/z) *44($C^{12}O^{16}O^{16}$)/ 45($C^{13}O^{16}O^{16}$, $C^{12}O^{16}O^{17}$) (upper frame) of Cassiar Tunnel source sample showing individual NMHC. Compound identification is presented in Table 2.1.*

3 Results

This chapter is an overview of the results of concentration and isotope ratio measurements made in the Lower Fraser Valley (LFV) and Greater Toronto Area (GTA) 2003 sampling campaign. Complete data sets are presented in Appendix 1. The mean concentrations and mean carbon isotope ratios presented in this chapter are not time weighted. A graphical overview of results is presented in Section 3.3.

3.1 Concentration Measurements

Mean NMHC mixing ratios are presented in Section 3.1. The mean over the daily sampling period, standard deviation (std. dev.), standard error (std. er.), minimum daily mixing ratio (min), maximum daily mixing ratio (max), and the measurement range of mixing ratios are reported in pptv, whereas the source study emissions are reported in ppbv. The number of measurements (n) for the individual NMHC in each study is also reported.

3.1.1 Concentration Measurements: Traffic Related Sources Study

NMHC concentrations found in the November 2003 traffic related sources study are presented in Table 3.1. Mixing ratios for traffic related source samples collected in the LFV are not available. On average, concentration measurements in the source study are a factor of ten greater than mixing ratios found in GTA ambient urban air (see Table 3.2).

3.1.2 Concentration Measurements: Urban Toronto

Mean concentrations of NMHC found in urban Toronto daily intensive sampling regimes in 2003 are summarized in Table 3.2. With few exceptions, mean mixing ratios for alkane compounds are highest in July. Aromatic compounds exhibit higher mixing ratios in June. The greatest range in NMHC concentrations was observed in the month of June.

3.1.3 Concentration Measurements: York University (Suburban)

Summarized in Table 3.3 are concentration measurements of NMHC found suburban ambient air collected at York University in the summer of 2003. Ambient air collected in June show, on average, highest NMHC mixing ratios. With the exception of *iso*-butane, *n*-butane and *m,p*-xylene, no significant difference in concentrations between months exists.

3.1.4 Concentration Measurements: Suburban/Rural Toronto

NMHC concentrations found in the summer of 2003 Suburban/Rural daily sampling campaign are summarized in Table 3.4. Values in August are the result of ambient air collected over two consecutive days. Ambient air samples most concentrated in NMHC were observed in July. Biogenic isoprene emissions are present in highest concentrations in July (Rudolph et al., 2003; Martin et al., 1991).

Table 3.1: Average mixing ratios (ppbv) observed in air samples collected at the Union Station Overpass (GTA), November, 2003.

	Mean	Std Dev.	Std. Er.	Min	Max	Range	N
Compound	**ppbv**						
nC2	15	8	2	8	30	23	16
nC3	28	27	7	7	107	100	16
nC4	52	48	12	9	160	151	16
nC5	12	10	2	2	37	35	16
nC6	5	5	1	1	21	19	16
nC7	2	2	0	0	8	8	16
iC4	8	6	2	2	24	22	16
iC5	21	17	4	4	65	62	16
23DMC4	2	2	0	0	8	7	16
2MC5	8	7	2	2	30	28	16
3MC5	4	4	1	1	16	15	16
iC8	5	6	1	1	24	23	16
Ace	22	27	7	4	111	107	16
Propene	16	12	3	4	46	42	16
1-butene	3	2	1	1	9	8	16
ibutene	4	3	1	1	12	11	16
Benz	8	7	2	2	26	24	16
Tol	15	13	3	3	55	52	16
C2Benz	2	2	1	0	9	9	16
mpXyl	6	8	2	0	29	28	16
oxyl	2	3	1	0	11	11	16

Table 3.2: Average mixing ratios (pptv) observed in Urban Toronto air samples collected in Summer 2003.

	June							July							August						
Compound	Mean	Std. Dev.	Std. Er.	Min	Max	Range	N	Mean	Std. Dev.	Std. Er.	Min	Max	Range	N	Mean	Std. Dev.	Std. Er.	Min	Max	Range	N
			pptv							pptv							pptv				
nC2	2797	412	66	1969	3862	1893	39	3992	748	176	2112	5099	2987	18	5318	1518	331	2061	6990	4929	21
nC3	1798	788	126	1060	4988	3928	39	2260	778	183	1174	3558	2384	18	2378	1298	283	741	5280	4539	21
nC4	1211	445	71	523	2190	1667	39	1725	1546	364	559	5199	4640	18	1337	679	148	372	2837	2465	21
nC5	602	320	51	90	1252	1162	39	886	637	150	305	2518	2213	18	778	437	95	146	1494	1348	21
nC6	899	3061	490	29	18858	18829	39	478	363	86	147	1641	1494	18	333	200	44	54	628	574	21
nC7	123	196	31	7	1256	1249	39	158	121	28	40	450	410	18	155	157	34	22	676	654	21
nC8	46	26	4	4	115	111	39	78	106	25	1	366	365	18	53	23	5	8	97	89	21
iC4	426	209	33	139	1264	1125	39	636	420	99	240	1550	1310	18	559	359	78	166	1538	1372	21
iC5	986	549	88	152	2298	2146	39	1600	1365	322	547	4678	4131	18	1228	651	142	255	2455	2200	21
2MC5	446	934	150	29	5884	5855	39	339	209	49	137	848	711	18	330	173	38	62	596	534	21
3MC5	481	1464	234	20	9057	9037	39	239	134	32	95	550	455	18	224	125	27	36	407	371	21
23DMC4	102	135	22	6	868	862	39	98	64	15	41	223	182	18	86	49	11	17	171	154	21
Ace	958	535	86	351	3403	3052	39	870	460	108	498	2623	2125	18	1050	458	100	346	1939	1593	21
Propene	323	219	35	9	911	902	39	340	159	38	109	738	629	18	544	373	81	58	1358	1300	21
1-butene	65	35	6	6	151	145	39	90	66	15	28	261	233	18	73	41	9	15	160	145	21
ibutene	113	55	9	22	279	257	39	130	70	17	49	284	235	18	122	68	15	47	331	284	21
Isoprene	103	65	10	19	298	279	39	160	142	33	46	522	476	18	381	177	39	143	697	554	21
CYC5	518	1151	184	51	5250	5199	39	2214	6991	1648	101	29572	29471	18	163	91	20	20	306	286	21
MCYC5	255	717	115	7	4458	4451	39	161	74	17	69	279	210	18	127	75	16	15	248	233	21
Benz	309	100	16	105	560	455	39	293	99	23	164	595	431	18	428	179	39	171	733	562	21
Tol	4479	15769	2525	105	98055	97950	39	1573	620	146	570	2881	2311	18	4046	3033	662	323	11908	11585	21
C2Benz	210	176	29	8	747	739	38	166	104	25	53	364	311	18	149	132	29	14	548	534	21
oXyl	216	186	30	4	764	760	38	153	86	20	40	353	313	18	120	97	21	6	314	308	21
mpXyl	708	715	114	8	2781	2773	39	550	392	92	141	1378	1237	18	337	258	56	11	811	800	21
CH_3Cl	466	59	9	313	618	305	39	454	91	22	339	643	304	18	419	54	12	331	543	212	21

Table 3.3: Average mixing ratios (pptv) observed in York University air samples collected in Summer 2003.

	May							June							July							August						
	Mean	Std Dev.	Std. Er.	Min	Max	Range	N	Mean	Std Dev.	Std. Er.	Min	Max	Range	N	Mean	Std Dev.	Std. Er.	Min	Max	Range	N	Mean	Std Dev.	Std. Er.	Min	Max	Range	N
Compound	pptv							pptv							pptv							pptv						
nC2	1876	198	36	1658	2286	628	30	786	616	112	279	2836	2557	30	1295	326	60	657	2010	1353	30	1423	590	170	947	2959	2012	12
nC3	744	138	25	488	1011	523	30	1377	1086	198	386	4027	3641	30	911	1205	220	169	6355	6186	30	1832	2303	665	258	7867	7609	12
nC4	1475	1086	198	413	4983	4570	30	931	658	120	282	2788	2506	30	321	158	29	106	652	546	30	735	408	118	269	1734	1465	12
nC5	631	330	60	204	1448	1244	30	631	539	98	148	2258	2110	30	281	227	41	71	1037	966	30	554	340	98	208	1286	1078	12
nC6	343	259	47	105	1305	1200	30	244	160	29	70	612	542	30	150	81	15	39	306	267	30	356	295	85	69	835	766	12
nC8	19	12	2	4	41	37	29	46	42	8	6	142	136	30	41	106	19	10	598	588	30	43	63	18	11	239	228	12
iC4	475	355	65	159	1856	1697	30	309	207	38	87	801	714	30	125	60	11	38	244	206	30	290	185	53	86	728	642	12
iC5	1096	711	130	334	3239	2905	30	904	718	131	223	2976	2753	30	423	269	49	119	1071	952	30	1039	640	185	394	2625	2231	12
2MC5	225	81	15	119	460	341	30	224	196	36	38	650	612	30	136	100	18	35	418	383	30	302	177	51	99	574	475	12
3MC5	177	58	11	87	296	209	30	153	135	25	26	450	424	30	89	60	11	25	247	222	30	213	141	41	58	419	361	12
Ace	643	229	42	406	1347	941	30	2115	826	151	898	4090	3192	30	410	261	48	1	1091	1090	30	542	316	91	247	1118	871	12
Propene	191	72	13	110	425	315	30	311	322	59	28	1112	1084	30	307	195	36	97	743	646	30	520	571	165	118	2183	2065	12
1-butene	97	38	7	41	203	162	30	66	56	10	12	192	180	30	43	26	5	15	112	97	30	125	173	50	29	660	631	12
Benz	188	52	9	102	344	242	30	293	199	36	95	750	655	30	215	233	42	76	1298	1222	30	292	163	47	148	584	436	12
Tol	521	264	48	68	1034	966	30	951	734	134	165	2526	2361	30	447	246	45	153	1214	1061	30	724	603	174	303	2317	2014	12
C2Benz	39	33	6	1	119	118	30	171	130	24	11	430	419	30	251	1032	188	13	5709	5696	30	120	209	60	5	769	764	12
OXyl	36	30	6	1	105	104	28	178	142	26	8	502	494	30	50	33	6	2	138	136	30	107	217	63	6	786	780	12
MpXyl	116	100	18	4	363	359	30	610	494	90	27	1769	1742	30	157	107	19	15	441	426	30	293	592	171	2	2138	2136	12
CH_3Cl	354	102	19	14	580	566	30	405	141	26	19	563	544	30	416	112	20	234	812	578	30	323	95	27	180	482	302	12

Table 3.4: Average mixing ratios (pptv) observed in Suburban/Rural Toronto air samples collected in Summer 2003.

	July							August						
Compound	Mean	*Std* Dev.	*Std.* Er.	Min	Max	Range	N	Mean	*Std* Dev.	*Std.* Er.	Min	Max	Range	N
	pptv							pptv						
nC2	1431	131	31	1263	1711	448	18	1275	156	26	989	1576	587	36
nC3	675	244	58	399	1075	676	18	499	216	36	265	1152	887	36
nC4	343	171	40	127	610	483	18	248	174	29	124	791	667	36
nC5	198	108	26	61	388	327	18	135	97	16	52	411	359	36
nC6	84	60	14	16	199	183	18	54	47	8	19	185	166	36
nC7	30	20	5	5	62	57	18	27	17	3	9	64	55	36
nC8	14	8	2	3	29	26	18	25	23	4	5	109	104	36
iC4	153	97	23	58	361	303	18	123	84	14	62	375	313	36
iC5	331	204	48	46	647	601	18	252	160	27	95	725	630	36
2MC5	81	48	11	21	169	148	18	61	46	8	22	188	166	36
3MC5	55	37	9	13	126	113	18	36	29	5	12	117	105	36
23DMC4	26	16	4	8	60	52	18	15	10	2	7	44	37	36
Ace	344	108	26	207	569	362	18	280	143	24	2	714	712	36
Propene	95	44	10	40	173	133	18	160	318	53	42	1887	1845	36
1butene	17	7	2	4	29	25	18	46	107	18	6	629	623	36
Ibutene	54	25	6	25	121	96	18	64	70	12	28	454	426	36
Isoprene	991	616	145	158	2279	2121	18	690	519	86	82	1805	1723	36
Benz	127	44	10	68	202	134	18	120	47	8	67	240	173	36
Tol	361	193	46	108	737	629	18	270	128	21	90	615	525	36
C2Benz	32	26	6	6	87	81	18	30	47	8	5	227	222	35
oXyl	23	19	5	4	65	61	18	17	31	5	1	155	154	35
mpXyl	95	78	18	11	240	229	18	47	103	17	4	456	452	35
CH_3Cl	408	65	15	344	548	204	18	403	87	15	284	734	450	36

3.2 Carbon Isotope Ratios

The following section is a statistical summary of carbon isotope ratios observed in the GTA and LFV (2003). Statistics are performed on isotopic measurements made in a given study without concentration weighting. In instances where the compound specific stable carbon isotope ratios are not reported, the NMHC ambient mixing ratio was below limits of GC-IRMS detection. The daily mean for the sample period, standard deviations (std. dev.), standard error (std. er.), minimum daily carbon isotope ratio (min), maximum daily carbon isotope ratio (max), and range in measured carbon isotope ratios ($\delta^{13}C$) are reported in ‰ units. The number of measurements made (N) in each daily study for the individual NMHC is also reported. Complete details of isotopic data is included in Appendix 1.

3.2.1 Carbon Isotope Ratios of Traffic Related Emissions in the GTA and LFV

Carbon isotope ratios of NMHC found in the November 2003 traffic related source study in the GTA and LFV are summarized in Table 3.5. Results are discussed in Chapter 4.

Table 3.5: Average carbon isotope ratios observed at Union Station Overpass (GTA) and Cassiar Tunnel (LFV), N=16 samples. All isotope ratios are reported in per mil units (‰ vs. PDB).

	GTA							LFV						
Compound	Mean	Std Dev.	Std. Er.	Min	Max	Range	N	Mean	Std Dev.	Std. Er.	Min	Max	Range	N
			‰								‰			
nC3	-27.8	1.3	0.3	-30.7	-26.1	4.6	15	-30.8	0.9	0.3	-32.8	-29.2	3.6	11
nC4	-28.1	0.4	0.1	-28.7	-27.0	1.7	13	-29.7	1.1	0.3	-31.7	-28.7	3.0	11
nC5	-27.3	0.4	0.1	-28.0	-26.6	1.4	16	-28.6	0.7	0.2	-29.8	-27.2	2.6	10
nC6	-26.8	0.8	0.2	-28.8	-25.8	3.0	16	-26.6	0.9	0.4	-27.6	-25.3	2.4	5
nC7	-26.2	0.4	0.1	-26.8	-25.5	1.3	14	-26.0	1.4	0.6	-27.4	-23.4	4.0	6
iC4	-24.6	3.3	0.9	-30.4	-15.7	14.7	15	-24.4	2.2	0.7	-27.8	-21.2	6.6	10
iC5	-28.7	0.4	0.1	-29.3	-27.8	1.5	16	-27.8	0.9	0.4	-29.0	-26.6	2.4	5
23DMC4	-25.3	0.5	0.2	-26.1	-24.4	1.7	11	-	-	-	-	-	-	-
2MC5	-28.1	0.7	0.2	-30.2	-27.3	2.9	16	-	-	-	-	-	-	-
3MC5	-26.7	1.0	0.3	-29.8	-25.5	4.3	16	-26.9	0.4	0.2	-27.4	-26.4	1.0	5
iC8	-28.4	2.0	0.5	-32.6	-26.5	6.1	14	-26.9	1.6	0.8	-28.2	-24.8	3.4	4
ace	-14.0	2.6	0.6	-20.0	-10.9	9.1	16	-14.9	1.0	0.3	-16.2	-12.6	3.6	12
propene	-23.6	0.5	0.1	-24.9	-23.0	1.9	16	-24.2	1.3	0.4	-26.1	-22.0	4.1	9
1-butene	-24.4	1.4	0.7	-25.7	-22.5	3.2	4	-24.2	1.5	0.9	-25.1	-22.5	2.6	3
ibutene	-23.4	0.9	0.3	-24.8	-22.1	2.7	8	-29.8	0.5	0.1	-30.5	-28.9	1.6	10
Benz	-25.7	1.5	0.4	-28.8	-24.1	4.7	15	-24.3	1.6	0.6	-26.7	-22.2	4.5	8
Tol	-26.3	0.3	0.1	-26.8	-25.8	1.0	15	-27.4	0.7	0.2	-28.6	-26.3	2.3	14
C2Benz	-26.7	0.9	0.2	-28.4	-25.1	3.3	15	-27.9	0.4	0.1	-28.5	-27.3	1.2	11
mpXyl	-26.1	0.6	0.2	-26.8	-25.2	1.6	13	-25.7	1.5	0.4	-27.8	-22.2	5.6	12
oXyl	-25.5	0.5	0.2	-26.3	-24.6	1.7	11	-26.2	0.7	0.2	-27.5	-25.3	2.2	12

3.2.2 Carbon Isotope Ratios of NMHC in Urban Ambient Air

Carbon isotope ratios of NMHC in the summer of 2003 Urban Toronto ambient air are summarized in Table 3.6. The range in compound specific isotope ratio measurement (0.9‰-19‰) is outside the range of experimental uncertainty of 0.5‰, indicating that the compounds have undergone some photochemical processing. The largest range in isotopic composition is observed in June when daily conditions favoured the formation of a stable inversion layer. However, the variability may also be explained by the isotope fractionation with high seasonal OH-radicals concentration observed to be a factor of 5 higher at midlatitudes than the global daily average of 10^6 radicals cm^{-3} (Finlayson 2000).

3.2.3 Carbon Isotope Ratios of NMHC in Suburban Ambient Air

Carbon isotope ratios of NMHC measured in ambient air collected at York University (Petrie Roof) in the GTA are summarized in Table 3.7. Similar to urban samples, the range in compound specific isotope ratios (0.5‰-18 ‰) is outside the range of experimental uncertainty (0.5‰) and is greatest in June. For 2-methylpentane, 3-methylpentane and *o*-xylene, the range in compound specific isotope ratios is smaller than experimental uncertainty, however sample numbers are less than or equal to three. Compounds exhibiting significant differences in mean isotopic composition between months include: propane, *iso*-butane, *iso*-pentane, *n*-pentane and *m,p*-xylene.

3.2.4 Carbon Isotope Ratios of NMHC in Suburban/Rural Ambient Air

Carbon isotope ratios of NMHC measured in Suburban and Rural Toronto (2003) campaigns are summarized in Table 3.8. The range in compound specific isotope ratios is outside the range of experimental uncertainty, demonstrating that the compounds have undergone some amount of photochemical processing and/or contributions for sources other than traffic related emissions.

Table 3.6: Average carbon isotope ratios observed in Urban Toronto in Summer 2003. All isotope ratios are reported in per mil (‰ vs PDB).

	June							July							August						
Compound	Mean	Std Dev.	Std. Er.	Min	Max	Range	N	Mean	Std Dev.	Std. Er.	Min	Max	Range	N	Mean	Std Dev.	Std. Er.	Min	Max	Range	N
				‰							‰							‰			
nC3	-29.7	1.2	0.2	-31.9	-27.2	4.7	30	-29.5	0.8	0.2	-30.8	-27.2	3.6	16	-29.8	0.4	0.1	-30.5	-29.1	1.4	11
nC4	-30.9	0.7	0.1	-32.0	-29.4	2.6	26	-30.2	1.3	0.3	-33.3	-28.2	5.1	15	-30.6	1.1	0.3	-32.7	-28.7	4.0	11
nC5	-28.0	0.7	0.1	-29.4	-26.3	3.1	27	-27.3	1.2	0.3	-29.1	-24.3	4.8	16	-27.0	1.9	0.6	-28.5	-21.8	6.7	11
nC6	-25.7	1.0	0.2	-28.7	-24.6	4.1	25	-26.7	1.0	0.3	-28.2	-25.3	2.9	9	-26.1	0.8	0.3	-27.2	-24.8	2.4	8
nC7	*-21.8*	2.6	*1.2*	-24.6	*-18.1*	6.5	*5*	-	-	-	-	-	-	-	-	-	-	-	-	-	-
iC4	-10.8	6.7	2.1	-19.2	-0.2	19.0	10	-21.9	5.1	2.1	-27.4	-15.6	11.8	6	-20.3	7.2	3.2	-32.5	-15.2	17.3	5
iC5	*-28.9*	*0.6*	*0.1*	*-30.1*	*-27.7*	*2.4*	*27*	*-28.9*	*0.8*	*0.2*	*-30.2*	*-27.6*	*2.6*	*16*	*-28.7*	*0.7*	*0.2*	*-29.5*	*-27.5*	*2.0*	*11*
2MC5	-25.6	2.3	0.7	-28.6	-19.8	8.8	10	-27.2	0.9	0.4	-27.9	-26.0	1.9	4	-28.4	0.0	0.0	-28.4	-28.4	0.0	1
MCYCC5	-27.3	1.4	0.3	-31.3	-25.5	5.8	21	-27.8	1.0	0.4	-29.2	-25.8	3.4	8	-27.2	0.8	0.4	-28.3	-26.2	2.1	5
3MC5	-25.9	1.0	0.2	-28.5	-23.5	5.0	21	-26.2	0.4	0.2	-26.6	-25.7	0.9	6	-13.4	4.1	1.3	-17.8	-6.0	11.8	10
ace	-11.5	2.5	0.5	-15.6	-6.8	8.8	27	-12.2	1.9	0.5	-14.6	-9.0	5.6	15	-20.7	4.7	1.8	-24.2	-10.2	14.0	7
propene	-23.8	1.6	0.5	-26.9	-21.1	5.8	12	-22.6	2.2	1.1	-25.8	-21.2	4.6	4	-25.1	0.0	0.0	-25.1	-25.1	0.0	1
ibutene	-25.4	2.0	0.5	-28.6	-22.4	6.2	15	-	-	-	-	-	-	-	-25.9	0.2	0.1	-26.1	-25.7	0.4	5
Benz	*-22.0*	*1.4*	*0.3*	*-23.9*	*-18.6*	*5.3*	*29*	*-24.1*	*1.2*	*0.3*	*-26.3*	*-21.9*	*4.4*	*17*	*-21.1*	*1.7*	*0.5*	*-23.0*	*-17.5*	*5.5*	*10*
Tol	-27.6	1.2	0.2	-29.7	-25.4	4.3	25	-27.6	1.1	0.3	-28.9	-25.6	3.3	15	-27.5	0.9	0.3	-28.4	-25.2	3.2	11
C2Benz	-26.9	1.2	0.5	-28.9	-25.4	3.5	7	-27.9	0.5	0.2	-28.4	-27.3	1.1	5	-27.5	0.3	0.2	-27.7	-27.3	0.4	2
mpXyl	-27.4	1.4	0.3	-32.5	-25.6	6.9	27	-26.2	0.9	0.2	-27.5	-24.7	2.8	14	-26.0	0.7	0.2	-26.9	-24.3	2.6	11
oXyl	-24.4	1.7	0.4	-27.8	-21.2	6.6	16	-24.8	0.9	0.3	-26.5	-23.2	3.3	9	-24.1	1.3	0.5	-25.7	-22.5	3.2	7
CH_3Cl	-36.5	3.0	0.8	-40.5	-29.1	11.4	13	-34.4	1.9	1.1	-35.9	-32.2	3.7	3	-35.5	5.5	2.8	-40.8	-28.6	12.2	4

Table 3.7: Average carbon isotope ratios observed at York University in Summer 2003. All isotope ratios are reported in per mil (‰ vs PDB).

	May							June							July							August						
Compound	Mean	Std Dev.	Std. Er.	Min	Max	Range	N	Mean	Std Dev.	Std. Er.	Min	Max	Range	N	Mean	Std Dev.	Std. Er.	Min	Max	Range	N	Mean	Std Dev.	Std. Er.	Min	Max	Range	N
	‰							‰							‰							‰						
nC3	-29.0	0.8	0.2	-30.6	-27.9	2.7	17	-28.8	0.6	0.1	-29.6	-27.3	2.3	19	-28.2	0.6	0.2	-29.0	-27.1	1.9	11	-28.7	0.7	0.3	-29.4	-27.5	1.9	7
nC4	-31.5	0.8	0.2	-32.5	-28.9	3.6	17	-30.4	1.5	0.4	-33.2	-28.2	5.0	18	-30.3	2.1	0.8	-33.0	-26.8	6.2	6	-30.7	0.7	0.2	-31.3	-29.2	2.1	8
nC5	-28.8	0.9	0.2	-30.4	-26.2	4.2	16	-27.3	0.9	0.2	-28.9	-26.1	2.8	18	-27.4	0.7	0.2	-28.7	-26.4	2.3	12	-27.4	0.9	0.3	-29.1	-25.9	3.2	11
nC6	-26.5	1.3	0.4	-29.1	-24.6	4.5	10	-26.0	2.1	0.7	-28.0	-22.1	5.9	9	-24.9	0.6	0.4	-25.3	-24.5	0.8	2	-28.0	1.9	0.8	-31.0	-26.2	4.8	5
IC4	-19.2	5.0	1.6	-26.3	-11.1	15.2	10	-12.1	6.1	2.1	-23.7	-5.2	18.5	8	-	-	-	-	-	-	-	-	-	-	-	-	-	-
IC5	-29.7	0.6	0.2	-30.6	-28.6	2.0	16	-28.8	0.8	0.2	-30.1	-27.2	2.9	17	-29.0	0.7	0.2	-30.8	-28.2	2.6	11	-29.2	0.6	0.2	-30.1	-28.3	1.8	11
2MC5	-26.7	1.4	0.5	-30.1	-25.8	4.3	8	-28.6	1.0	0.4	-29.6	-27.1	2.5	6	-26.9	0.3	0.2	-27.1	-26.7	0.4	2	-31.1	0.0	0.0	-31.1	-31.1	0.0	1
3MC5	-26.3	1.0	0.4	-27.8	-24.7	3.1	8	-25.8	1.4	0.6	-27.1	-23.8	3.3	5	-25.4	0.4	0.3	-25.6	-25.1	0.5	2	-27.4	2.0	1.0	-30.0	-25.4	4.6	4
MCYCC5	-27.6	0.7	0.2	-28.6	-26.8	1.8	9	-27.0	0.9	0.4	-27.9	-25.8	2.1	6	-	-	-	-	-	-	-	-	-	-	-		-	-
ace	-8.8	4.8	1.2	-18.4	-3.4	15.0	16	-11.5	6.1	1.4	-28.1	-2.3	25.8	18	-13.2	3.6	1.5	-20.2	-10.8	9.4	6	-14.2	1.8	0.9	-16.9	-12.9	4.0	4
propene	-24.6	2.3	0.9	-27.0	-21.9	5.1	6	-23.7	1.6	0.6	-25.2	-20.0	5.2	8	-24.6	2.2	1.1	-27.0	-21.7	5.3	4	-24.9	1.3	1.0	-25.8	-23.9	1.9	2
ibutene	-26.0	1.5	0.4	-27.7	-22.1	5.6	12	-26.7	1.8	0.7	-28.4	-24.2	4.2	7	-29.7	0.0	0.0	-29.7	-29.7	0.0	1	-28.2	1.7	1.2	-29.4	-27.0	2.4	2
Benz	-23.4	1.9	0.5	-25.9	-20.1	5.8	12	-23.3	2.0	0.5	-26.2	-18.3	7.9	17	-24.8	0.7	0.4	-25.5	-24.2	1.3	3	-28.0	1.7	1.0	-29.4	-26.1	3.3	3
Tol	-28.1	1.1	0.3	-30.3	-26.4	3.9	17	-27.4	1.4	0.4	-29.9	-25.2	4.7	16	-22.1	2.2	0.4	-25.8	-17.9	7.9	24	-21.7	3.0	0.9	-26.1	-17.4	8.7	11
C2Benz	-	-	-	-	-	-	-	-26.6	1.3	0.5	-27.8	-24.3	3.5	6	-27.6	1.5	0.3	-31.0	-25.5	5.5	21	-26.6	1.2	0.4	-27.5	-24.0	3.5	8
mpXyl	-26.9	1.5	0.4	-28.8	-22.8	6.0	16	-26.8	1.8	0.4	-31.1	-22.3	8.8	19	-25.3	0.9	0.2	-26.5	-23.4	3.1	22	-25.4	0.7	0.2	-26.7	-24.0	2.7	11
oXyl	-25.4	2.2	1.2	-27.7	-23.4	4.3	3	-25.0	0.9	0.4	-26.2	-24.0	2.2	6	-24.0	0.0	0.0	-24.0	-24.0	0.0	1	-25.6	0.2	0.1	-25.8	-25.5	0.3	3
CH_3Cl	-35.4	5.0	2.9	-39.6	-29.9	9.7	3	-	-	-	-	-	-	-	-40.8	0.0	0.0	-40.8	-40.8	0.0	1	-35.6	4.5	3.2	-38.8	-32.4	6.4	2

Table 3.8: Average carbon isotope ratios observed in Suburban and Rural Toronto in Summer 2003. All isotope ratios are reported in per mil (‰ vs PDB).

	July							August						
Compound	Mean	Std Dev.	Std. Er.	Min	Max	Range	N	Mean	Std Dev.	Std. Er.	Min	Max	Range	N
	‰							‰						
nC3	-28.5	1.0	0.3	-29.6	-26	3.2	8	-28.7	0.7	0.2	-30.3	-27.5	2.8	13
nC4	-30.9	0.3	0.2	-31.2	-31	0.5	3	-30.2	1.1	0.4	-31.0	-27.9	3.1	7
nC5	-27.0	1.7	0.8	-28.8	-24	4.6	5	-27.9	1.0	0.4	-29.5	-26.7	2.8	6
nC6	-	-	-	-	-	-	-	-27.4	0.0	0.0	-27.4	-27.4	0.0	1
iC5	-27.7	0.7	0.4	-28.6	-27	1.5	4	-28.9	0.7	0.2	-29.9	-27.9	2.0	9
2MC5	-27.5	0.0	0.0	-27.5	-28	0.0	1	-27.8	0.7	0.4	-28.3	-27.0	1.3	3
ace	-9.2	1.4	0.6	-11.5	-8	3.5	5	-14.7	1.8	0.7	-18.0	-13.4	4.6	6
propene	-	-	-	-	-	-	-	-20.4	0.0	0.0	-20.4	-20.4	0.0	1
ibutene	-28.0	2.0	1.4	-29.4	-27	2.8	2	-30.1	2.8	1.3	-33.3	-26.2	7.1	5
isoprene	-27.6	1.5	0.5	-29.3	-25	4.8	10	-27.1	1.4	0.5	-28.6	-25.2	3.4	8
CYCC3	-27.0	0.5	0.4	-27.3	-27	0.7	2	-	-	-	-	-	-	-
CYCC5	-22.2	0.0	0.0	-22.2	-22	0.0	1	-	-	-	-	-	-	-
Benz	-23.0	2.3	0.7	-28.5	-21	7.9	11	-25.7	2.3	0.6	-28.6	-19.8	8.8	14
Tol	-28.6	1.4	0.5	-30.5	-26	4.7	7	-27.1	0.9	0.3	-28.5	-25.8	2.7	8
mpXyl	-25.9	1.4	0.4	-28.2	-23	5.2	11	-26.6	0.7	0.2	-28.1	-25.7	2.4	14
oXyl	-24.9	0.0	0.0	-24.9	-25	0.0	1	-33.0	0.0	0.0	-33.0	-33.0	0.0	1
CH_3Cl	-37.3	0.9	0.4	-38.0	-37	1.5	4	-	-	-	-	-	-	-

3.3 Compound Specific Isotope Ratio Results

For the 2003 sampling campaign, two trends demonstrating photochemical processing are observed consistently throughout the isotope ratio data set. Firstly, for most NMHC the ambient measurements exhibit a higher overall variability than the source composition. The average daily range in compound specific stable carbon isotope ratio is 3.6 ‰ in source samples, whereas for ambient air the range is 4.6 ‰. Secondly, the range in ambient samples is outside the range of experimental uncertainty (0.5 ‰). Compounds that have relatively large ^{OH}KIE show a large range in isotopic composition, although changes in isotope ratios from source values are also dependant on OH-radical reactivity. Unsaturated and alkane compounds a show larger total variability in isotope ratios than aromatics (see Table 3.9). The average daily range in compound specific isotopic ratios for diurnal cycles in the GTA is 4. 6‰.

Table 3.9 : Isotope Ratios of compounds measured in the GTA in Summer 2003.

	Mean	Std. Dev.	Std. Er	Max	Min	Range	N
CH_3Cl	-35.6	3.3	0.5	-40.8	-28.6	12.2	38
ALKANES	-27.4	4.1	0.1	-33.3	-3.2	30.1	741
ISOPRENE	-27.1	1.3	0.2	-29.3	-24.5	4.8	30
AROMATICS	-25.5	2.5	0.1	-33	-17.4	15.6	509
UNSATURATES	-25.1	3.0	0.3	-33.3	-10.2	23.1	96
ETHYNE	-11.6	4.0	0.4	-28.1	-2.3	25.8	107

In the GTA, the average isotope ratio of all ambient measurements of NMHC, including halogenate NMHC is –25.7 ± 3.4 ‰. The most ^{12}C enriched compound is CH_3Cl (–35.6 ± 3.3 ‰), followed by alkanes (–27.4 ± 4.1 ‰), isoprene (-27.1 ± 1.3 ‰), aromatics (–25.1 ± 3.0 ‰), unsaturates (–25.1 ± 3.0 ‰) and ethyne (–11.6 ± 4.0 ‰). A box and whisker plot data summary is shown is Figure 3.1 CH_3Cl is most enriched in ^{12}C because of biogenic source contributions (Thompson 2002). Alkanes, aromatics and unsaturated compounds fall within the range reported for crude oils: -23.3 ‰ to –32.5 ‰ (Yeh 1981). Isoprene falls within range expected for plants utilizing a C_4 photosynthetic pathway: -21‰ to 35 ‰ (Rudolph 2003).

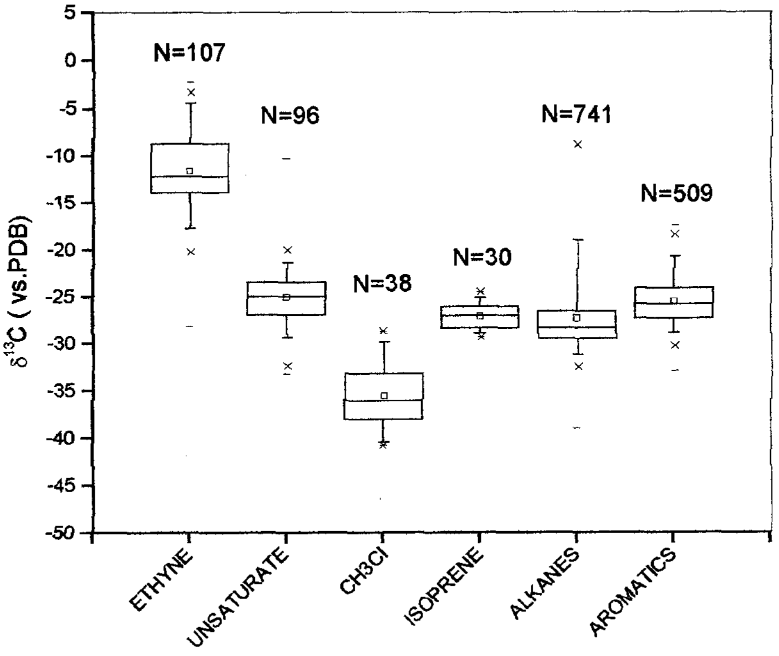

Figure 3.1 . Box and Whisper Plot of all isotope ratio measurements of NMHC made in the GTA in Summer 2003. Boxes represent the 25th and 75th percentiles, whiskers the 5th and 95th percentiles and (x), *the 1st and 99th percentiles. Maximum (-) , Minimum (-) and mean values (small squares) are also shown.*

3.3.1 Source Emissions

Compound specific isotopic analyses of NMHC in samples collected in the LFV and GTA were made to assess spatial differences in isotope ratios of traffic related source emissions. The mean compound specific stable carbon isotope ratios and mixing ratios are presented in Figure 3.2. For NMHC showing a significant spatial difference in isotopic composition, compounds are depleted in ^{13}C in LFV traffic related emissions relative to GTA emissions. Average mixing ratios and average stable carbon isotope ratios in GTA traffic related emissions display a slight inverse relationship at the 95% significance level. The spatial differences in compound specific isotope ratios are discuss in greater detail in Section 4.1.

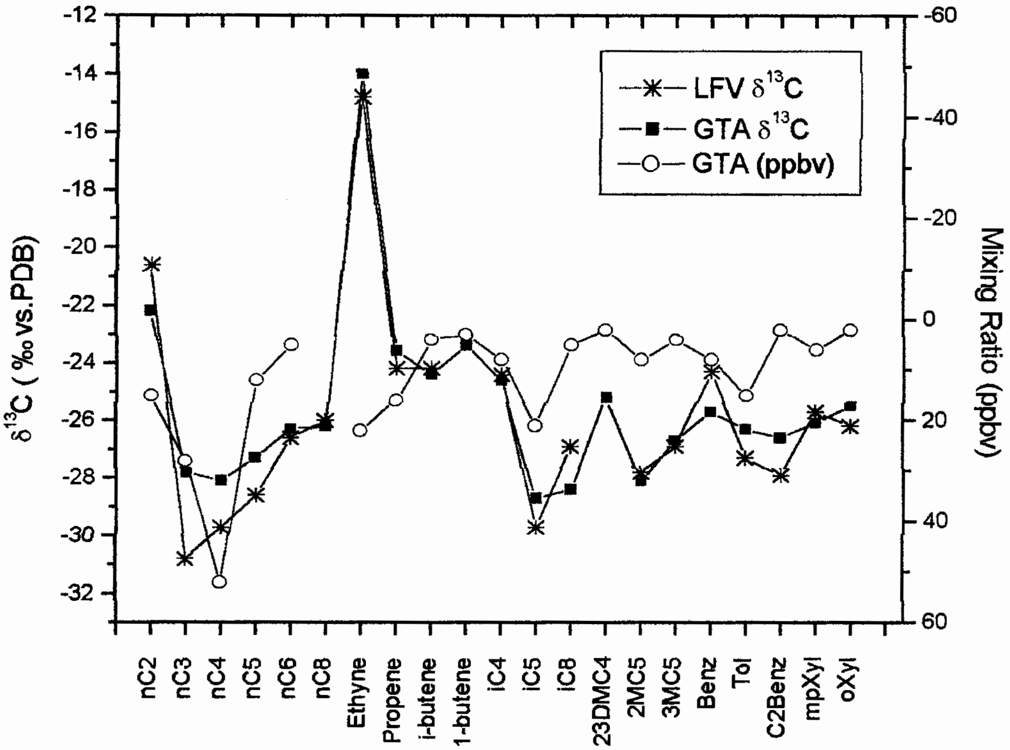

Figure 3.2: Averages of stable carbon isotope ratios (‰ vs. PDB) and mixing ratios (ppbv) for NMHC at locations heavily influenced by transport related emissions in the GTA (Union Station) and LFV (Cassiar Tunnel).

3.3.2 Alkanes

As shown in Figure 3.3 (a), with few exceptions, the compound specific isotope ratios of alkane compounds follow a similar pattern between compounds in all studied air parcels, although the isotopic offsets between compounds differ in details. *N*-hexane (YU Aug), more deplete in ^{12}C relative to n-pentane, and 2-methylpentane (Urban Jun), more deplete in ^{12}C relative to 3-methylpentane, are exceptions to the overall trend.

Compound specific stable carbon isotope ratios showing the largest range between locations is iso-butane (-10.9 ‰ in Urban June samples to –19.2 ‰ in YU May samples). The range can be attributed to the low OH-radical reactivity of alkanes and the magnitude of KIE_{OH} for iso-butane (9.29‰). The smallest daily average range (3.9‰) in carbon isotope ratios is observed for alkane compounds.

If anthropogenic NMHC sources have exclusively origins in urban Toronto, then through reactions with OH radicals, NMHC in rural and suburban air parcels would be deplete in ^{12}C. However, no isotope ratio offset pattern is observed between locations suggesting anthropogenic NMHC contributions from rural and suburban locations (see Figure 3.4 a). The small sample pool for air collected at Suburban/Rural sites may not be reflective of differences in isotopic composition between locations as recent emission events in rural areas and/or transport of photochemically aged emission into urban core would yield similar results.

In Figure 3.3 (b) there is an overall decrease in mixing ratios with increasing carbon number for straight-chain compounds at all locations. This pattern does not exist for branched alkane compounds, where iso-pentane is at highest ambient concentrations for all temporal and spatial variations. Lowest mixing ratios exist in rural and suburban locations (see Figure 3.4 b).

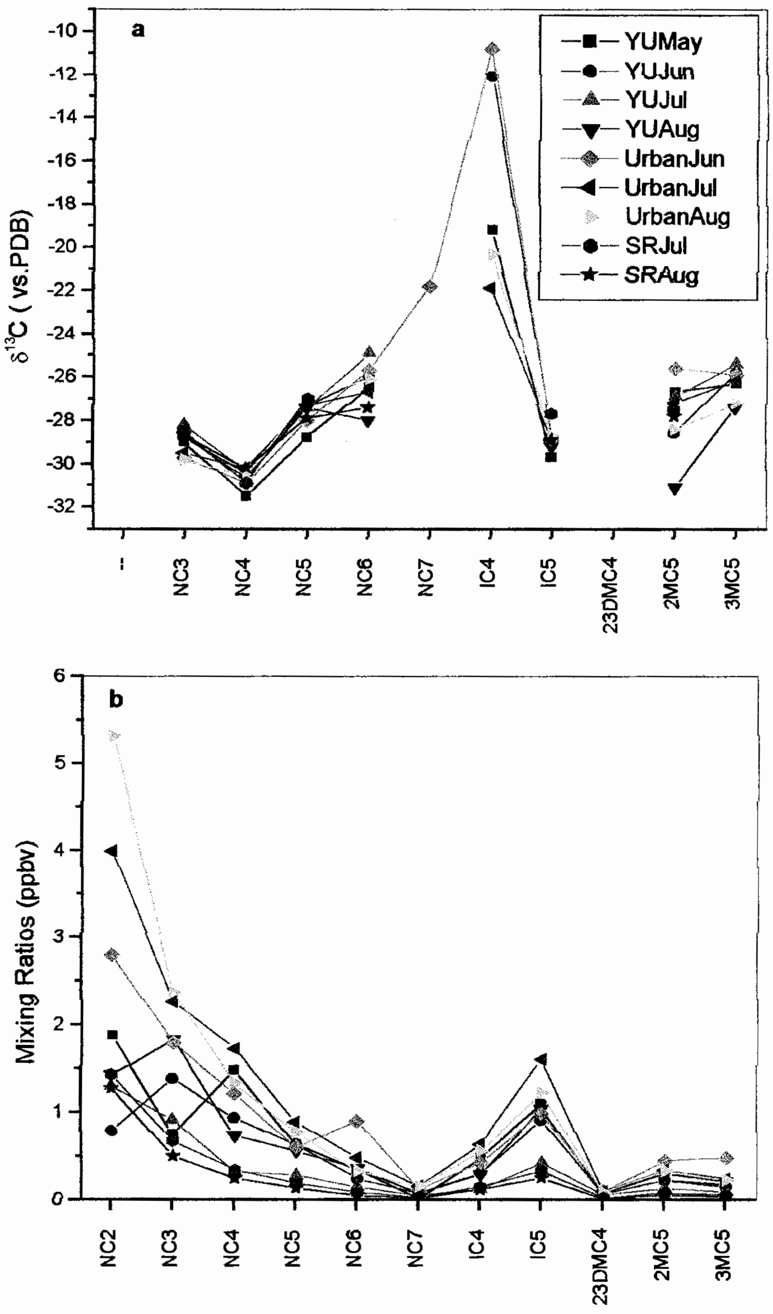

Figure 3.3: (a) Averages of stable carbon isotope ratios (‰ vs. PDB) and (b) mixing ratios (ppbv) of individual alkanes in Summer 2003.

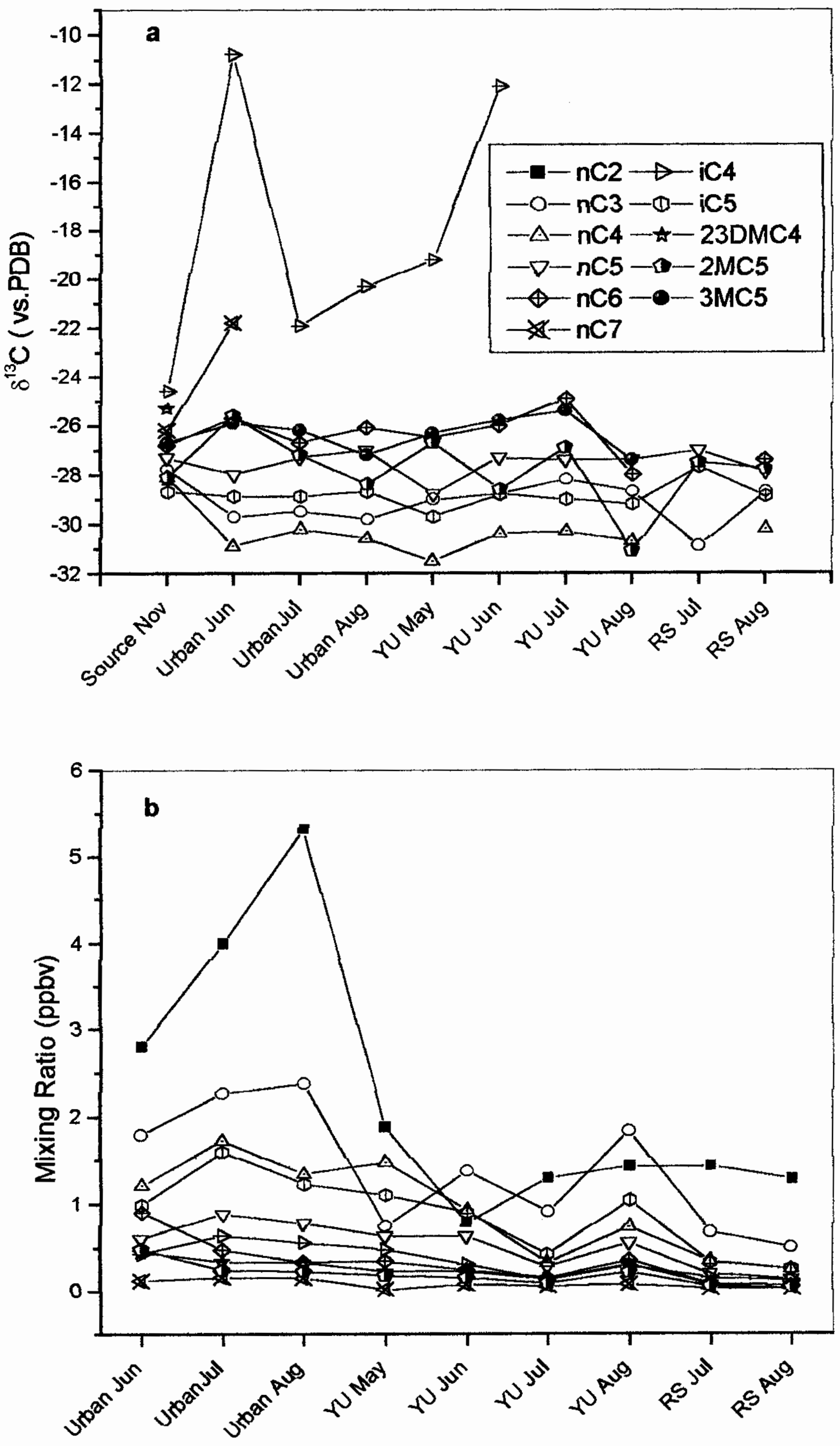

Figure 3.4: (a) Averages of stable carbon isotope ratios (‰ vs. PDB) and (b) mixing ratios (ppbv) of alkane compounds for all air parcels measured in Summer 2003.

3.3.3 Unsaturated, Cyclic and Halogenated NMHC

Unsaturated and halogenated compounds show a greater average range (5.7 ‰) in $\delta^{13}C$ compared to alkanes (3.9‰). The variability in unsaturated NMHC can be explained by the large KIE_{OH} associated with the double and triple bonds (see Table 1.2). Ethyne is most enriched in ^{13}C relative to other NMHC, whereas CH_3Cl is the least. Rudolph *et al* (2000) have been attributed to the formation of substantially enriched ethyne during incomplete combustion processes. Origins from emissions other than traffic related sources is responsible for the observed isotopic values of CH_3Cl as origins, including biomass burning, oceanic emissions and salt marsh emissions as major source sectors, are biogenic (Thompson, 2002).

In Figure 3.5 (a) for June and July months $\delta^{13}C$ are most negative in urban Toronto and, within a specific month, become increasing positive with increasing distance from the urban core. The observation is consistent with the expectation that anthropogenic emissions are greatest in urban centres and undergo photochemical processing while being transported away from the urban core.

Mixing ratios display considerable variability across samples types, with rural air containing the lowest concentrations of NMHC on average. An exception is high biogenic isoprene emissions in rural locations (see Figure 3.5 b). In July, mixing ratios decrease with distance from downtown Toronto. In other months, no significant difference between background (rural) and non background air is observed.

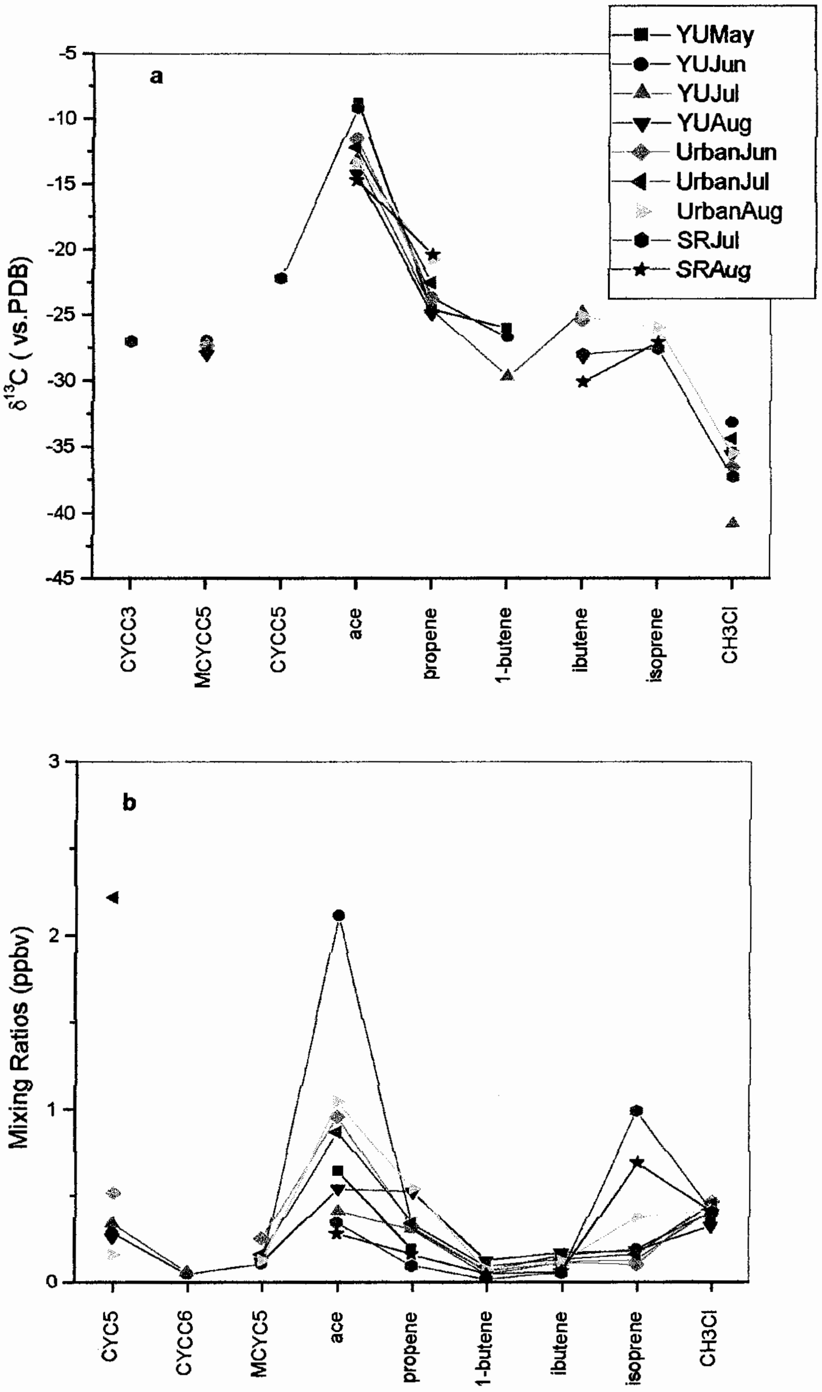

Figure 3.5: (a) Averages of stable carbon isotope ratios (‰ vs. PDB) and (b) mixing ratios (ppbv) of individual unsaturated, cyclic and halogenated nonmethane hydrocarbons in Summer 2003.

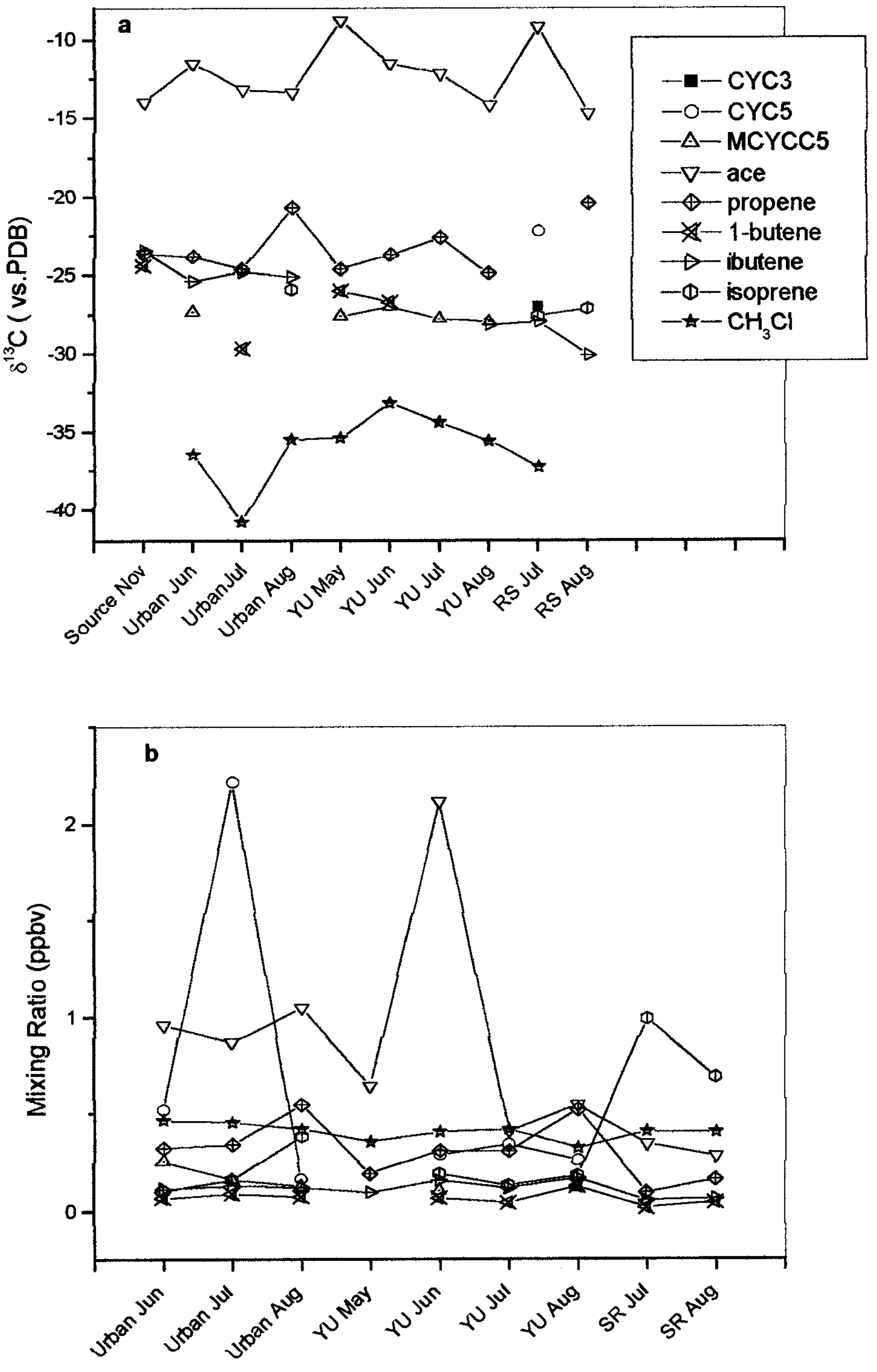

Figure 3.6: (a) Averages of stable carbon isotope ratio (‰ vs. PDB) and (b) mixing ratios (ppbv) of individual alkene, alkyne, cyclic and halogenated compounds for all air parcels in Summer 2003.

3.3.4 Aromatics

The isotopic variability (std dev = 2.5 ‰) of aromatic compounds is the smallest of all compound families (Table 3.9). The average daily range in stable carbon isotope ratio is 4.3 ‰. The isotopic composition of *o*-xylene is on average 2 ‰ heavier than *m*-xylene and *p*-xylene isomers (see Figure 3.7 a). The mean isotopic composition of benzene is the heaviest of all aromatic compounds analyzed. As with alkanes, the smallest variability in isotopic composition is in source study air parcels (See Figure 3.8 a). No overall difference in isotopic composition is observed for urban, suburban and rural air types.

The mean mixing ratios of aromatic compounds show small variability between compound and location with the exception of high toluene in urban locations (see Figure 3.7 b). The increased mixing ratios for *m*-xylene and *p*-xylene are attributed to the concentration summation for the isomers. In Figure 3.8 b, the NMHC concentration of air decreased with increasing distance from the urban core over all months.

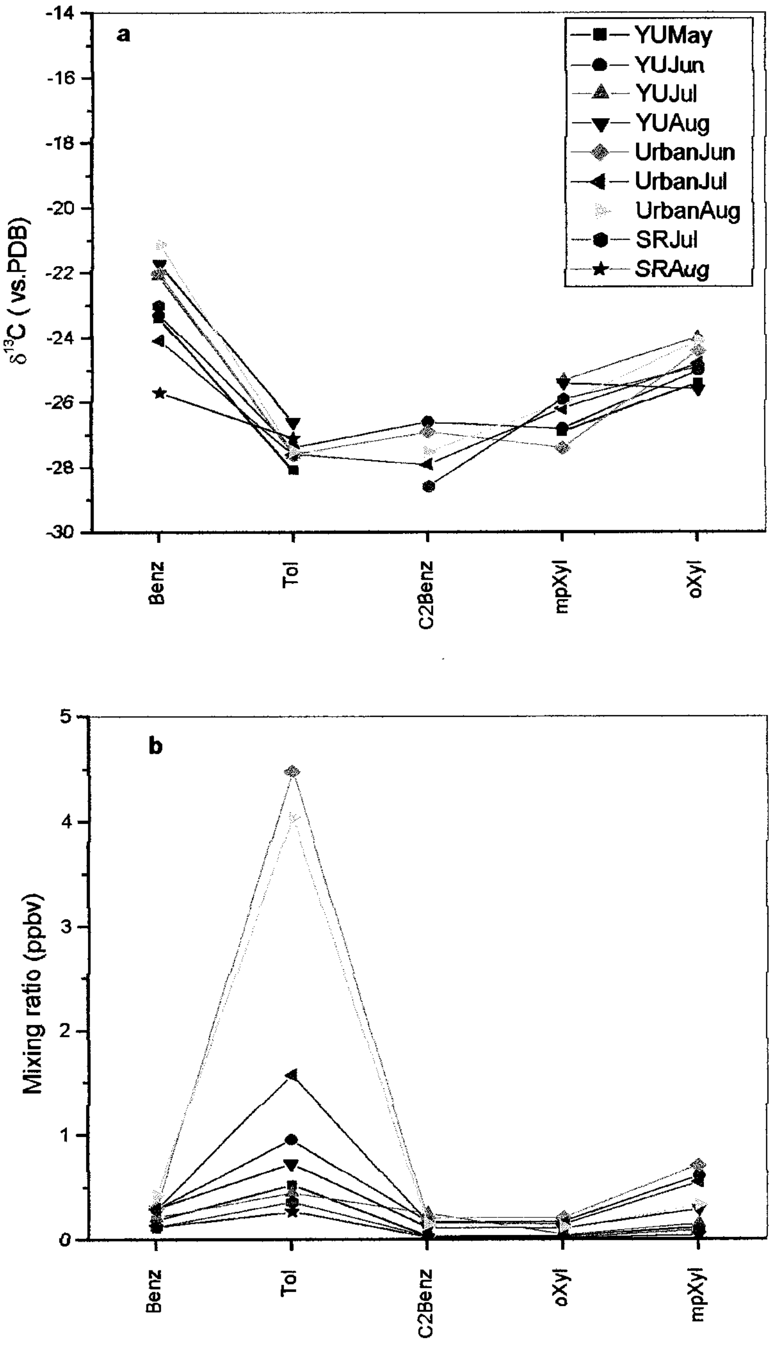

Figure 3.7: (a) Averages of stable carbon isotope ratio (‰ vs. PDB) and (b) mixing ratios (ppbv) of individual aromatic compounds in Summer 2003.

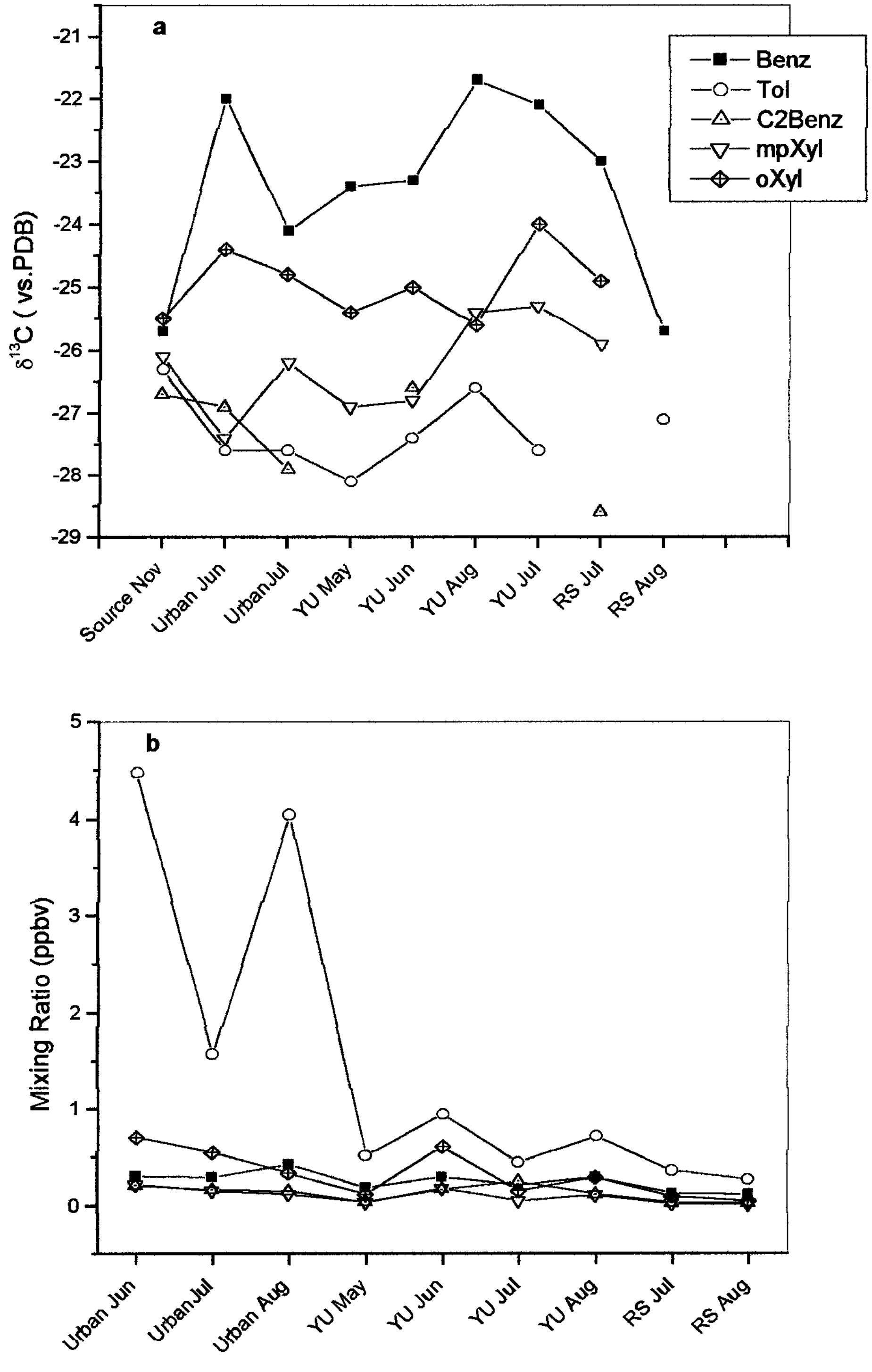

Figure 3.8: (a) Averages of stable carbon isotope ratio (in ‰ relative to PDB) and (b) mixing ratios (ppbv) of individual aromatic compounds for all air parcels in Summer 2003.

4 Discussion

4.1 Average stable carbon isotope ratio of NHMC in traffic related emissions

The analytical method described by Rudolph et al. (1997) for measuring stable isotope ratios of NMHC at ambient atmospheric concentrations has proven useful in elucidating information on atmospheric processing of the compounds (Tsunogai and Yoshida, 1999; Rudolph et al., 2000; Thompson et al., 2002; Rudolph et al., 2003). However, few papers on this subject have been reported and the information needed to interpret the isotopic measurement is extremely limited. Specifically, Rudolph and Czuba (2002) suggested that isotopic composition of NMHC can be used to determine the photochemical age of individual NMHC in a air parcel. To accurately determine the photochemical age of NMHC, the kinetic isotope effect (KIE_{OH}) of individual NMHC reacting with their primary sink, OH radicals, as well as atmospheric source carbon isotope ratio measurements must be known. Much of the ambiguity in calculating the photochemical age lies in the uncertainty associated with the stable carbon isotope ratio of source composition. In urban areas, traffic related emissions are the major source sector, accounting for 43% of NMHC emissions (Environment Canada 2003). Available information on isotope composition of traffic related sources of NMHC is limited to studies in the Greater Toronto Area and Wellington, New Zealand (Rudolph et al., 1997, 2002).

To elucidate information on the isotopic composition of NMHC source emissions, ambient air from traffic sources was collected and analyzed by the method described in Chapter 2. The following section describes in greater detail the spatial differences in results presented in Chapter 3 of samples collected in the Greater

Toronto Area and Lower Fraser Valley in November 2003. Isotopic variability of NMHC emissions caused by changes in fuel composition in the GTA are also examined.

The results of the source studies at the Union Station Overpass (GTA) and the Cassiar Tunnel (LFV) are presented in Table 4.1. Results of emission studies in the GTA by Czuba (1998) and Thompson (2003) are shown for comparison. Figure 4.1 shows the frequency distributions of the isotopic composition for all compounds families measured in the LFV and GTA. The observed distributions for all measured alkanes can be described by a Gaussian function with one standard deviation (σ) values of 3.6 ‰ and 2.0 ‰ and centers of –27.3 ‰ and –27.0 ‰ in the LFV and GTA respectively. Results for aromatic compounds show less variation in isotopic composition with values of –26.4 ± 1.6 ‰ [LFV] and –26.1 ± 0.9 ‰ [GTA]. The normal distribution of NMHC in emissions suggests no degradation by OH-radicals.

The distribution for alkenes tends to be more enriched in ^{13}C than alkane and aromatics in both locations with σ values of 1.3 ‰ and 0.8 ‰ and centers of –24.2 ‰ and –23.6 ‰ in the LFV and GTA. On average, the isotopic composition of alkenes are 3 ‰ more enriched in ^{13}C than alkane and aromatic compounds. The results are compatible with a small though statistically significant average difference of 2.4 ‰ reported by Rudolph et al (2002). Possible explanations for the shift include isotope fractionation during incomplete combustion or preferred removal of isotopically light alkenes by catalytic converters (Rudolph 2002).

In contrast to all other compounds in the study, ethyne from emissions is substantially more enriched in ^{13}C than any other NHMC in the study. The isotopic compositions of ethyne are –14.8 ± 1.0 ‰ [LFV] and -14.0 ± 2.6 ‰ [GTA] with no significant difference found between locations. When ethyne measurements are omitted from calculations of averages, the $\delta^{13}C$ average values are –26.5 ± 1.8 ‰ [GTA] and -27.1 ± 2.3 ‰ [LFV] (see Figure 4.2). The carbon isotope ratios are fully compatible with $\delta^{13}C$ values of crude oil ranging from –23.3 to –32.5‰ reported by Yeh and Epstein in 1981.

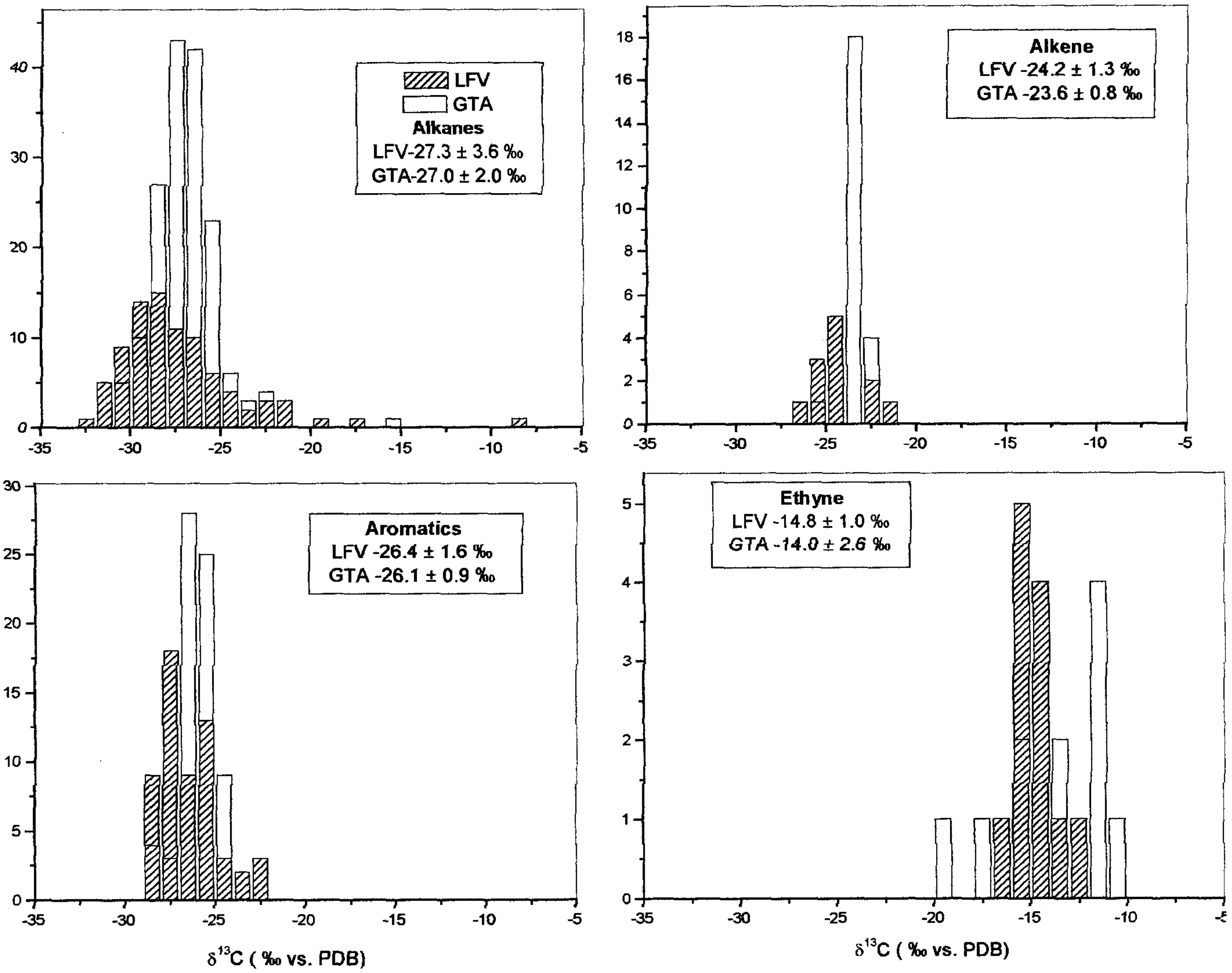

Figure 4.1: Frequency distributions of the isotopic composition over all compounds measured in the Cassiar Tunnel (LFV) and Union Station Overpass (GTA). Averages and standard deviations are given for all populations. Vertical axis is N.

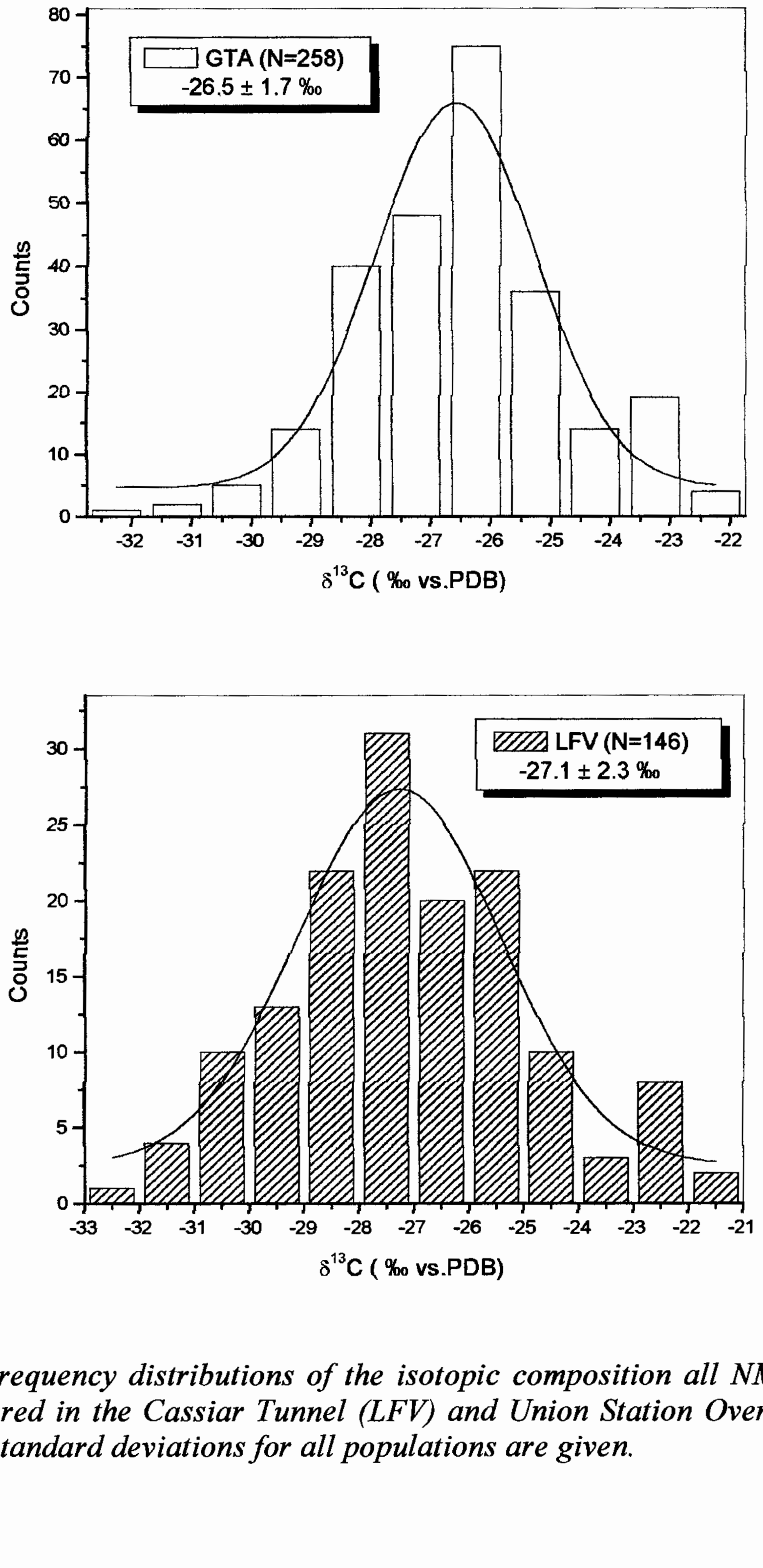

Figure 4.2: Frequency distributions of the isotopic composition all NMHC, ethyne omitted, measured in the Cassiar Tunnel (LFV) and Union Station Overpass (GTA). Averages and standard deviations for all populations are given.

Table 4.1: Averages and standard deviations of stable carbon isotope ratio (in ‰ relative to PDB) for NMHC at locations influenced by transport related emissions in the GTA (Union Station) and LFV (Cassiar Tunnel). Isotopic composition measurements made by Czuba in 1999 (b) and Thompson in 2003 (c) are shown for comparison.

COMPOUND	CASSIAR TUNNEL NOVEMBER 2003 (N=16)	UNION STATION NOVEMBER 2003 (N=16)	TORONTO TUNNEL JANUARY 1998 (N=3)[B]	TORONTO TUNNEL AUGUST 1998 (N=3)[B]	TORONTO TUNNEL FEBRUARY 2001 (N=2)[C]	TORONTO TUNNEL SEPTEMBER 2000 (N=6)[C]
Propane	-30.8 ± 0.9	-27.8 ± 1.3		-25.0 ± 4.3		-25.6 ± 0.9
n-Butane	-29.7 ± 1.1	-28.1 ± 0.4		-30.6 ± 1.2		
n-Pentane	-28.6 ± 0.7	-27.3 ± 0.4	-27.7 ± 1.1	-29.0 ± 1.1	-27.0	-25.5
n-Hexane	-26.6 ± 0.9	-26.8 ± 0.8	-25.5 ± 1.1	-26.4±1.8		
n-Heptane	-26.0 ± 1.5	-26.2 ± 0.4	-25.7 ±1.0		-26.9 ± 2.5	-24.1 ± 2.7
Ethyne	-14.8 ± 1.0	-14.0 ± 2.6			-16.8 ± 2.1	-10.2 ± 2.0
Propene	-24.2 ± 1.3	-23.6 ± 0.5	-25.2 ± 1.9		-22.4	-23.4
i-butene	-24.2 ± 1.5	-24.4 ± 1.4		-22.2 ± 1.6		
1-butene		-23.4 ± 0.9		-26.8 ± 3.1		
i-Butane	-24.4 ± 2.2	-24.6 ± 3.3				
i-Pentane	-29.7 ± 0.4	-28.7 ± 0.4	-28.7 ± 1.2	-29.7 ± 0.5		-27.4
i-Octane	-26.9 ± 1.6	-28.4 ± 2.0		-30.4 ± 1.0		
2,3-Dimethylbutane		-25.2 ± 0.5	-28.5 ± 0.6			
2-Methylpentane	-27.8 ± 0.9	-28.1 ± 0.7	-27.7 ±0.7	-29.1± 0.7		
3-Methylpentane	-26.9 ± 0.4	-26.7 ± 1.0	-27.7 ± 2.0	-28.1 ± 0.2		
Benzene	-24.3 ± 1.6	-25.7 ± 1.5	-27.0 ±1.4	-26.6 ±1.1	-26.1 ± 0.8	-24.5 ± 1.2
Toluene	-27.3 ± 0.7	-26.3 ± 0.3	-27.4 ± 1.1	-27.7 ±1.1	-27.2 ± 0.3	-25.7 ± 1.5
Ethylbenzene	-27.9 ± 0.4	-26.6 ± 0.9	-26.8 ± 1.1	-27.0	-24.3 ± 0.5	-25.4 ± 1.2
m + p-Xylene	-25.7 ± 1.5	-26.1 ± 0.6	-26.9 ± 3.0	-26.8 ±0.8	-27.3 ± 0.1	-26.6 ± 0.5
o-Xylene	-26.2 ± 0.7	-25.5 ± 0.5	-27.3± 0.6	-27.4 ± 0.4	-24.9 ± 0.2	-23.5 ± 1.0
Total average	-25.9 ± 4.2	-25.7 ± 3.5				
Total average[a]	-27.1 ± 2.3	-26.5 ± 1.8				
n-alkanes	-27.4 ± 4.0	-27.0 ± 1.6			-28.0 ± 2.0	-25.5 ± 2.0
i-alkanes	-27.1 ± 3.1	-26.7 ± 3.1				-27.5 ± 0.8
Alkanes	-27.3 ± 3.6	-27.0 ± 2.0				-25.7 ± 2.1
Alkenes	-24.2 ± 1.3	-23.6 ± 0.8			-21.7 ± 1.4	-21.9 ± 2.1
Aromatic	-26.4 ± 1.6	-26.1 ± 0.9			-25.9 ± 1.5	-25.4 ± 1.6

[a] Total average omitting ethyne measurements, b Rudolph et al. 2003, c Thompson 2003.

Due to high concentrations of unprocessed emissions, it is assumed that photochemical aged NMHC collected at close proximity to source emission have minimal effects on carbon isotopic composition. To satisfy this assumption, concentrations of samples were considered in the simple linear mixing model described in Equation 4.1. Assuming the only influence on the concentration and stable carbon isotope ratios is mixing of background and source emissions, the measured isotope ratio is a function of the concentration of the sample at the time of collection. Figure 4.3 shows a mixing model that predicts, over a range of concentration ratios, the change in isotopic ratio of the sample from the source value caused by sample mixing with background air. Background air is arbitrarily assigned $\delta^{13}C$ values that are 5 ‰, 10 ‰ , 15 ‰, and 20 ‰ more deplete in ^{12}C than the $\delta^{13}C$ of the source emissions. The model predicts that for sample with NMHC concentrations that are 30 time greater than background levels, to cause a difference in $\delta^{13}C$ that is greater than the sampling and analytical experiment uncertainty (0.5 ‰), the values of the background air would have to be 10 ‰ heavier than the sample. Considering source emission mixing ratios were on average a factor of ten greater than mixing ratios found in GTA ambient urban air (see Section 3.1.1), background air would have to be 5 ‰ heavier than the sample to cause a 0.5 ‰ change (Thompson 2003).

$$\text{Eq 4.1} \quad \delta^{13}C_{sample} = \frac{\delta^{13}C_{background} \times [NMHC]_{background} + \delta^{13}C_{source} \times [NMHC]_{source}}{[NMHC]_{sample}}$$

Given the elevated mixing ratios found in source studies and that variations in the isotopic range of a NMHC is, on average 4.6 ‰ and seldom exceed the 5 ‰, it is likely that mixing with background air has minimal effect on the isotopic composition of emissions. However, the possibility that tunnel samples were impacted by mixing of air parcels from other nearby sources cannot be ruled out.

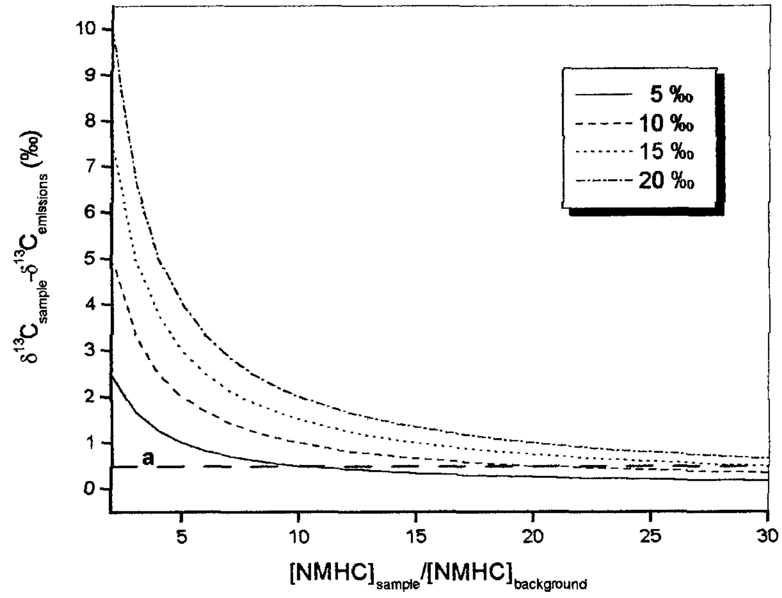

Figure 4.3: Mixing model of the change caused by sample mixing with background air over a range of concentration ratios for a compound that is 5 ‰, 10 ‰, 15 ‰ and 20 ‰ more enriched in the background air compared to source emissions. The experimental uncertainty (0.5 ‰) is shown by the dashed line labelled (a).

4.1.2 Spatial Differences in Stable Carbon Isotope Ratios

The average isotope ratio of NMHC in this study does not exhibit a significant difference between locations: –25.7 ± 3.5 ‰ and -25.9 ± 4.2. ‰ (relative to PDB) in the GTA and the LFV respectively. Despite the small spread in isotopic composition of NMHC between locations, differences for individual compounds are evident. Propane, *n*-pentane and *iso*-pentane, toluene and ethylbenzene exhibit differences between locations at the 95% significance level (Figures 4.4 and 4.5). All compounds are heavier in emissions in the Greater Toronto Area. A similar comparison was made by Thompson (2003) between tunnel samples taken in Toronto and samples taken from a tunnel site in Wellington, New Zealand (Rudolph et al. 2002, 1997). Thompson found that no significant difference existed in samples over all compounds studied with the exception of propane and *m,p*-xylene where a 1.6 ± 1.3 ‰ difference was found. Given that systematic differences between the isotopic composition of fossil fuels with location exist (Sofer 1984, Epstein 1981), the more negative isotopic values found in the LFV are most likely due to differences in fuel compositions. Given the normal distribution of compound specific isotope ratios, it is unlikely that degradation by OH radicals and/or other sinks contribute to the shift in mean isotope ratio between locations.

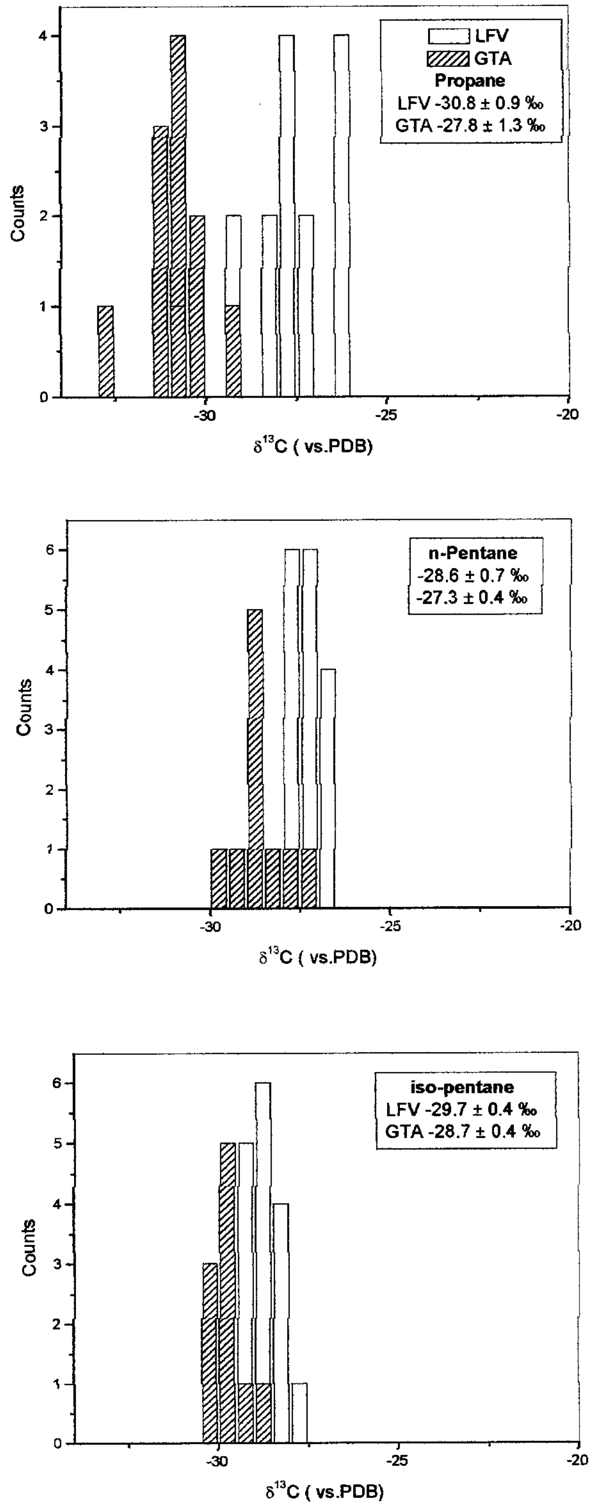

Figure 4.4: Frequency distribution of the isotopic composition of alkanes showing significant differences in LFV and GTA tunnel samples. Averages and standard deviations are shown.

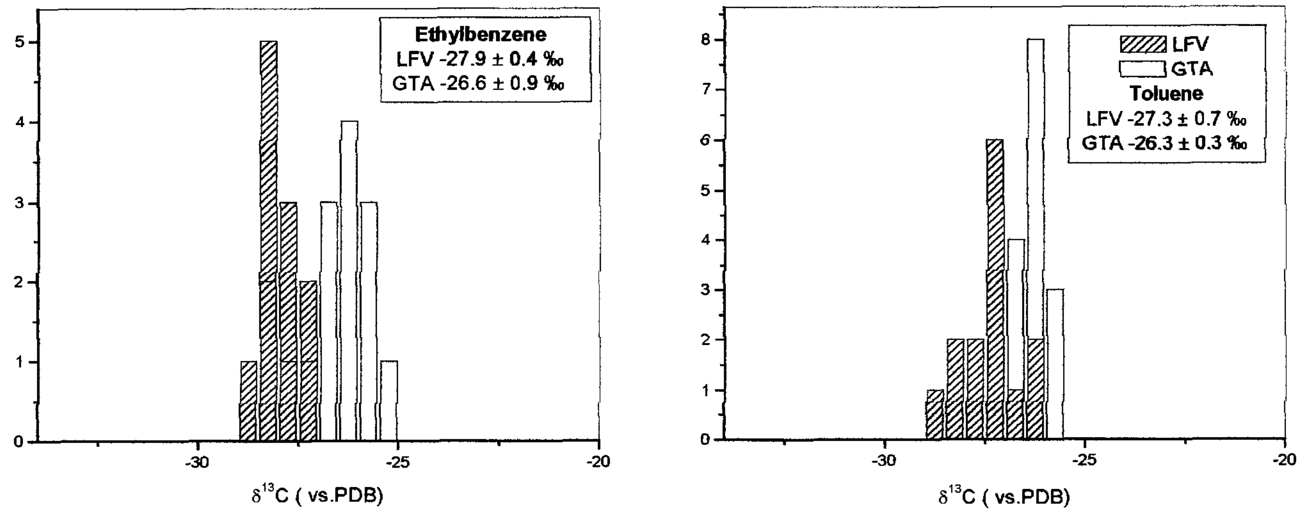

Figure 4.5: Frequency distribution of the isotopic composition of aromatics showing significant differences in LFV and GTA tunnel samples. Counts are represented on the vertical axis. Averages and standard deviations are shown. Vertical axis is N.

A correlation matrices showing the Pearson's correlation coefficients (R) for each sample pair of variables is shown in Table 4.2 for the LFV and GTA. For the construction of the matrix, 16 ambient air samples of source emissions were used. For, R-values subscripted with double asterisk there is a 99.9% confidence that the coefficient is in fact smaller or higher than zero. The values subscripted with a single asterisk have a confidence level of 99.5% (2-tailed F-test). N designates the number of samples in the dataset. For half the combinations of straight chain alkanes in GTA samples, a direct linear relationship exists (r=.578-0.788). In the LFV only propene, n-hexane and n-heptane exhibit significant correlation at the 99.9% confidence level. Unfortunately, given the small number of discrete measurements in the LFV, the results are of low significance.

Whiticar & Snowdon (1999) have applied compound specific isotope correlations as a diagnostic tool for petroleum characterization. Specifically, the isotopic separation between n-alkanes ($\delta^{13}C_5$- $\delta^{13}C_6$;$\delta^{13}C_5$-$\delta^{13}C_7$, etc.) can distinguish between oils of different sources because they are expected to have a systematic offset based on generation from a similar kerogen type and thermal history. However, alkane differences in this study show no systematic offset.

NMHC exhibiting significant correlation in both the GTA and LFV are shown in Figure 4.6. For C_6 isomers there is no difference in isotopic composition between locations (see Figure 4.6 a). In Figure 4.6 (b) and (c) there is considerable shift between GTA (open circles) towards heavier isotopic ratios relative to LFV (dark squares). The shift may be attributed to (1) atmospheric degradation due to OH-radical processing or and (2) differences in source material. Considering the normal distribution in isotope ratios, the shift is most likely caused by differences in source material. However, given the small sample number and the experimental uncertainty (0.5‰), it is inconclusive as to what is contributing to the shifts in isotope ratios between locations. In Figure 4.6, isotope ratios from the ambient air collected in the GTA are plotted for comparison. Samples were plotted because they are more concentrated and ^{12}C enriched than samples collected immediately prior, suggesting recent emission events. Isotope ratios of iso-pentane in ambient air are within the range of November emissions, however toluene and n-pentane are enriched in ^{12}C. The offset suggests contribution from sources other than traffic related emissions and/or temporal differences in source emissions. In this study there is no depletion in

^{13}C for *n*-pentane versus *iso*-pentane that is greater than the experimental uncertainty for these compounds in either the GTA or the LFV.

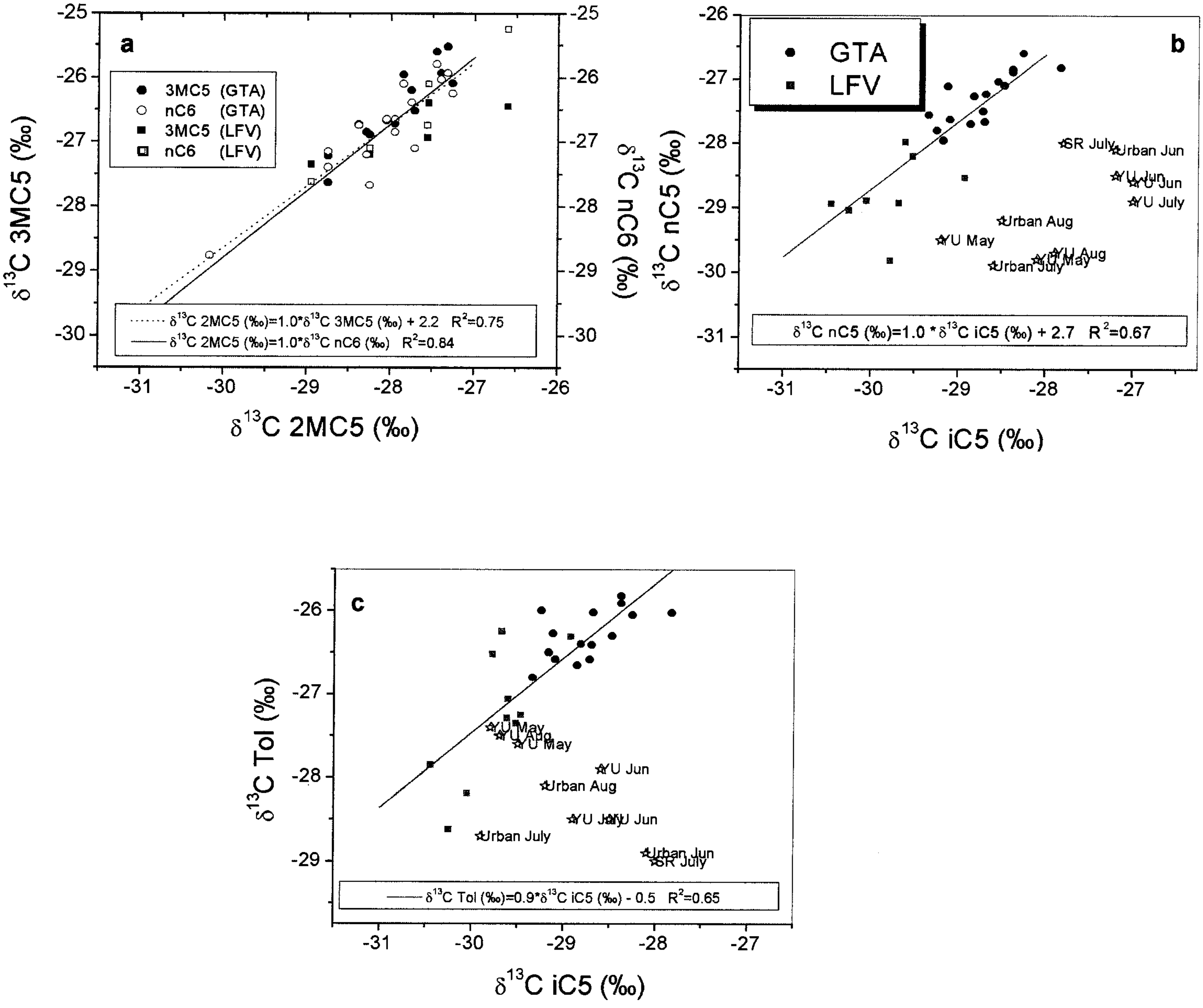

Figure 4.6: NMHC showing linear correlations in the GTA (circles) and LFV (square). In (b) and (c), isotope ratios of NMHC in GTA ambient air are shown for comparison.

Table 4.2: Union Station correlation matrix showing the Pearson's correlation coefficients (R) for each pair of variables, with the negative correlations showing up as negative numbers. For the construction of the matrix 16 ambient air samples taken at Union Station Overpass were used. For the R-values subscripted by a double asterisk there is a 99.9% confidence that the coefficient is in fact smaller or higher than zero. The values subscripted by a single asterisk have a confidence level of 99.5% (2-tailed F-test). N designates the number of samples in the dataset.

		ace	nC3	propene	iC4	nC4	iC5	nC5	23DMC4	2MC5	3MC5	nC6	nC7	Benz	nC8	Tol	C2Benz	M.pXyl	oxyl
ace	Cor.	1																	
	N	16																	
nC3	Cor.	.221	1																
	N	15	15																
propene	Cor.	-.455	.352	1															
	N	16	15	16															
iC4	Cor.	.056	.079	-.147	1														
	N	15	14	15	15														
nC4	Cor.	.020	-.003	.065	-.008	1													
	N	14	13	14	13	14													
iC5	Cor.	.352	.151	-.084	.262	.355	1												
	N	16	15	16	15	14	16												
nC5	Cor.	.459	.286	-.027	.151	.531	.787(**)	1											
	N	16	15	16	15	14	16	16											
23DMC4	Cor.	.212	.143	-.257	.170	.609	.704(*)	.788(**)	1										
	N	11	11	11	10	10	11	11	11										
2MC5	Cor.	.567(*)	.202	-.253	-.336	.260	.426	.539(*)	.858(**)	1									
	N	16	15	16	15	14	16	16	11	16									
3MC5	Cor.	.573(*)	.115	-.210	-.391	.286	.275	.498(*)	.797(**)	.963(**)	1								
	N	16	15	16	15	14	16	16	11	16	16								
nC6	Cor.	.562(*)	.153	-.079	-.401	.285	.331	.525(*)	.617(*)	.897(**)	.936(**)	1							
	N	16	15	16	15	14	16	16	11	16	16	16							
nC7	Cor.	.123	-.032	-.187	.474	.578(*)	.579(*)	.750(**)	.845(**)	.227	.184	.267	1						
	N	14	13	14	13	12	14	14	9	14	14	14	14						
Benz	Cor.	.596(*)	.332	-.074	.064	.178	.478	.678(**)	.334	.589(*)	.529(*)	.456	.456	1					
	N	15	14	15	14	13	15	15	10	15	15	15	14	15					
nC8	Cor.	.845(**)	.237	-.288	.041	.286	.510	.686(**)	.466	.670(**)	.618(*)	.579(*)	.386	.943(**)	1				
	N	14	13	14	13	12	14	14	10	14	14	14	13	13	14				
Tol	Cor.	.530(*)	.053	-.204	.030	.258	.596(*)	.659(**)	.570	.469	.414	.433	.463	.726(**)	.762(**)	1			
	N	15	14	15	14	14	15	15	10	15	15	15	13	14	13	15			
C2Benz	Cor.	.553(*)	.541(*)	-.183	-.058	.005	.043	.104	.222	.514	.438	.458	-	.372	.495	.227	1		
	N	15	14	15	14	13	15	15	10	15	15	15	13	14	13	14	15		
x.m-Xyl	Cor.	-.561(*)	-.085	.382	-.438	.403	.149	-.055	.273	.054	.007	-.015	-	-.194	-.304	.173	-.283	1	
	N	13	12	13	12	11	13	13	8	13	13	13	11	12	11	12	13	13	
o-Xyl	Cor.	.095	.402	-.052	.242	.001	.163	-.059	.276	-.103	-.232	-.154	.056	.123	.184	-	.595	-.084	1
	N	11	11	11	10	9	11	11	7	11	11	11	9	10	9	10	11	11	11

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

Table 4.3: Cassiar correlation matrix showing the Pearson's correlation coefficients (R) for each pair of variables, with the negative correlations showing up as negative numbers. For the contruction of the matrix 16 ambient air samples taken at Cassiar were used. For the R-values subscripted by a double asterisk there is a 99.9% confidence that the coefficient is in fact smaller or higher than zero. The values subscripted by a single asterisk have a confidence level of 99.5% (2-tailed F-test). N designates the number of samples in the dataset.

		ace	nC3	propene	iC4	nC4	iC5	nC5	2MC5	3MC5	nC6	nC7	Benz	nC8	Tol	C2Benz	mpXyl	oXyl
ace	Pearson	1																
	N	12																
nC3	Pearson	.669(*)	1															
	N	11	11															
propene	Pearson	.596	.901(**)	1														
	N	9	9	9														
iC4	Pearson	.230	.382	.657	1													
	N	10	10	9	10													
nC4	Pearson	.079	.599	.134	.537	1												
	N	11	11	9	10	11												
iC5	Pearson	-.143	-.065	.158	.611	.405	1											
	N	10	10	8	9	10	10											
nC5	Pearson	-.042	-.031	-.312	.371	.403	.364	1										
	N	10	10	9	9	10	9	10										
2MC5	Pearson	-.126	-.113	.195	-.788	-.484	-.825	-.433	1									
	N	5	5	5	5	5	4	5	5									
3MC5	Pearson	-.179	.340	.446	-.743	-.126	-.909	-.626	.863	1								
	N	5	5	5	5	5	4	5	5	5								
nC6	Pearson	-.094	.152	.450	-.703	-.460	-.931	-.653	.962(**)	.927(*)	1							
	N	5	5	5	5	5	4	5	5	5	5							
nC7	Pearson	.089	.541	.858(*)	.564	.116	.436	-.434	.966(**)	.939(*)	.989(**)	1						
	N	6	6	6	6	6	5	6	5	5	5	6						
Benz	Pearson	.404	.829(*)	.858(*)	.643	.344	.436	-.374	-.189	.803	.245	.736	1					
	N	7	6	6	6	6	5	6	3	3	3	4	8					
nC8	Pearson	-.420	.501	.022	-.843	.939	.455	.006	-.114	.463	-.014	.051	.713	1				
	N	4	4	4	4	4	3	4	4	4	4	4	3	4				
Tol	Pearson	-.618(*)	-.419	-.024	.354	.196	.722(*)	-.012	-.842	-.559	-.828	.606	-.030	.679	1			
	N	12	11	9	10	11	10	10	5	5	5	6	8	4	14			
C2Benz	Pearson	-.238	-.431	-.691	-.200	-.196	-.182	.535	-.581	-.880(*)	-.727	-.671	-.832	-.568	-.004	1		
	N	10	9	7	8	9	8	8	5	5	5	6	5	4	11	11		
x.m-Xyl	Pearson	-.011	.478	.722	.611	.524	.659	-.094	-.092	.478	.283	.916(*)	.555	.903	.403	-.478	1	
	N	10	9	7	8	9	8	8	4	4	4	5	6	3	12	10	12	
o-Xyl	Pearson	-.155	.090	.202	.637	.612	.487	.411	-.848	-.765	-.784	.089	-.657	.763	.435	.480	.172	1
	N	10	9	7	8	9	9	8	4	4	4	5	6	3	12	10	11	12

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

Table 4.4: The Pearson's correlation coefficients (R) for each pair of variables showing significant correlation, with the negative correlations showing up as negative numbers. For the R-values subscripted by a double asterisk there is a 99.9% confidence that the coefficient is in fact smaller or higher than zero. The values subscripted by a single asterisk have a confidence level of 99.5% (2-tailed F-test). N designates the number of samples in the dataset.

LFV		
Compound Pair	**Pearson Cor.**	**N**
nC3/ace	0.669(*)	11
Propene/nC3	0.901(**)	9
NC6/2MC5	0.962(**)	5
NC6/3MC5	0.927(*)	5
NC7/propene	0.858(*)	6
NC7/2MC5	0.966(**)	5
NC7/3MC5	0.939(*)	5
Benz/MC3	0.829(*)	6
Benz/propene	0.858(*)	6
Tol/ace	-0.618(*)	12
Tol/iC5	0.722(*)	10
C2Benz/3MC5	-0.880(*)	5
Xm-xyl/NC7	0.916(*)	5

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

GTA		
Compound Pair	**Pearson Cor.**	**N**
NC5/iC5	0.787(**)	16
23DMC4/iC5	0.704(*)	11
23DMC4/nC5	0.788(**)	11
2MC5/ace	0.567(*)	16
2MC5/nC5	0.539(*)	16
2MC5/23DMC4	0.858(**)	11
3MC5/ace	0.573(*)	16
3MC5/nC5	0.498(*)	16
3MC5/23DMC4	0.797(**)	11
3MC5/2MC5	0.963(**)	16
NC6/ace	0.562(*)	16
NC6/nC5	0.525(*)	16
NC6/23DMC4	0.617(*)	11
NC6/2MC5	0.897(**)	16
NC6/3MC5	0.936(**)	16
NC7/nC4	0.578(*)	12
NC7/iC5	0.579(*)	14
NC7/nC5	0.750(**)	14
NC7/23DMC4	0.845(**)	9
Benz/ace	0.596(*)	15
Benz/nC5	0.678(**)	15
Benz/2MC5	0.589(*)	15
Benz/3MC5	0.529(*)	15
NC8/ace	0.845(**)	14
NC8/nC5	0.686(**)	14
NC8/2MC5	0.670(**)	14
NC8/3MC5	0.618(*)	14
NC8/nC6	0.579(*)	14
NC8/Benz	0.943(**)	13
Tol/ace	0.530(*)	15
Tol/iC5	0.596(*)	15
Tol/nC5	0.659(**)	15
Tol/Benz	0.726(**)	14
Tol/nC8	0.762(**)	13
C2Benz/ace	0.553(*)	15
C2Benz/nC3	0.541(*)	14
Xm-Xyl/ace	-0.561(*)	13

4.1.3 Temporal Difference in Isotopic Composition of Source Emissions

In Canada, fuel composition is altered to suit regional temperature conditions (Canadian Petroleum Products Institute 1993). To investigate isotopic variability resulting from changes in fuel composition, the November 2003 emission study was compared to tunnel studies in the GTA by Czuba 1999 (January and August 1998) and Thompson 2002 (August 2000 and February 2001). Anova results show differences in monthly means and standards deviations at the 95% significance level for the compounds shown in Figure 4.7. Although differences for individual NMHC were found, no systematic changes in isotopic composition between months was observed. Given the limited sample size, it is inconclusive whether changes in fuel composition with season cause any significant shift towards heavier or lighter isotopic ratios.

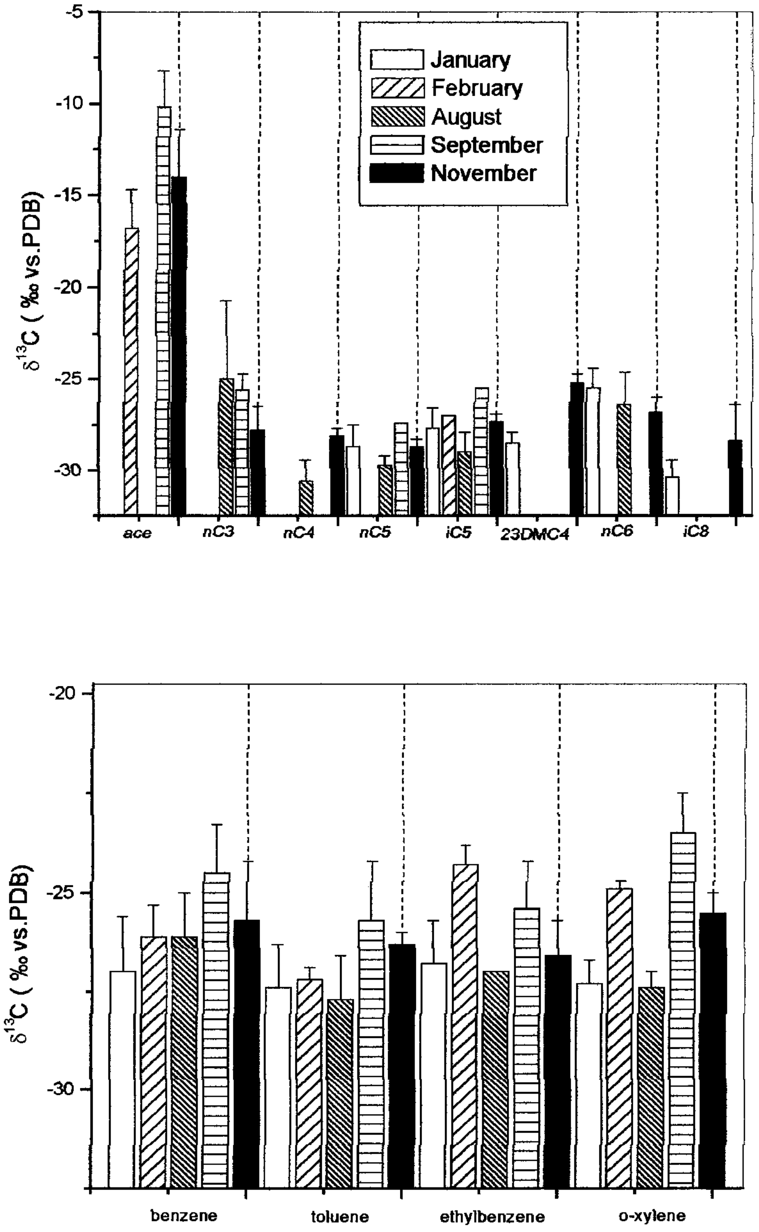

Figure 4.7: Average isotopic ratios for each month of NMHC showing significant temporal differences in GTA tunnel samples. Error bars show standard deviations of measurement.

4.2 Diurnal Cycles

Diurnal variations in the stable carbon isotope ratios and mixing ratios of NMHC from ambient air samples collected at York University in the summer of 2003 are discussed in the following section. Photochemical ages of NMHC in these samples are derived using the isotopic hydrocarbon clock method first described by Rudolph *et al.* in 2000. The average photochemical age of NMHC in air samples collected at York University during the summer of 2003 is 10^{11} cm^{-3} s.

Based on derived photochemical ages, the use of NMHC as probes for long range transport and local atmospheric events is discussed. From the maximum observed compound specific photochemical age it is concluded that NMHC with low OH• reactivity (e.g. benzene) are appropriate for probing long range atmospheric processes, whereas short lived compounds such as toluene are appropriate for probing local events.

4.2.2 Diurnal Variations in Mixing Ratios

The concentration data for a diurnal study conducted at York University are presented in Figures 4.8-4.11. Samples were analyzed according to the analytical method outlined in Chapter 2. Complete data is listed in Appendix 1. Figures 4.8-4.11 are comprised of representative plots of NMHC mixing ratios and isotope ratios for which photochemical processing data are available. Between 0600 local time (LT) and 2000 LT, an average coefficient of variance of 85% was observed in NMHC mixing ratios at a set location in all months investigated. Early morning concentration conditions of NMHC are, on average, a factor of ten higher than midday conditions. The high morning concentrations have been attributed to the accumulation of NMHC at night during the formation of a stable inversion layer (Rudolph 2002). The largest average range in daily mixing ratios of 1.4 ppb was observed in the month of June. In June, the largest variation in daily temperature and the greatest maximum temperatures is observed (Figure 4.12). The mixing ratios of all compounds show a noon hour minimum that has been attributed to fast atmospheric removal and dispersion of gases (Rudolph 2000). In conjunction with temperature variations, mixing ratio results support a hypothesis of increased horizontal convection associated with high surface temperatures

It is known that seasonal variations in NMHC may be influenced by one or all of three factors: (1) seasonal abundance of the OH radicals caused by seasonal abundance of solar insolation, (2) changing hydrocarbon source strengths, and (3) changing atmospheric mixing patterns such as enhancement of vertical mixing through increased convection during summer months (Singn and Zimmerman, 1992). However, with few exceptions, no significant difference in the mean mixing ratios of NMHC between months in the Summer 2003 GTA study was observed (see Section 3.1.3). Similar summer seasonal effects reported by Cheng et al. (1997) for studies conducted in Edmonton have been accounted for by increased industrial emissions in summer months.

4.2.3 Diurnal Variations in Isotopic Ratios

Diurnal variations in NMHC isotopic composition are presented in Figures 4.8-4.11. Samples were analyzed according to the analytical method outlined in Chapter 2. The largest daily range in isotopic composition observed was 25‰ for ethyne. For volatile alkanes of relatively high atomic mass (nC_5 and nC_6), the smallest range was observed (0‰-5‰). No significant correlation was found between concentration and isotopic composition, with the exceptions of *iso*-pentane and ethyne, with correlation coefficients of (–0.35) and (–0.79) respectively.

NMHC atmospheric mixing ratios in midday conditions are often lower than the IRMS instrumental detection limits. However, when concentrations in midday conditions are high enough for accurate instrumental detection, the isotope ratio are enriched in ^{12}C relative to other isotope ratios for the investigated compound. The enrichment in ^{12}C is therefore indicative of a recent emission event (Figures 4.8-4.11). Unexpected by Rayleigh fractionation, the addition of recent emissions to an air parcel causes NMHC mixing ratios to be independent of carbon isotope ratios. Mixing of air parcels containing NMHC with different compound specific carbon isotope ratios would also result in air parcels containing NMHC with carbon isotope ratios that are independent of concentration measurements.

For comparison, in Figures 4.8-4.11, the isotopic compositions (solid lines) and standard deviations (dashed lines) of NMHC in traffic related emissions collected in the GTA in November 2003 are shown. As predicted by the Rayleigh Equation (Equation 1.13), the preferential abstraction of ^{12}C from NMHC by OH radicals results in a NMHC air sample deplete in ^{12}C relative to initial source material. All compounds, however, with the exceptions of benzene and ethyne, exhibit ambient isotopic composition more enriched in ^{12}C than the lower limits of traffic related emissions (see Table 4.1 in Section 4.1). As the preferential abstraction of ^{12}C results in a ^{13}C enriched atmospheric NMHC sample pool, ambient NMHC more enriched in

^{12}C than the lower limits of traffic related emissions reflect uncertainty in source assignment.

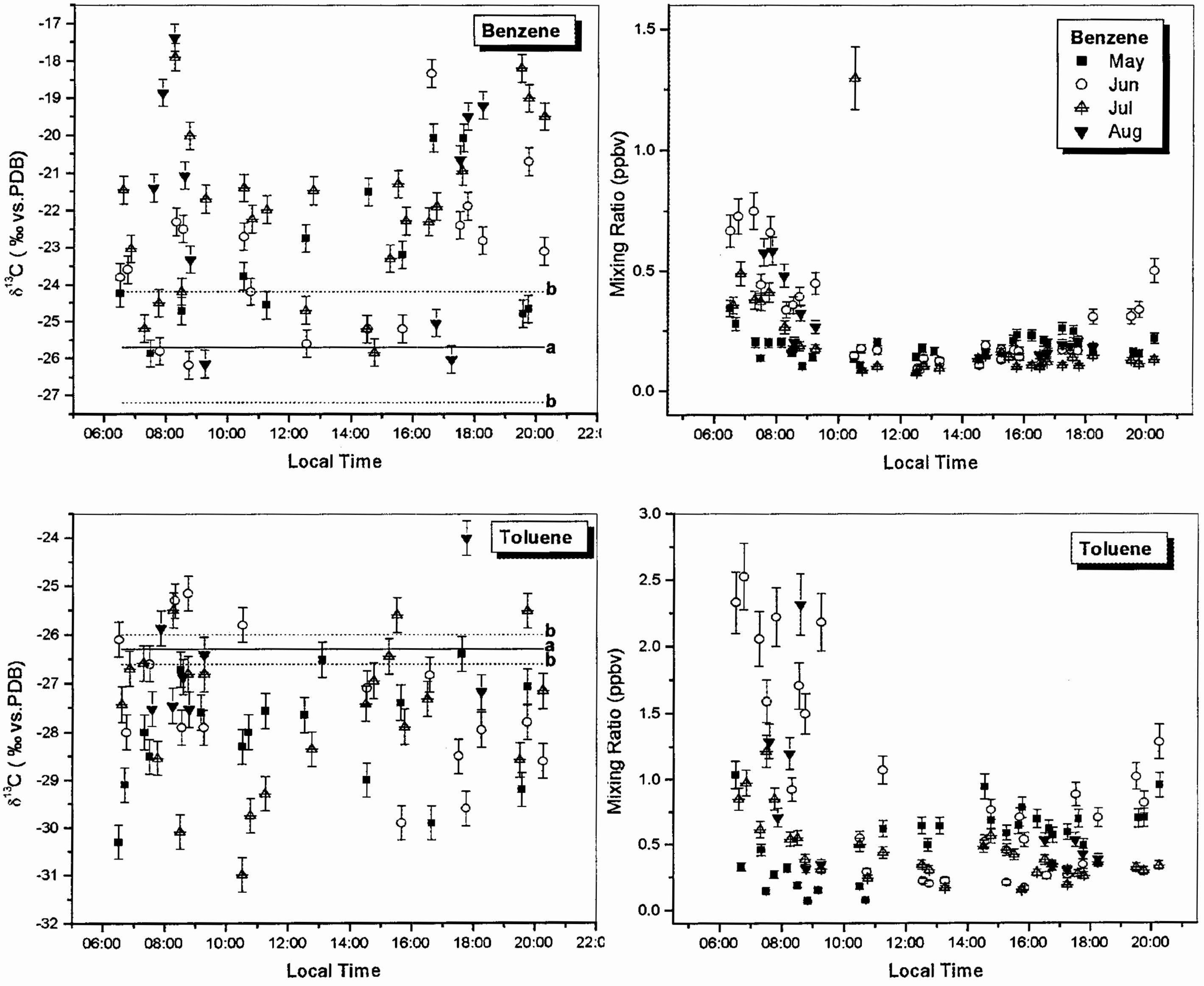

Figure 4.8: Diurnal variations in isotope ratios and mixing ratios of benzene and toluene measured at York University in May (dark squares), June (open circle), July (hatched triangles) and August (dark triangles) 2003. The unbroken line (a) is the isotopic ratios for Nov 2003 source study. Dashed lines (b) are the standard deviations of the source emissions.

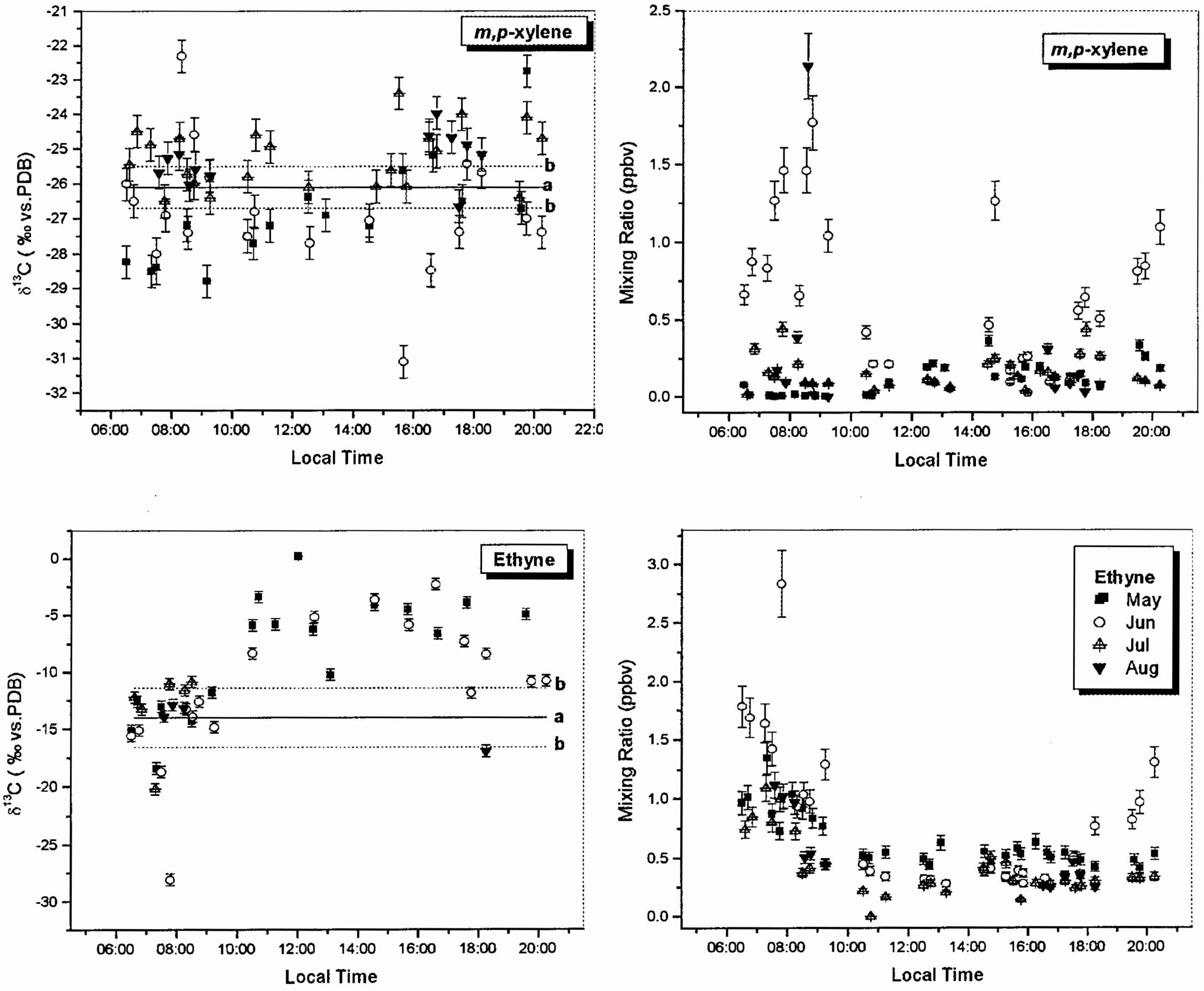

Figure 4.9: Diurnal variations in isotope ratios and mixing ratios of m,p-xylenes and ethyne measured at York University in May (dark squares), June (open circles), July (hatched triangles) and August (dark triangles) 2003. The unbroken line (a) is the isotopic ratios for Nov 2003 source study. Dashed lines (b) are the standard deviations of the source emissions.

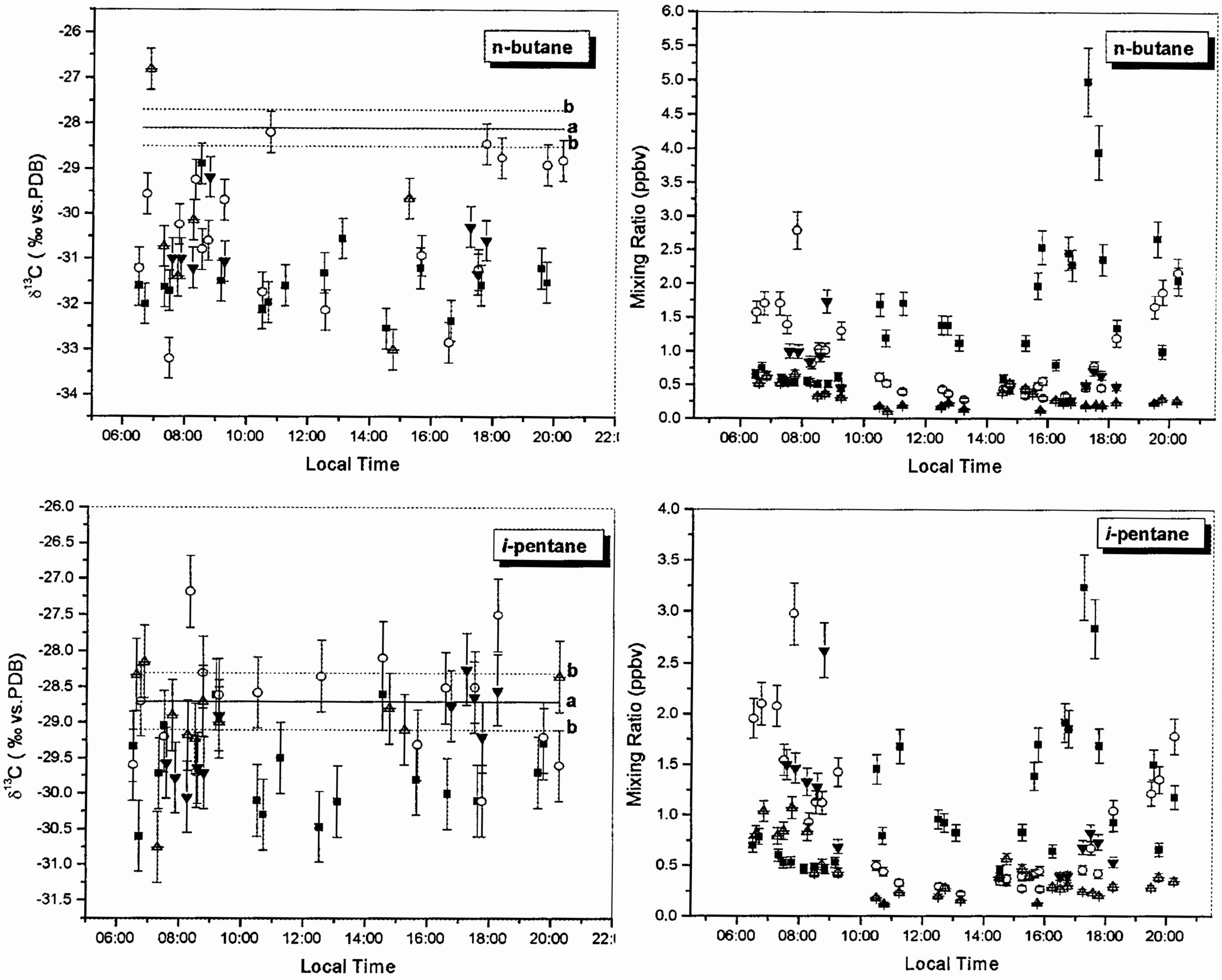

Figure 4.10: Diurnal variations in isotope ratios and mixing ratios of n-butane and iso-pentane measured at York University in May (dark squares), June (open circle), July (hatched triangles) and August (dark triangles) 2003. The unbroken line (a) is the isotopic ratios for Nov 2003 source study. Dashed lines (b) are the standard deviations of the source emissions.

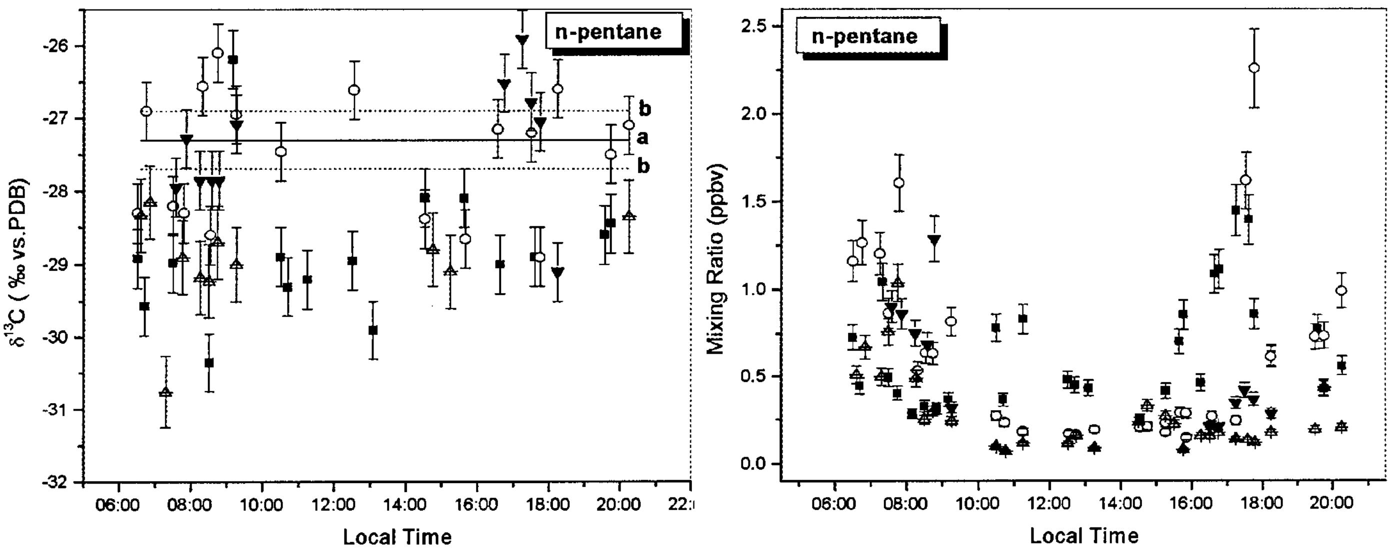

Figure 4.11: Diurnal variations in isotope ratios and mixing ratios of n-pentane measured at York University in May (dark squares), June (open circle), July (hatched triangles) and August (dark triangles) 2003. The unbroken line (a) is the isotopic ratios for Nov 2003 source study. Dashed lines (b) are the standard deviations of the source emissions.

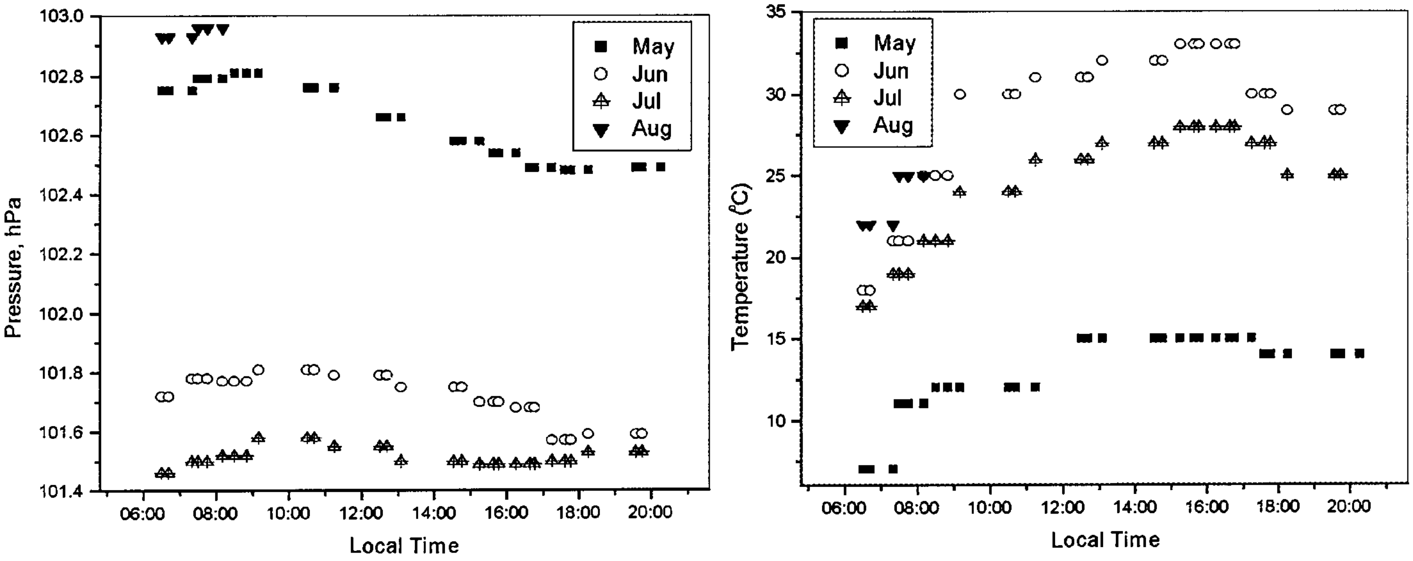

Figure 4.12: Temperature and pressure condition measured at York University in May (dark squares), June (open circles), July (hatched triangles) and August (dark triangles) 2003.

Equation 1.14 predicts that the difference between the isotopic ratio of source emissions and photochemically aged emissions is dependant on the magnitude of KIE_{OH} and the OH radical reaction rate (k_{OH}). As benzene and ethyne are similar compounds in their OH radical reactivity and large KIE_{OH} values (see Table 1.2), the observed depletion in ^{12}C relative to the source material may reflect misassignment in isotopic source composition. Considering a OH-radical abundance of 10^6 molecules cm^{-3} and the atmospheric lifetime of benzene of ten days (Atkinson 1990), the change in isotope ratio resulting from Equation 1.14 is 8.6 ‰ over the ten day lifetime of atmospheric benzene, assuming no air parcel mixing. Although Canadian national inventories identify the transportation sector as the most significant source of VOC, the sector accounts for only 43% of total emissions (Environment Canada, 2003). Considering the magnitude of the offset in stable carbon isotope ratio, national VOCs inventories and the discrepancy in source composition found in Figure 4.8-4.11, it cannot be ruled out that source material other than traffic related emissions contribute to source emissions.

The daily mean NMHC isotope ratios in four consecutive months at York University are shown in Figures 3.5 (a), 3.6 (a) and 3.7 (a). Significant differences exist in mean isotopic composition between months for the following compounds: propane, *iso*-butane, *iso*-pentane, *n*-pentane and *mp*-xylene. For compounds in which significant differences exist, NMHC exhibiting the least amount of photochemical processing were observed in May when the most ^{12}C enriched isotope ratios are apparent. The largest variation observed in June samples is indicative of a greater degree of photochemical processing associated with OH radical abundance in the month (Spivalovsky et al., 1990).

4.2.4 Photochemical ages

Photochemical ages of compounds were calculated by inserting measured isotope ratios and experimentally derived KIE_{OH} and k_{OH} values listed in Table 1.2 into Equation 1.14 (Table 1.2) KIE_{OH} and k_{OH} are values derived from chamber experiments of a mixture of NMHC and OH-radicals, accounting for OH-radical loss in a mixture of atmospheric sinks (Rudolph 2000). KIE_{OH} and k_{OH} are temperature dependant (Atkinson 2003). Temperature corrections factors were not applied because KIE_{OH} temperature variability data is not presently available.

Eq. 1.14

$$t[OH]_{av} = (\delta_{ct2} - \delta_{ct1}) / (KIE_{OH} \times k_{OH})$$

The uncertainty of calculated photochemical ages depends on the variability of source composition relative to the magnitude of the KIE_{OH}, the uncertainty in KIE_{OH} and k_{OH} for the reaction of NMHC with the OH-radical as well as measurement error.

The uncertainty in the mean photochemical age of NMHC derived from Equation 1.14 can be expressed by the following Gaussian error propagation (Rudolph 2003):

Eq 4.1

$$\Delta(t \times [OH]_{av}) = \{(\Delta^2 \delta c_{c_{t1}} - \Delta^2 \delta_{c_{t2}}) / (KIE_{OH} \times k_{OH})^2 + (\Delta^2 KIE_{OH} / KIE_{OH}{}^2 + \Delta^2 k_{OH} / k_{OH}{}^2) \times (t \times [OH]_{av})^2\}^{1/2}$$

where Δ indicate the errors of the values. Gaussian error propagation is applied to non linear functions containing multivariables when multivariables are uncorrelated with each other. For a list of errors used in photochemical age calculations, see Table 1.2 and Table 2.1.

Equation 1.14, used for determining the photochemical age of an air mass, is valid only under the assumption that the stable carbon isotope ratio of emissions is known. Given the limited amount of information available on source composition, in calculations of photochemical age, the mean value of emissions for an individual compound, minus one σ was used. For the determined photochemical age of *mp*-xylene, the $\delta^{13}C$ value is a mean measurement of both isomers, and *p*-xylene k_{OH} and KIE_{OH} values were used in calculations. Consequentially, error assignment according to equation 4.1 for these compounds does not include error contributions from NMHC sources other than traffic related emissions.

The uncertainties in photochemical age smaller than 1% were observed for n-butane and toluene. The small error for these NMHC is primarily driven by the small relative error in KIE_{OH} measurement for the compounds. Unfortunately, for all other compounds relative errors as high as 20% were observed. However, the average daily range in isotope ratio for NMHC measured at York University is 4.9‰. The large range in isotopic composition for NMHC with high relative measurement error, makes distinguishing between air parcels of different photochemical ages possible in diurnal cycles.

The KIE_{OH} used in the calculation of the photochemical age of a NHMC was determined at 298K using chamber experiment methods. Although KIE_{OH} and k_{OH} are kinetic properties influenced by temperature, given the limited amount of available data, correction factor were ignored. However, changes in reaction rates over the entire temperature range are estimated to be less than 10% (Atkinson 1994).

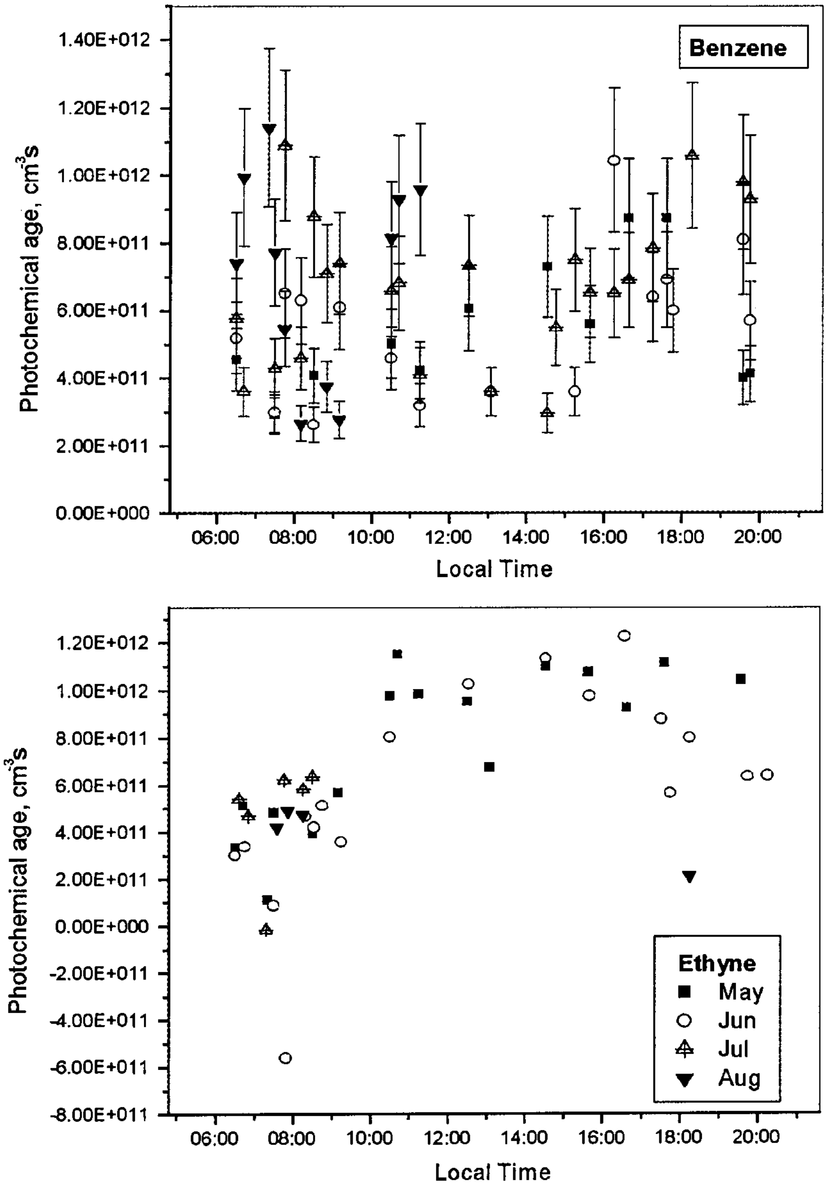

Figure 4.13: Photochemical age of benzene and ethyne derived from the stable carbon isotope ratios in Figure 4.8 and Figure 4.9. The calculations are based on measured ^{OH}KIE values for the reaction of NMHC with OH-radicals and the lower limits of source composition. The error bars indicate the uncertainty from ^{OH}KIE, ^{OH}k and measurement error contributions. For ethyne, uncertainty data is not available.

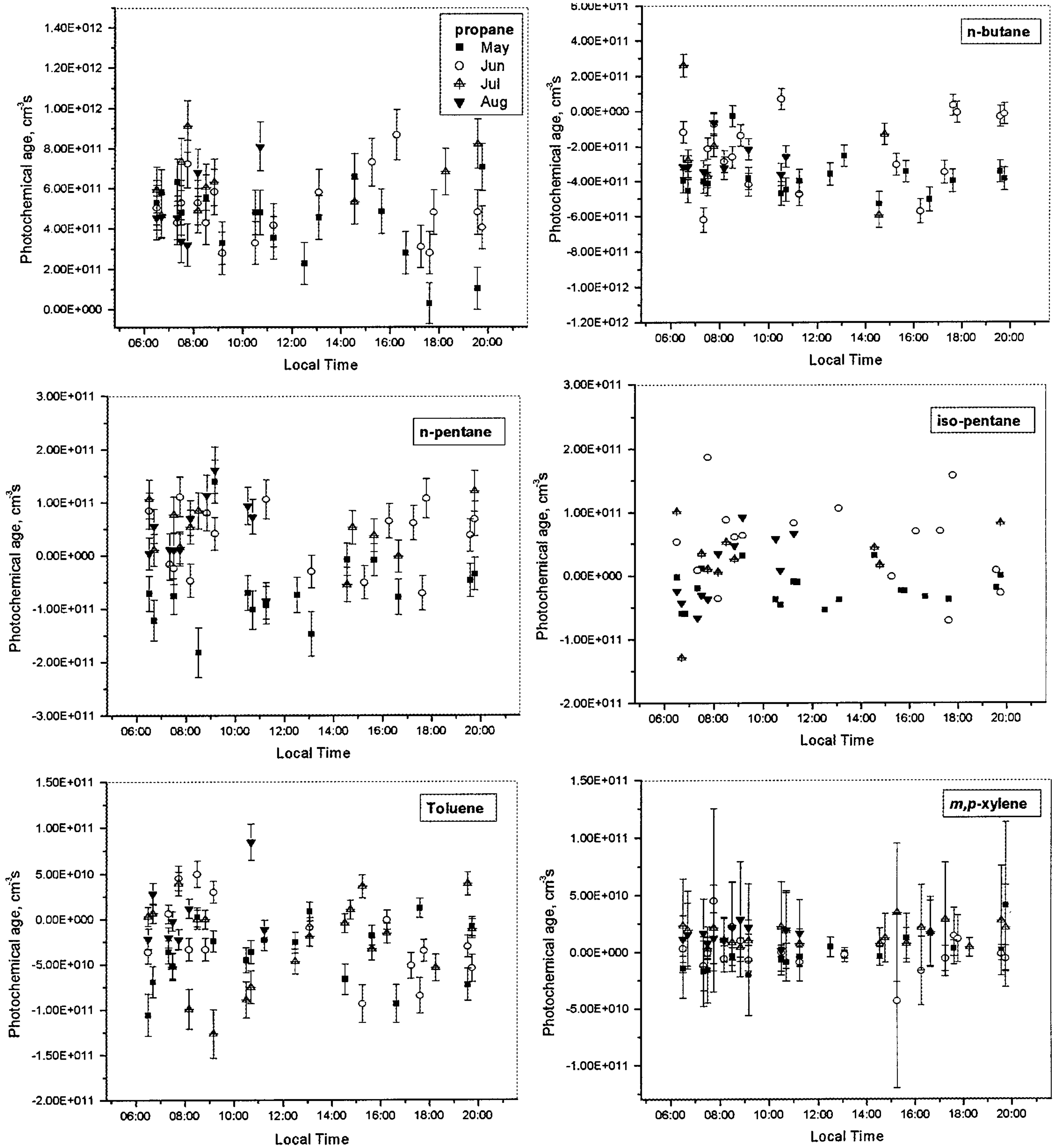

Figure 4.14: Photochemical age of alkanes and aromatics derived from the stable carbon isotope ratios in Figure 4.8-4.11. The calculations are based on measured ${}^{OH}KIE$ values for the reaction of NMHC with OH-radicals and the lower limits of source composition. The error bars indicate the uncertainties from ${}^{OH}KIE$, ${}^{OH}k$ and measurement error contributions. For iso-pentane, uncertainties data is not available.

The true linear average photochemical ages of NMHC at York University are presented in Figures 4.13 and 4.14. Chemical processing of NMHC is observed over a considerable range. The highest amount of photochemical aging (10^{12} cm^{-3} s) is observed for compounds exhibiting similarly low reactivity towards OH-radicals: benzene, ethyne and propane. Assuming the global OH-radical concentration of 10^{6} cm^{-3} s, the maximum observed photochemical age and the corresponding atmospheric age of NMHC are shown in Table 4.5. Photochemical ages of the magnitude observed in propane, ethyne and benzene (10^{12} cm^{-3} s) correspond to an atmospheric age greater than or equal to 12 ± 2 days using a daily global average OH-radical abundance of 10^{6} molecules cm^{-3}. In this case, error in atmospheric lifetimes is the error in photochemical age propagated as the squared relative standard deviation. Estimated local OH-radical average of (2×10^{6} molecules cm^{-3}) for 40°N in June corresponds to an atmospheric age of 5 ± 1 days for the photochemical ages of 10^{12} cm^{-3} s (Spivalovsky et al., 1990).

The results provide additional evidence of the contention that NMHC with long residence times will exhibit the largest amount of chemical processing. The time necessary for an air parcel containing NMHC to cross over York University from the Toronto's downtown core is approximately two hours given wind average wind speeds of 15 km h^{-1}. It is most likely that long range transport processes contribute to the NMHC mix of photochemically aged compounds in the suburban air sheds. The least amount of photochemical aging (10^{10} cm^{-3}s) was observed for molecules with high OH-radical reactivity (e.g. *m,p*-xylene and toluene), reflecting chemical processing on an hourly time scale.

Table 4.5: Highest degree of photochemical aging and maximum observed atmospheric age of NMHC compounds measured at York University in Summer 2003.

Compound	Photochemical Age (10^{11}) cm^{-3} s	Maximum observed atmospheric age (days)
toluene	1.1 ± 0.2	1 ± 0.2
n-pentane	2.1 ± 0.4	2 ± 0.4
iso-pentane	2.1 ± 0.4	2 ± 0.4
n-butane	2.5 ± 0.5	3 ± 0.6
ethyne	10	12
propane	11 ± 2.2	13 ± 2.6
benzene	14 ± 2.8	16 ± 3.2

Assuming a global OH-radical concentration of 10^6 molecules cm^{-3}, the atmospheric lifetime in days was calculated from stable carbon isotope ratios derived photochemical ages (see Equation 1.14). Under average wind speed conditions (15 km h^{-1}) at York University in Summer 2003, the limit of transport for each NMHC was estimated. Shown by the arrow in Figure 4.15 are transport distance limits for each compound based on the largest observed photochemical age. Considering the range in photochemical processing and the reactivity of NMHC with OH-radicals, information derived from isotopic composition of long-lived compounds such as benzene, ethyne and propane reflect regional conditions and possible trans-boundary transport. Toluene and other short-lived compounds are more reflective of local conditions. The mixing ratios of these compounds in urban air parcels are higher than the instrumental detection limits of 0.1 ppbv C (see Table 1.1)

For all NMHC, the air samples with the most chemically processed compounds are observed in morning conditions when NMHC accumulation is greatest. If an average global OH-radical concentration of 10^6 molecules cm^{-3} and an average NMHC photochemical age of 10^{11} $cm^{-3}s$ are specified, then the mean age of NMHC in the suburban airshed is approximately 1 ± 0.2 day. Considering this estimate, it is reasonable that the high photochemical ages observed for NMHC in morning samples result from the accumulation of chemically processed compounds in a nightime inversion layer. Changes in isotopic composition from reaction with ground level O_3 at night may also contribute to the mix. However, these changes are anticipated to be small as reaction rates with O_3 are on average a factor of six lower than with OH radicals (Iannone 2003). Daily maxima in photochemical age do not occur consistently in morning or evening hours over the sample period. The lack of a consistent daily asymptote associated with a Rayleigh curve in diurnal trends is indicative that samples showing the least amount of photochemical processing are the result of recent emissions events.

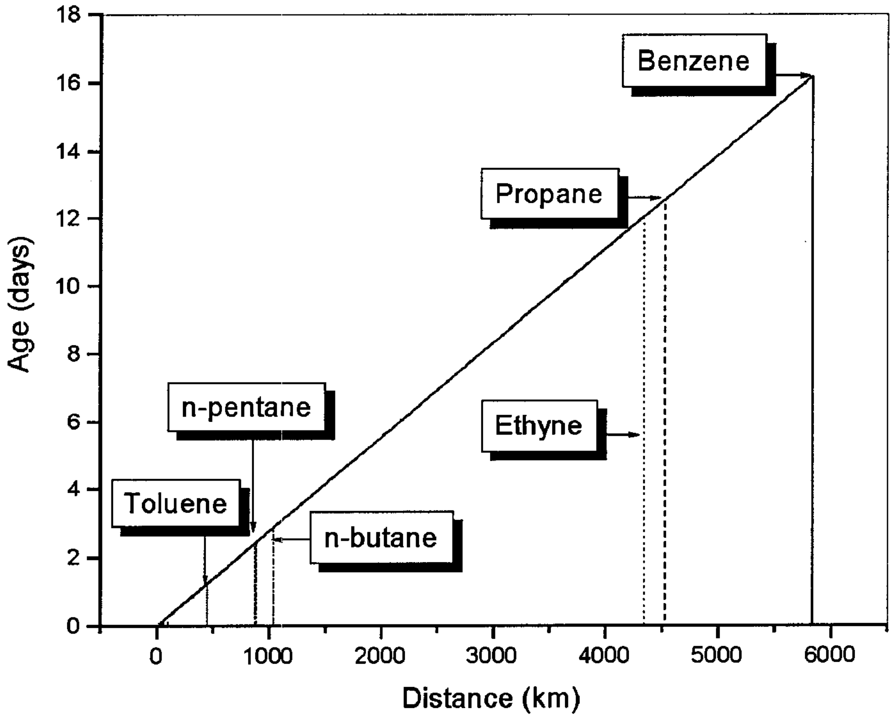

Figure 4:15. NMHC atmospheric age and distance model derived from photochemical ages.

4.3 Photochemical Aging and Dilution Processes

Removal of NMHC from an air parcel in the lower troposphere is primarily governed by two mechanisms: the first is by dilution processes and the second is by photochemical loss through reactions with OH radicals (Rudolph 2000). The following section will address how stable carbon isotope ratios can be used in conjunction with ambient NMHC concentration measurements to quantify and differentiate proportions of these two NMHC removal processes in suburban and rural locations in the GTA. Assuming other atmospheric NMHC removal processes are insignificant, by conventional mass balance, the average daily NMHC loss from the urban GTA air parcel travelling to suburban and rural locations 30-75 km upwind is 50 ± 10%. Relative to the monthly average urban GTA air parcel, the air parcel gains 2 ± 8 % in NMHC through chemical emissions in the summer of 2003.

4.3.1 Photochemical Processing

The Raleigh equation (Eq. 1.13) first described in Section 1.4 becomes Equation 4.2 by simple rearrangement.

Eq 1.13
$$\delta_{ct2} = -KIE_{OH} \times \ln\left(\frac{c_{t2}}{c_{t1}}\right) + \delta_{ct1}$$

Eq 4.2
$$\left(\frac{c_{t2}}{c_{t1}}\right)_{chem} = EXP\left(\frac{\delta c_{t2} - \delta c_{t1}}{{}^{OH}KIE}\right)$$

By substituting measured $\delta^{13}C$ values and experimentally derived ${}^{OH}KIE$ values into Equation 4.2, concentration loss due to photochemical oxidation is expressed as a ratio of the concentration of NMHC remaining at t_2 to the concentration of NMHC at t_1.

A model calculation for atmospheric loss by photochemical oxidation by OH-radicals is shown in Figure 4.16 . For the model, the KIE_{OH} value of 8.13 for benzene was used. Shown in the figure is the average range in compound specific isotopic ratios for diurnal cycles in the GTA (4.6‰). Corresponding to this value, the maximum daily concentration loss ratio (0.5_6) caused by photochemical oxidation for benzene in Summer 2003 is shown.

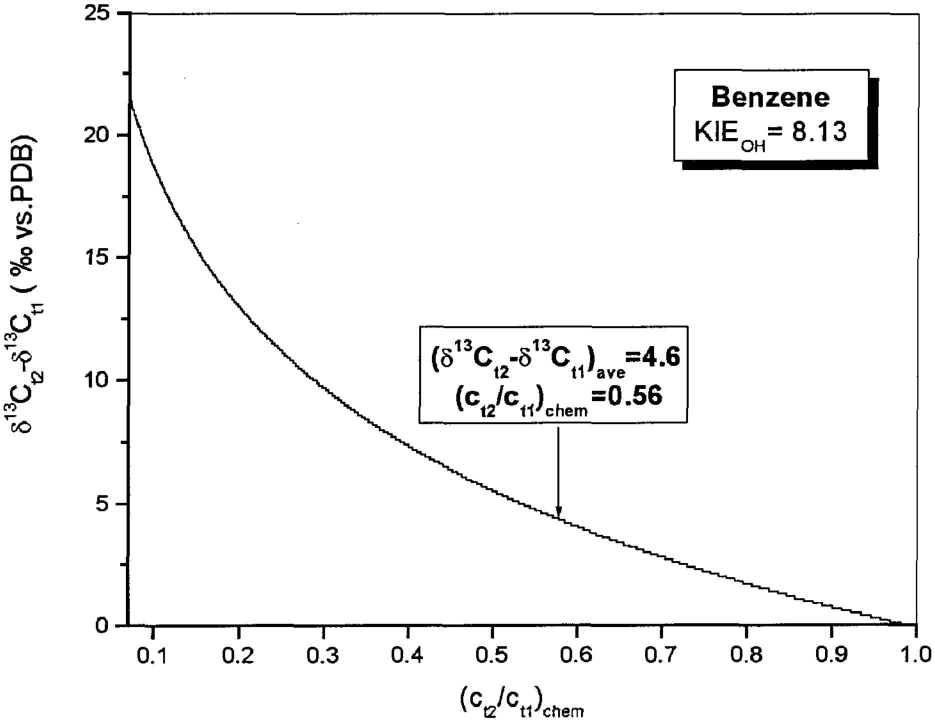

Figure 4:16. Rayleigh fractionation curve for benzene. The maximum benzene loss corresponding to a daily isotope ratio range of 4.6 ‰ at York University is indicated by the arrow.

4.3.2 Air Parcel Mixing

The Rayleigh curve described in Equation 4.2 accounts for atmospheric NMHC loss by photochemical removal processes only. However, if concentration measurements are made in ambient air, information on the loss processes due to air parcel mixing or dilution can be estimated. By conventional mass balance, if only dilution and chemical processing by OH-radicals contributed to a decrease in NMHC concentration since time t_1, the observed NMHC mixing ratio can be expressed as follows:

Eq 4.3
$$\left(\frac{c_{t2}}{c_{t1}}\right)_{meas} = 1 - \left(\frac{c_{t2}}{c_{t1}}\right)_{chem} - \left(\frac{c_{t2}}{c_{t1}}\right)_{dil}$$

where c_{t1} is the concentration at t_1 and c_{t2} is the concentration remaining in the measured air sample, or chemically processed and diluted air parcel. In applying Equation 4.3 in the following analysis, the concentration and isotopic composition at t_1 was taken to be the average concentration and isotopic composition of the urban air mass for the given month. Mixing ratios used are presented in Table 3.2 in Section 3.1. Daily average carbon isotope ratios for NMHC in urban Toronto are reported in Table 3.6. NMHC changes in the air parcel therefore reflect processing relative to the urban Toronto.

Analogous to calculating photochemical ages, the validity of Equation 4.3 depends on the uncertainty in KIE_{OH}, in stable carbon isotope ratios at t_1 and t_2, and in concentration measurement at t_1 and t_2. Consequently variations in these measurements will contribute to the overall uncertainty in quantifying NMHC removal by chemical and dilution processes. From Equation 4.2, the daily average chemical gain as an urban air parcel travels upwind to suburban and rural locations is 2 %. Assuming an experimental uncertainty of 0.5‰, by propagation of uncertainty, the associated error in this calculation is 8 %. From Equation 4.3, the daily average removal by dilution processes is 50 ± 10% as an urban air parcel travels upwind to suburban and rural locations.

The average impact of chemical removal derived from the isotopic data is compared to contributions from dilution derived from Equation 4.3 for diurnal studies in the GTA in the summer of 2003. Results from samples collected at York University are shown in Figure 4.17. Rural/Suburban air sheds are represented in Figure 4.18. Open squares indicate the percent loss due to photochemical removal by OH-radicals, whereas dark squares are indicative of dilution processes. Error bars indicate the standard deviation of the mean.

For dilution processes, negative values may reflect uncertainties in t_1 value assignment. However, given diurnal patterns, negative contributions most likely reflect addition of NMHC source material to the air parcel through air parcel mixing. The most negative values occurred during periods of low or cooling temperatures and anticipated high automotive activity, (6:00-9:00 and 17:00-20:00 LT). During these time periods, atmospheric concentrations double the average urban mixing ratios are observed. The maximum loss processes by dilution is observed near noon hours when horizontal convection processes associated with high temperatures are expected to be greatest (Singn and Zimmermann, 1992). Unfortunately, short sampling periods and low atmospheric NMHC concentrations in rural/suburban samples make analysis of considerably aged air parcels difficult. With the exception of ethyne and isoprene atmospheric concentrations fall below the 0.1 ppbV C detection limit in rural and suburban samples. Unlike York University samples, concentration loss from dilution processes in rural/suburban samples are not negative, reflecting small input from air parcel mixing processes.

Because the chemical loss fraction is derived from the Rayleigh equation, negative values may be indicative of uncertainty in source emission assignment, whereas positive values are reflective of photochemically aged air parcels. The quantification of photochemical loss may be underestimated as concentrations in noon hour samples, when it is anticipated that OH radical concentrations are maximum, are often below instrumental detection limits. Nevertheless, it should be noted that values assigned for t_1 are averages of diurnal measurements made in urban GTA. As a result, negative values greater may be regarded as possible recent emission events relative to daily averages in the urban core.

At York University, the air samples exhibiting a high degree of chemical processing (high positive values) occur near 15:00 LT in both June and July. As this time occurs near rush hour, the event occurs when NMHC are exposed to the anticipated largest integrated amount of OH-radicals. For both June and July, between 7:30-8:30 LT, large negative values for chemical loss processing are observed. Large negative value are also observed in afternoon hours in June between 15:40-17:45 LT, and in July between 14:30-15:00 LT. Though standard deviations of the mean, shown as error bars in Figure 4.17, indicate no significant difference for this time interval in June, the error bars show significant differences in July near rush hour. The values are reflective of a synoptic episode of high NMHC atmospheric emissions from traffic related sources. Given the small temporal increments for which input emissions are observed in diurnal patterns, concentration ratios derived from the Rayleigh equation can serve to distinguish recent emission events from more aged air parcels.

The application of Equation 4.3 is useful for assessing the loss contributions from air parcel mixing and photochemical oxidation by OH-radicals. The model does not however account for chemical loss by at night by ozone (Iannone 2003). However, as the rate constants for NMHC reaction with ozone are six orders of magnitude lower than with OH-radicals, the expected contributions to chemical processing are expected to be negligible. From averages in Summer 2003, the total input of emissions is 2 ± 8% as the urban air parcel mixes with suburban and rural air. The average loss due to dilution processes in suburban and rural location is 50 ± 10% that of the original urban concentration.

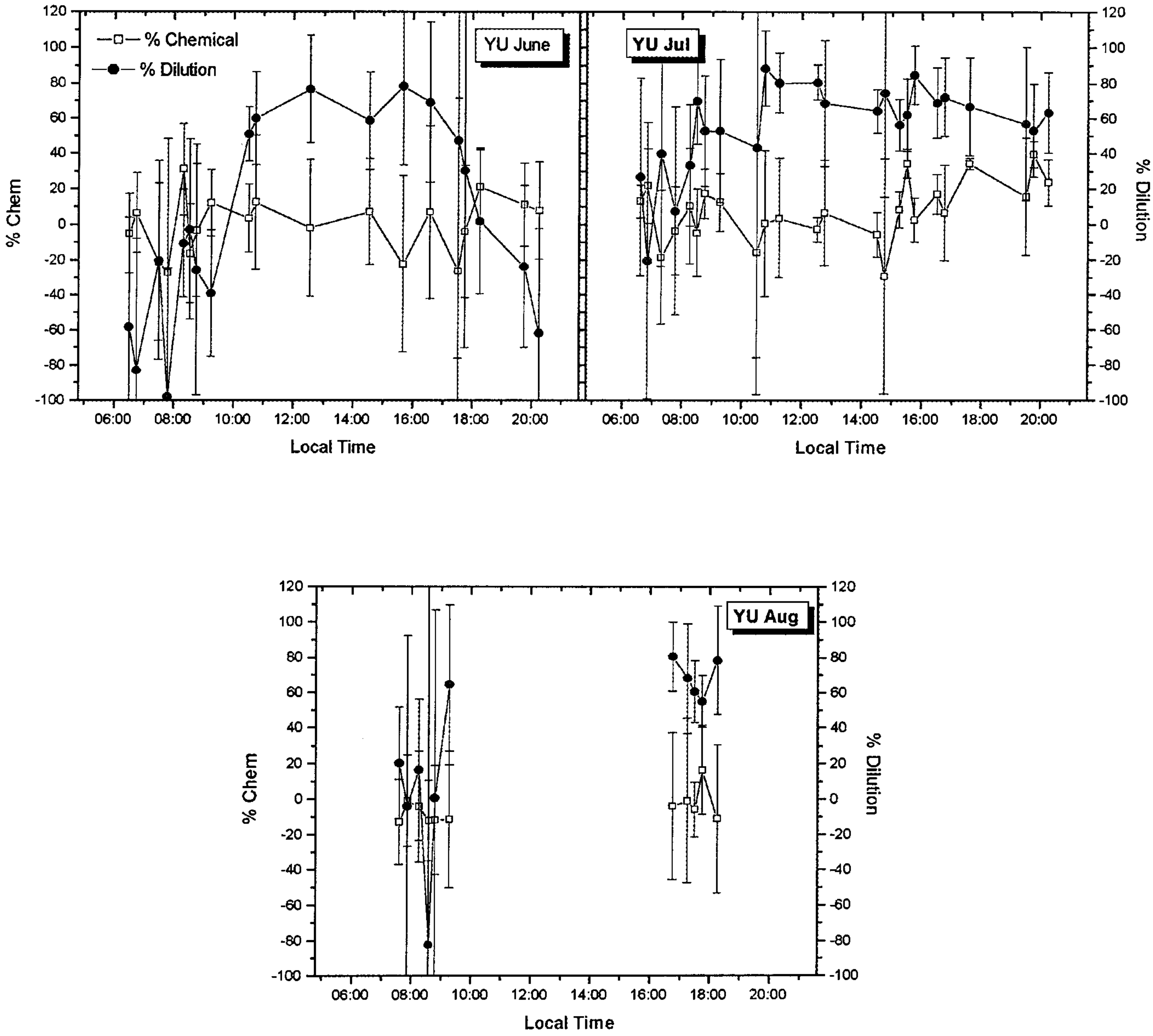

Figure 4:17. Diurnal variations in mean NMHC loss percentages for dilution (dark circles) and chemical (open squares) processing at York University. Values are derived from isotope ratios and mixing ratio measurements made in ambient air collected at York University in June, July and August 2003. Error bars indicate the standard deviation of the mean.

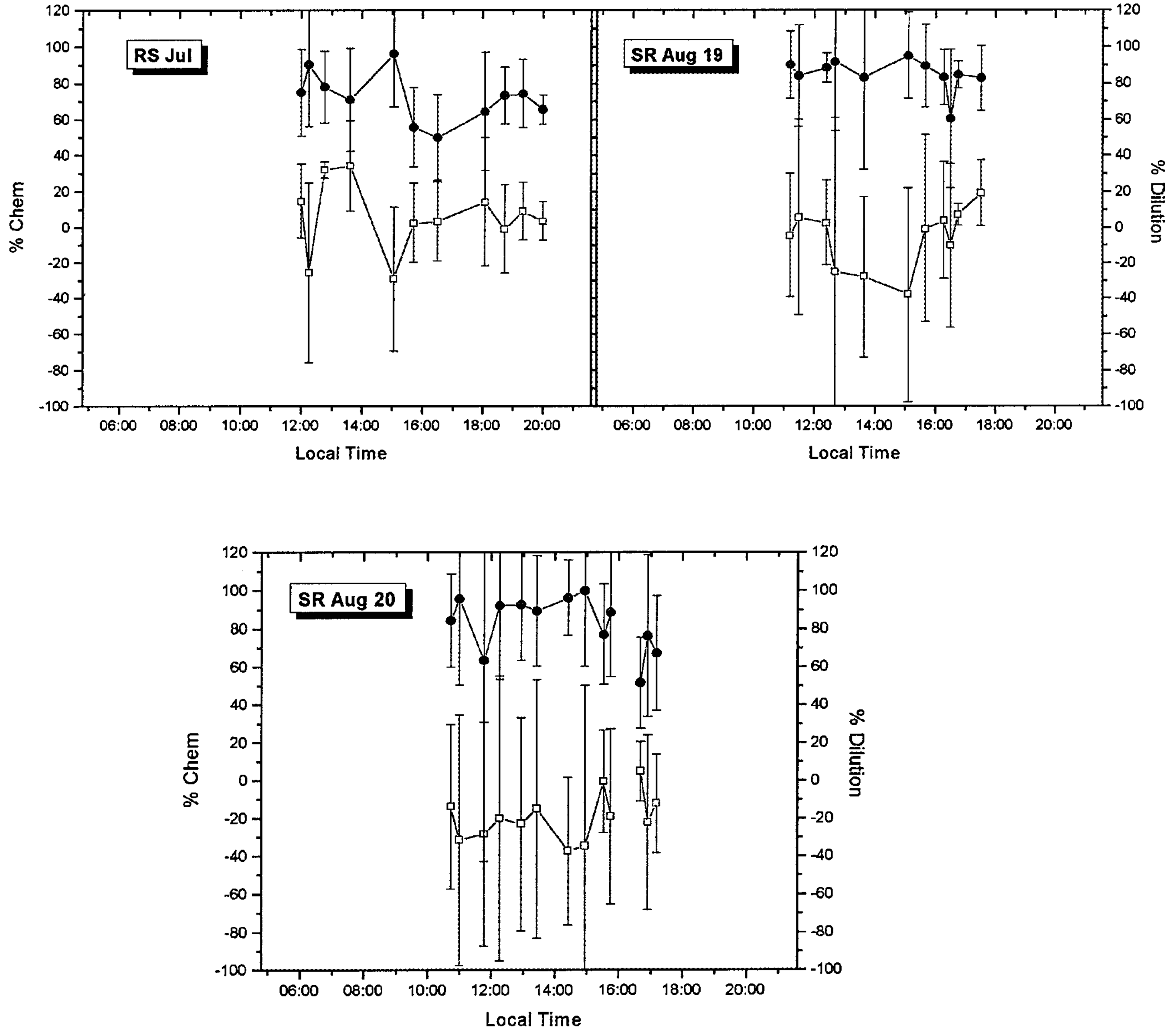

Figure 4.18: Diurnal variations in the mean NMHC loss percentages for dilution (dark circles) and chemical (open squares) processing in Rural/Suburban GTA. Values are derived from isotope ratios and mixing ratio measurements made in ambient air collected in suburban and rural location in the GTA in June and August 2003. Error bars indicate the standard deviation in the mean.

5 Conclusions

Average stable carbon isotope ratios of ambient alkane and aromatic nonmethane hydrocarbons from traffic related emissions are -27.1 ± 2.3 ‰ in the Lower Fraser Valley and –26.5 ± 1.7‰ in the Greater Toronto Area. The values fall in the same range as crude oils (–23.3 to –32.5‰) reported by Yeh and Epstein (1981). Although specific NMHC are heavier in the GTA, no significant spatial difference is observed between the average isotopic composition of traffic related emission of NMHC in the LFV and GTA. No systematic monthly variation in the NMHC isotope ratio in traffic related emissions was found. $\delta^{13}C$ information derived from the study of the isotopic composition of traffic related emission are useful in providing additional parameters for photochemical aging models.

In the GTA, the average isotope ratio of all ambient measurements of NMHC, including halogenate NMHC is –25.7 ± 3.4 ‰. The most ^{12}C enriched compound is CH_3Cl (–35.6 ± 3.3 ‰), followed by alkanes (–27.4 ± 4.1 ‰), isoprene (-27.1 ± 1.3 ‰), aromatics (–25.1 ± 3.0 ‰), unsaturates (–25.1 ± 3.0 ‰) and ethyne (–11.6 ± 4.0 ‰).

In ambient air, atmospheric removal processes cause changes as small as 0.5 ‰ (n-butane in June, Suburban/ Rural locations) and as large as 18.5 ‰ (ethyne, June, York University) in daily NMHC isotope ratios. The average range in compound specific isotopic ratio for diurnal cycles in the GTA is 4.6‰. The differences in carbon isotopic ratio between source composition and ambient observations rarely exceed 3‰ for alkane compounds. For unsaturated and aromatic compounds the changes are considerably larger and are sometimes as large as 10‰.

The magnitude of the change in isotopic composition is dependant on both the reactivity of the compound with OH-radical and the kinetic isotope effect for the reaction with OH-radicals. Considerable uncertainty in $\delta^{13}C$ source values is possibly due the emission contributions from sources other than the transportation sector.

Small changes in isotopic composition of most alkane compounds contribute to considerable uncertainty in derived photochemical ages. However, compounds for which the relative uncertainty in experimentally derived ^{OH}KIE values is small, relative errors in photochemical ages are lower than 1%. Given the large changes in isotopic composition in diurnal cycles, the changes in photochemical ages are sometimes a factor of ten greater than the uncertainty.

Despite uncertainty in isotopic composition of source emission, given the relative changes in isotopic composition and atmospheric lifetimes, it is apparent that compounds with low OH reactivity (e.g. benzene) are appropriate for probing long-range atmospheric processes, whereas compounds with considerable OH reactivity (e.g. toluene) are appropriate for probing more local events. Furthermore, the analytical method allows for the simultaneous probing of atmospheric processes over a wide temporal range of hours to months.

Detailed analysis of available data assists in understanding changes in concentration and $\delta^{13}C$. Specifically, the daily average fraction due to photochemical aging accounts for 2 ± 8% gain of NMHC in rural and suburban areas relative to urban areas located 30-75 km downwind. Given the analytical detection limits (0.1 ppbv), the value measured are most likely directly impacted by local emissions and are not reflective of average background conditions. The average loss due to dilution processes in suburban and rural location is considerably larger. The loss fraction caused by dilution is, on average, 50 ± 10% that of the original urban concentration.

Although data on the carbon isotope ratios of NMHC are limited, the analytical method is appropriate for detecting isotopic composition of source emissions and diurnal variability in the photochemical ages. The use of stable isotope ratio measurements most likely will be of equal value for studying atmospheric processing of other trace gases such as halocarbons and NMHC oxidation products. As well, kinetic isotope effects for chemical processing other than OH-radical loss can be derived to advance the understanding of the atmospheric lifetimes of these compounds.

6 References

Anderson, Rebecca. Personal communication.

Anderson, R., Czuba, E., Ernst, D., Huang, L., Thompson, A., Rudolph, J. Method for Measuring the Carbon Kinetic Isotope Effects of Gas-Phase Reactions of Light Hydrocarbons with the Hydroxyl Radical. *J. Phys. Chem.* **107**, 6191-6199.

Anderson, R.S. , Iannone, R., Thompson, A.E., Rudolph, J., Huang, L. Carbon kinetic isotope effects in the gas-phase reactions of aromatic hydrocarbons with the OH radical at 296 ± 4K. (submitted)

Atkinson, R., Gas Phase tropospheric chemistry of organic compounds, *Journal of Physical and Chemical Reference Data,* Monograph 2, 1-216, 1994.

Atkinson, R. Kinetic and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds. *Journal of Physical and Chemical Reference Data,* Monograph 1, 1-246, 1989.

Atkinson, R., Arey, J. Atmospheric Degradation of Volatile Organic Compounds. *Chem. Rev.* **103**, 4605-4638, 2003.

Atkinson, R. Atmospheric chemistry of VOCs and NO_x, *Atmospheric Environment.* **34,** 2063-2101, 2000.

Brenninkmeijer, C.A.M., Lowe, D.C., Manning, M.R., Sparks,R.J., van Velthoven, P.F.J., The ^{13}C, ^{14}C, and ^{18}O isotopic composition of CO, CH_4 and CO_2 in the higher southern latitudes lower stratosphere. *Journal of Geophysical Research*, **100**, D12, 26,163-26,172, 1995.

Calvert, J.G., Hydrocarbon involvement in photochemical smog formation in Los Angeles atmosphere. *Environmental Science Technology.* **10**, 256-262, 1976.

Cheng, L., Fu, L., Angle, P., Sandhu, H.S. Seasonal Variations of Volatile Organic Compounds in Edmonton, Alberta. **31**, 239-246, 1997.

Clarkson, S., Martin, R.J., Rudolph, J. Ethane and propane in the Southern marine troposphere. *Atmospheric Environment.* **31**, 3763-3771, 1997.

Conny, J.M., Currie, L.A., The isotopic characterization of methane, non-methane hydrocarbons and formaldehyde in the troposphere. *Atmospheric Environment.* **30**, 621-638, 1996.

Craig H. Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. *Geochim, Cosmochim. Acta.* **12**, 1330149. 1957.

Czuba, E. Development of a technique to study stable carbon isotope composition of NMHCs in ambient air, M.Sc. thesis, York Univerisity, Toronto, 1999.

Environment Canada. Future Canadian Measures for Reducing Emissions of Volatile Organic Compounds (VOC) from Consumer and Commercial Products, 2003.

Faure, Gunter. Principles of Isotope Geology, 2nd Edition. P 429 John Wiley and Sons, Inc. USA 1986.

Finlayson-Pitts, B.J., and J.N. Pitts, Jr. Chemistry of the Upper and Lower Atmosphere: Theory, Experiments and Applications. Academic Press, San Diego, CA, 2000.

Greenberg, J.P., Guenther, A., Zimmerman, P., Baugh, W., Geron, C., Davis, K. Tethered balloon measurements of biogenic VOCs in the atmospheric boundary layer. *Atmospheric Environment.* **33**, 855-867, 1999.

Goldstein, A., Shaw, S., Isotopes of Volatile Organic Compounds: An Emerging Approach for Studying Atmospheric Budgets and Chemistry., *Chem. Rev.* **103**, 5025-5048, 2003.

Heddle, J.A., Shepson, J.D., Gingerich, J.D., So, K.W. The mutagenicity of peroxylacetyl nitrate (PAN) *in vivo,* tests for somatic mutations and chromosomal aberrations. *Environ. Molec.Mitagen.*, **21**, 58-66, 1993.)

Iannone, R. Anderson, R.S., Rudolph, J. The carbon kinetic isotope effect of ozone-alkene reactions in the gas-phase and the impact of ozone reactions on the stable carbon isotope ratios of alkenes in the atmosphere. *Geophysical Research Letters*, **30**, 13, 1684, 2003.

Kleinman, L.I., Daum, P.H., Lee, Y.N., Nunnermacker, L.J., Springston, S.R., Weinstein-Loyd, J., Hyde, P., Doskey, P., Rudolph, J. Berkowitz, C. Photochemical age determinations in the Phoenix metropolitan area. *Journal of Geophysical Research*, 108 (D3) 4094, 2003

Martin, R.S., Westberg, H., Allwine, E., Ashman, L., Farmer, J.C., Lamb, B. Measurements of isoprene and its atmospheric oxidation products in a central Pennsylvania deciduous forest. *Journal of Atmospheric Chemistry* **13**: 1-32, 1991.

Matthews, D.E., Hayes, A.J. Isotope monitoring gas chromatography-mass spectrometry. *Analytical Chemistry*, **50**, 1465-1473,1978.

Merrit, D.A., Freeman K.H., Ricci, M.R., Studley, S.A., Hayes, J.M. Performance and optimization of a combustion interface for isotope ratio monitoring gas chromatography/mass spectrometry, *Analytical Chemistry.*, **67**, 2461-2473, 1995.

Rudolph, J., Czuba, E. On the use of isotopic composition measurements of volatile organic compounds to determine the "photochemical age" of an air mass. *Geophysical Research Letters*, **27**, 3865-3868, 2000.

Rudolph, J., Czuba, E., Huang, L. The stable carbon isotope fractionation for the reactions of selected hydrocarbons with OH-radicals and its relevance for atmospheric chemistry. *Journal of Geophysical Research*, **105**(D24), 29,329-29,346, 2000.

Rudolph, J. Lowe, D.C., Martin, R.J., Clarkson, T.S. A novel method for the compound specific determination of $\delta^{13}C$ in volatile organic compounds at ppt levels in ambient air. *Geophysical Research Letters*, **24**, 659-662, 1997.

Rudolph, J., Czuba, E., Norman, A.L, Huang, L., Ernst, D. Stable carbon isotope composition of nonmethane hydrocarbons in emissions from transportation related sources and atmospheric observations in an urban atmosphere. *Atmospheric Environment*, **36**, 1173-1181, 2002

Rudolph, J., Anderson, R.S., Czapiewski, K.V., Czuba, E., Ernst, D., Gillespie, T., Huang, L., Rigby, C. The stable carbon isotope ratio of biogenic emissions of isoprene and the potential use of stable carbon isotope ratio measurements to study photochemical processing of isoprene in the atmosphere. *Journal of Atmospheric Chemistry*, **44**, 39-55, 2003.

Rudolph, J., Stupak, J. Determination of Aromatic Acids and Nitrophenols in Atmopheric Aerosols by Capillary Electrophoresis. *Journal of Chromatographic Science*, **40**, 207-213, 2002.

Singh, H.B., Zimmerman, P.B. Atmospheric distribution and sources of Nonmethane hydrocarbons, in Gaseous Pollutants: Characterization and Cycling. John Wiley and Sons, 177-235, 1992.

Spivalovsky, C.M., Yevich, R., Logan J.A, Wofsky S.C., McElroy, M.B., Prather, M.J. Tropospheric OH in a three-dimensional chemical tracer model: An assessment based on observations of CH_3CCl_3, *Journal of Geophysical Research,* 95, 18,441-18,471, 1990.

Temple, P.J., Taylor, O.C. World wide measurements of peroxylacetylnitrate (PAN) and implications for plant injury, *Atmospheric Environment,* **17**, 1583-1587, 1983.

Thompson, A.E., Rudolph, J., Rohrer, F., Strein, O. Concentration and stable carbon isotopic composition of ethane and benzene using a global three-dimensional isotope inclusive chemical tracer model. *Journal of Geophysical Research,* **108**(D13), 4373, doi:10.1029/2002JD002883, 2003.

Thompson, A.E., Anderson, R.S. Rudolph, J., Huang, L. Stable carbon isotope signatures of background tropospheric chloromethane and CFC113. *Biogeochemistry,* **60**, 191-211, 2002.

Thompson, A.E. Stable Carbon Isotope Ratios of Nonmethane Hydrocarbons and Halocarbons in the Atmosphere, Ph.D. thesis, York Univerisity, Toronto, 2003.

Tsunogai, U., Yoshida, N. Carbon isotopic composition of C2-C5 hydrocarbons and methyl chloride in urban, coastal, and marine atmospheres over the western North Pacific., *Journal of Geophysical Research,* **104**, 16033-16039, 1999

Whiticar, M.J. and Snowdon. Geochemical characterization of selected Western Canada oils by C_5-C_8 compound specific isotope correlation (CSIC), *Organic Geochemistry,* **30**, 1127-1162, 1999.

Yeh, H.-W., Epstein, S., 1981. Hydrogen and carbon isotopes of petroleum and related organic matter. Geochimica et Cosmochimica Acta , **45**, 753-762.

Appendix 1

Table A1: Sampling Information, GTA Source Study, Nov 2003.

Lab #	site	canister	date	time -start	time-end	time [min]	temp[°C]	wind direct.	sp.[km/h]
TT-03-001	Union Station	Y251	20/11/2003	7:35	8:30	0:55	2.5	24	11
TT-03-002	Union Station	Y354	20/11/2003	7:45	7:50	0:05	2.5	24	11
TT-03-003	Union Station	Y258	20/11/2003	8:00	8:05	0:05	3.5	26	17
TT-03-004	Union Station	Y280	20/11/2003	8:15	8:19	0:04	3.5	26	17
TT-03-005	Union Station	Y426	20/11/2003	8:25	9:30	1:05	3.5	26	17
TT-03-006	Union Station	Y488	20/11/2003	8:45	8:50	0:05	3.5	26	17
TT-03-007	Union Station	Y245	20/11/2003	9:00	9:04	0:04	5	27	19
TT-03-008	Union Station	Y478	20/11/2003	9:15	9:19	0:04	5	27	19
TT-03-009	Union Station	Y300	20/11/2003	15:30	16:30	1:00	10	21	11
TT-03-010	Union Station	Y360	20/11/2003	15:45	15:49	0:04	10	21	11
TT-03-011	Union Station	Y514	20/11/2003	16:00	16:04	0:04	9.6	19	15
TT-03-012	Union Station	Y288	20/11/2003	16:15	16:19	0:04	9.6	19	15
TT-03-013	Union Station	Y497	20/11/2003	16:35	17:35	1:00	9.6	19	15
TT-03-014	Union Station	Y257	20/11/2003	16:50	16:54	0:04	9.6	19	15
TT-03-015	Union Station	Y309	20/11/2003	17:05	17:09	0:04	8.6	20	11
TT-03-016	Union Station	Y289	20/11/2003	17:20	17:24	0:04	8.6	20	11

Table A2: NMHC isotopic composition ($\delta^{13}C$ ‰), GTA Source Study, Nov 2003.

Lab#	ace	nC3	propene	iC4	nC4	1-butene	ibutene	iC5	nC5	23DMC4	2MC5	3MC5	nC6	nC7	Benz	iC8	Tol	C2 Benz	mpXyl	oXyl
TT-03-001	-20.0	-28.1	-23.1	-22.7	-27.0	LOD	LOD	-28.9	-27.7	LOD	-30.2	-29.8	-28.8	-26.2	-28.8	-32.6	-26.7	-28.3	-25.7	-25.1
TT-03-002	-18.0	-27.5	-23.4	-22.8	-28.2	LOD	LOD	-29.1	-27.6	LOD	-28.3	-26.9	-27.7	-26.7	-26.5	-30.8	-26.6	-27.6	-25.5	-25.9
TT-03-003	-15.9	-28.1	-23.2	-23.1	-27.8	LOD	LOD	-28.7	-27.5	LOD	-28.0	-26.7	-26.7	-26.0	-25.1	LOD	-26.6	-26.0	-26.1	-24.7
TT-03-004	-15.7	-27.5	-23.0	-25.3	-28.4	LOD	LOD	-29.3	-27.6	-26.1	-28.8	-27.2	-27.2	LOD	LOD	-29.9	-26.8	-27.2	-26.6	-26.1
TT-03-005	-14.6	-27.9	-23.9	-25.8	-28.5	-24.5	-24.8	-29.2	-28.0	-25.3	-28.1	-26.7	-26.7	-26.8	-28.5	-30.9	-26.5	-25.1	LOD	LOD
TT-03-006	-11.5	-27.6	-24.0	-25.7	-28.1	LOD	-23.3	-28.7	-27.7	-25.8	-28.0	-26.7	-26.9	-26.6	-25.8	-27.7	-26.4	LOD	LOD	LOD
TT-03-007	-13.5	-30.7	-24.0	-24.7	-28.0	LOD	-22.8	-28.5	-27.1	-25.2	-27.9	-26.0	-26.1	-26.0	-27.1	-29.6	-26.3	-28.4	-26.4	-26.3
TT-03-008	-14.5	-29.3	-23.2	-28.6	-28.7	LOD	LOD	-29.3	-27.8	-26.0	-28.4	-26.7	-26.8	-26.8	-25.6	-28.0	-26.0	-27.0	-25.4	-25.6
TT-03-009	-11.5	-27.3	-23.6	-15.7	LOD	LOD	LOD	-28.4	-26.9	LOD	-28.8	-27.6	-27.4	-25.8	-24.1	-26.8	-25.8	-26.5	-26.7	-25.5
TT-03-010	-13.2	-29.3	-24.9	LOD	-28.1	LOD	LOD	-28.7	-27.2	-24.9	-27.7	-26.5	-27.1	-25.8	-24.2	-26.7	-26.0	-26.4	-26.3	-25.4
TT-03-011	-14.1	-28.0	-23.4	-25.7	LOD	LOD	-22.1	-28.3	-26.6	-24.4	-27.3	-25.5	-25.9	-25.5	-24.9	-26.7	-26.1	-26.7	-25.3	-25.7
TT-03-012	-15.0	-26.4	-23.1	-30.4	-28.4	LOD	LOD	-28.4	-26.9	-24.9	-27.4	-25.9	-26.0	LOD	-24.4	LOD	-25.9	-26.5	-25.2	-25.8
TT-03-013	-10.9	-26.2	-23.9	-23.6	LOD	LOD	-23.5	-28.6	-27.0	-25.0	-27.8	-26.2	-26.4	-26.2	-24.9	-27.3	LOD	-25.8	-26.3	-24.6
TT-03-014	-11.3	LOD	-23.6	-26.7	-28.0	-22.5	-23.1	-28.8	-27.3	LOD	-28.3	-26.9	-27.2	-26.8	-25.4	-26.9	-26.4	-26.4	-26.5	LOD
TT-03-015	-12.3	-26.5	-23.2	-22.7	-27.9	-25.0	-23.3	-27.8	-26.8	-25.0	-27.3	-26.1	-26.3	-26.2	-24.6	-26.5	-26.0	-26.2	LOD	LOD
TT-03-016	-11.9	-26.1	-23.5	-25.5	-27.8	-25.7	-24.5	-29.1	-27.1	-25.2	-27.5	-25.6	-25.8	-26.0	-25.0	-27.2	-26.3	-25.7	-26.8	LOD

Table A3: NMHC Mixing Ratio (ppbv), GTA Source Study, Nov 2003.

Lab#	nC2	ace	nC3	propene	iC4	nC4	1-butene	ibutene	iC5	nC5	23DMC4	2MC5	3MC5	nC6	nC7	Benz	iC8	Tol	C2Benz	mpXyl	oXyl
TT-03-001	8.711	5.335	9.498	3.747	2.356	9.925	0.577	0.775	4.673	2.570	0.438	1.894	1.125	1.317	0.476	1.963	0.800	3.671	0.433	1.248	0.411
TT-03-002	8.627	4.653	7.020	3.588	2.847	11.360	0.600	0.786	6.190	3.069	0.575	2.790	1.500	1.563	0.549	2.200	0.843	4.046	0.616	1.893	0.642
TT-03-003	8.359	6.516	9.091	3.663	2.078	8.889	0.522	0.858	3.794	2.032	0.394	1.936	0.992	1.362	0.388	2.274	0.792	3.420	0.480	1.348	0.469
TT-03-004	10.987	7.289	16.787	6.162	4.383	23.564	1.178	1.436	9.697	4.802	0.912	5.691	2.520	4.225	1.248	3.386	1.797	7.018	0.608	1.744	0.614
TT-03-005	8.243	5.648	15.355	5.702	4.294	19.200	0.910	1.306	10.627	5.730	0.705	3.116	1.854	2.005	0.868	3.451	1.709	7.225	0.360	0.945	0.302
TT-03-006	10.631	10.251	15.466	6.715	5.258	25.234	1.075	1.583	8.017	4.184	0.550	3.168	1.250	2.123	0.685	3.308	1.453	6.579	0.939	2.932	1.025
TT-03-007	9.254	4.906	38.141	5.476	4.365	19.692	0.857	1.110	8.330	3.941	0.662	3.131	1.520	2.155	0.944	2.500	1.735	7.201	0.640	1.913	0.683
TT-03-008	7.597	3.923	8.331	4.716	5.070	25.591	1.015	1.091	8.707	4.793	0.567	2.257	1.343	1.544	0.504	2.497	1.092	4.889	0.827	2.575	0.871
TT-03-009	19.170	35.175	36.021	20.904	8.830	54.350	3.099	4.488	27.265	14.807	2.535	8.086	5.603	5.335	2.173	8.247	6.078	16.141	3.047	10.012	3.703
TT-03-010	19.707	32.726	51.493	24.132	8.280	52.817	3.304	4.746	26.549	14.843	2.551	7.999	5.895	5.385	1.953	9.351	7.206	9.163	0.147	0.360	0.125
TT-03-011	15.753	28.089	13.079	23.795	10.184	58.076	3.990	4.886	31.734	17.725	2.486	10.622	6.492	7.387	3.783	12.588	5.279	26.887	3.613	10.434	3.650
TT-03-012	8.257	13.813	27.766	21.118	9.387	53.746	3.884	4.546	23.693	13.481	1.918	7.982	4.987	5.100	2.329	8.681	4.744	19.478	3.358	9.791	3.468
TT-03-013	22.383	46.477	20.573	26.622	13.326	92.720	5.009	6.202	39.565	22.106	3.823	14.733	8.464	10.287	3.938	14.088	10.398	27.597	5.292	17.807	6.602
TT-03-014	23.052	110.855	8.606	45.725	20.863	159.454	8.918	11.509	65.485	37.459	7.646	29.828	15.993	20.790	8.136	26.395	23.620	55.271	8.659	28.517	11.182
TT-03-015	29.150	18.428	107.192	24.628	9.265	58.655	3.596	4.464	24.143	13.038	2.249	9.724	5.062	6.814	2.305	10.276	5.077	16.726	3.396	3.988	4.125
TT-03-016	30.208	12.217	65.251	26.103	23.601	159.600	5.548	7.110	41.720	21.842	2.829	12.643	6.153	7.792	2.401	13.814	7.336	16.848	0.671	1.601	0.570

Table A4: Sampling Information, LFV Source Study, Nov 2003.

Lab#	Sampling Date	time -start	time-end	time [min]	Canister #	location	Temp. (C) (Person)	Wind Spd (Kph)	Wind Dir
CFC-03-001	20/11/2003	7:10	7:55	0:45	Y206	Cassiar Tunnel	8.7	20	8
CFC-03-002	20/11/2003	7:22	7:26	0:04	Y441	Cassiar Tunnel	8.7	20	8
CFC-03-003	20/11/2003	7:39	7:43	0:04	Y228	Cassiar Tunnel	8.7	20	8
CFC-03-004	20/11/2003	7:49	7:54	0:05	Y201	Cassiar Tunnel	8.7	20	8
CFC-03-005	20/11/2003	8:00	8:52	0:52	Y330	Cassiar Tunnel	9.5	20	12
CFC-03-006	20/11/2003	8:14	8:18	0:04	Y319	Cassiar Tunnel	9.5	20	12
CFC-03-007	20/11/2003	8:35	8:39	0:04	Y501	Cassiar Tunnel	9.5	20	12
CFC-03-008	20/11/2003	8:45	8:49	0:04	Y455	Cassiar Tunnel	9.5	20	12
CFC-03-009	20/11/2003	15:20	16:15	0:55	Y467	Cassiar Tunnel	14.4	17	21
CFC-03-010	20/11/2003	15:35	15:38	0:03	Y318	Cassiar Tunnel	14.4	17	21
CFC-03-011	20/11/2003	15:50	15:54	0:04	Y320	Cassiar Tunnel	14.4	17	21
CFC-03-012	20/11/2003	16:04	16:08	0:04	Y528	Cassiar Tunnel	14.2	11	19
CFC-03-013	20/11/2003	16:20	17:11	0:51	Y370	Cassiar Tunnel	14.2	11	19
CFC-03-014	20/11/2003	16:35	16:38	0:03	Y285	Cassiar Tunnel	14.2	11	19
CFC-03-015	20/11/2003	16:50	16:55	0:05	Y287	Cassiar Tunnel	14.2	11	19
CFC-03-016	20/11/2003	17:05	17:10	0:05	Y209	Cassiar Tunnel	13.5	19	17

Table A5: NMHC isotopic composition ($\delta^{13}C$ ‰), LFV Source Study, Nov 2003.

Lab #	ace	nC3	propene	iC4	nC4	1-butene	iC5	nC5	2MC5	3MC5	nC6	nC7	Benz	iC8	Tol	C2Benz	mpXyl	oXyl
CFC-03-001	-14.3	-30.9	-24.7	-27.8	-31.7	LOD	-30.3	-29.0	LOD	LOD	LOD	LOD	LOD	LOD	-28.6	-27.8	-27.8	-27.2
CFC-03-002	-14.6	-31.3	LOD	-22.1	-29.9	LOD	-29.5	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-27.3	-28.2	-27.4	-26.5
CFC-03-003	-15.8	-31.0	-25.1	-27.0	-29.5	LOD	-29.8	-29.8	LOD	LOD	LOD	LOD	-25.28	LOD	-26.5	LOD	LOD	LOD
CFC-03-004	-15.2	-30.8	-24.2	-25.1	-29.6	LOD	-30.5	-28.9	-26.6	-26.45	-25.25	-25.7	-25.85	-28.17	-27.9	-28.0	LOD	-26.0
CFC-03-005	-13.5	-30.9	-24.8	-24.7	-29.4	LOD	-29.5	-28.2	-28.25	-27.2	-27.1	-26.79	LOD	-28.09	-27.4	-27.6	-26.8	-25.9
CFC-03-006	-16.2	-32.8	LOD	LOD	-31.6	LOD	-29.7	-28.9	LOD	LOD	LOD	LOD	LOD	LOD	-26.3	-27.6	-26.4	-25.7
CFC-03-007	-15.6	-30.6	-24.8	-22.7	-28.8	-22.45	-29.6	-28.0	-28.95	-27.35	-27.62	-27.35	LOD	LOD	-27.1	-27.3	-25.7	-25.3
CFC-03-008	-12.6	-29.2	-22.0	-22.7	-29.3	-25.06	-30.1	-28.9	LOD	LOD	LOD	LOD	-23.95	LOD	-28.2	LOD	-25.3	-25.9
CFC-03-009	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-22.56	LOD	-27.6	LOD	-24.9	-27.3
CFC-03-010	-15.0	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-22.2	LOD	-27.4	-28.4	-24.8	-27.5
CFC-03-011	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-28.0	-28.0	-25.4	-25.8
CFC-03-012	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
CFC-03-013	-14.8	-30.1	-22.2	-21.2	-28.8	LOD	-28.9	-28.5	LOD	LOD	LOD	-23.35	-23.51	LOD	-26.3	-28.3	-22.2	-25.5
CFC-03-014	-15.1	-30.2	-24.3	-25.4	-28.7	LOD	LOD	-28.7	-27.55	-26.4	-26.1	-26.13	-24.15	-24.75	-27.2	-28.5	-25.3	LOD
CFC-03-015	-15.7	-31.4	-26.1	-25.2	-28.9	-25.07	-29.6	-27.2	-27.56	-26.94	-26.75	-26.59	-26.67	-26.67	-27.3	-27.4	-26.8	-25.8

Table A6: Sampling Information, York University, May 2003.

Lab #	site	canister	date	time -start	time-end	time [min]	weather	temp[°C]	humidity	wind direct.	sp.[km/h]	Atmos. Pre.
TS03-001	Petrie roof	Y251	22/05/2003	6:30	7:30	60	partly cloudy	7	64%	N	9	P:102.75 Kpa
TS03-002	Petrie roof	Y453	22/05/2003	6:42	6:46	4	partly cloudy	7	64%	N	9	P:102.75Kpa
TS03-003	Petrie roof	Y287	22/05/2003	7:20	7:24	4	partly cloudy	7	64%	N	9	P:102.75Kpa
TS03-004	Petrie roof	Y209	22/05/2003	7:30	8:15	45	partly cloudy	11	44%	NE	13	P:102.79Kpa
TS03-005	Petrie roof	Y270	22/05/2003	7:45	7:49	4	partly cloudy	11	44%	NE	13	P:102.79Kpa
TS03-006	Petrie roof	Y527	22/05/2003	8:10	8:13	3.5	partly cloudy	11	44%	NE	13	P:102.79Kpa
TS03-007	Petrie roof	Y202	22/05/2003	8:30	9:18	48	partly cloudy	12	37%	NE	22	P: 102.81Kpa
TS03-008	Petrie roof	Y226	22/05/2003	8:50	8:54	4	partly cloudy	12	37%	NE	22	P: 102.81Kpa
TS03-009	Petrie roof	Y222	22/05/2003	9:10	9:13	3	partly cloudy	12	37%	NE	22	P: 102.81Kpa
TS03-010	Petrie roof	Y467	22/05/2003	10:30	11:30	60	mainly sunny	13	35%	E	30	P: 102.76 Kpa
TS03-011	Petrie roof	Y353	22/05/2003	10:42	10:46	4	mainly sunny	13	35%	E	30	P: 102.76 Kpa
TS03-012	Petrie roof	Y248	22/05/2003	11:15	11:19	4	mainly sunny	13	35%	E	30	P: 102.76 Kpa
TS03-013	Petrie roof	Y455	22/05/2003	12:30	13:20	50	partly cloudy	15	37%	SE	20	P: 102.66 Kpa
TS03-014	Petrie roof	Y239	22/05/2003	12:42	12:46	4	partly cloudy	15	37%	SE	20	P: 102.66 Kpa
TS03-015	Petrie roof	Y258	22/05/2003	13:05	13:09	4	partly cloudy	15	37%	SE	20	P: 102.66 Kpa
TS03-016	Petrie roof	Y237	22/05/2003	14:32	15:27	55	partly cloudy	15	37%	SE	20	P: 102.58 Kpa
TS03-017	Petrie roof	Y332	22/05/2003	14:45	14:50	5	partly cloudy	15	37%	SE	20	P: 102.58 Kpa
TS03-018	Petrie roof	Y413	22/05/2003	15:15	15:19	4	partly cloudy	15	37%	SE	20	P: 102.58 Kpa
TS03-019	Petrie roof	Y488	22/05/2003	15:38	16:30	52	mainly sunny	15	36%	E	17	P: 102.54 Kpa
TS03-020	Petrie roof	Y386	22/05/2003	15:46	15:50	4	mainly sunny	15	36%	E	17	P: 102.54 Kpa
TS03-021	Petrie roof	Y304	22/05/2003	16:15	16:18	3	mainly sunny	15	36%	E	17	P: 102.54 Kpa
TS03-022	Petrie roof	Y268	22/05/2003	16:38	17:30	52	sunny	15	36%	E	20	P: 102.49 Kpa
TS03-023	Petrie roof	Y242	22/05/2003	16:46	16:49	3.5	sunny	15	36%	E	20	P: 102.49 Kpa
TS03-024	Petrie roof	Y512	22/05/2003	17:15	17:19	4	sunny	15	36%	E	20	P: 102.49 Kpa
TS03-025	Petrie roof	Y487	22/05/2003	17:36	18:36	60	sunny	14	39%	SE	19	P: 102.48 Kpa
TS03-026	Petrie roof	Y292	22/05/2003	17:46	17:49	3.5	sunny	14	39%	SE	19	P: 102.48 Kpa
TS03-027	Petrie roof	Y401	22/05/2003	18:15	18:18	3	sunny	14	39%	SE	19	P: 102.48 Kpa
TS03-028	Petrie roof	Y244	22/05/2003	19:34	20:34	60	sunny	14	40%	E	17	P: 102.49 Kpa
TS03-029	Petrie roof	Y283	22/05/2003	19:45	19:48	3.5	sunny	14	40%	E	17	P: 102.49 Kpa
TS03-030	Petrie roof	Y254	22/05/2003	20:16	20:19	3.5	sunny	14	40%	E	17	P: 102.49 Kpa

Table A7: NMHC Mixing Ratio (ppbv), York University, May 2003.

Lab #	ppbV	ace	nC2	propene	nC3	iso-butene	nC4	iC4	nC5	2MC4	Benz	MCYC5	nC6	2MC5	3MC5	Tol	C2Benz	oXyl	mpXyl	nC8	CH3Cl
TS03-001	ppbv	0.969	2.286	0.331	0.773	0.122	0.655	0.233	0.726	0.701	0.344	0.086	0.164	0.186	0.128	1.034	0.026	0.017	0.078	0.017	0.293
TS03-002	ppbv	1.015	2.226	0.425	0.906	0.133	0.755	0.237	0.446	0.785	0.279	0.102	0.175	0.221	0.148	0.327	0.004	0.002	0.014	0.007	0.483
TS03-003	ppbv	1.347	2.285	0.321	0.894	0.097	0.596	0.217	1.044	0.602	0.202	0.074	0.135	0.163	0.110	0.458	0.003	0.002	0.009	0.008	0.409
TS03-004	ppbv	0.875	2.182	0.243	0.750	0.095	0.525	0.221	0.494	0.527	0.137	0.122	0.338	0.164	0.155	0.141	0.001	0.001	0.004	0.004	0.355
TS03-005	ppbv	0.730	2.218	0.241	0.685	0.076	0.538	0.220	0.405	0.531	0.199	0.129	0.366	0.167	0.161	0.268	0.003	0.001	0.006	0.008	0.309
TS03-006	ppbv	1.038	2.057	0.213	1.011	0.066	0.552	0.204	0.286	0.463	0.201	0.150	0.492	0.163	0.176	0.317	0.005	0.004	0.017	0.007	0.271
TS03-007	ppbv	0.925	2.129	0.244	0.816	0.088	0.512	0.223	0.329	0.475	0.162	0.241	0.877	0.203	0.255	0.187	0.003	0.001	0.007	0.004	0.250
TS03-008	ppbv	0.837	1.871	0.209	0.793	0.065	0.513	0.214	0.315	0.463	0.102	0.298	1.305	0.197	0.259	0.068	0.002	LDL	0.005	LDL	0.289
TS03-009	ppbv	0.771	2.023	0.229	0.889	0.071	0.620	0.254	0.368	0.529	0.143	0.254	0.844	0.211	0.271	0.150	0.003	LDL	0.005	0.004	0.266
TS03-010	ppbv	0.524	1.766	0.144	0.699	0.129	1.686	0.473	0.782	1.456	0.133	0.100	0.237	0.255	0.179	0.177	0.004	0.002	0.012	0.007	0.295
TS03-011	ppbv	0.498	1.713	0.138	0.789	0.072	1.194	0.411	0.367	0.795	0.107	0.076	0.177	0.157	0.113	0.073	0.003	0.003	0.010	0.006	0.278
TS03-012	ppbv	0.547	1.781	0.143	0.597	0.082	1.705	0.480	0.831	1.681	0.200	0.102	0.232	0.271	0.185	0.620	0.035	0.024	0.094	0.017	0.275
TS03-013	ppbv	0.489	1.751	0.128	0.791	0.095	1.386	0.522	0.482	0.961	0.143	0.084	0.223	0.177	0.130	0.645	0.068	0.060	0.192	0.034	0.298
TS03-014	ppbv	0.440	1.700	0.123	0.741	0.078	1.383	0.578	0.450	0.926	0.178	0.079	0.201	0.169	0.121	0.496	0.071	0.066	0.216	0.041	0.014
TS03-015	ppbv	0.627	1.728	0.157	0.977	0.062	1.119	0.345	0.433	0.826	0.166	0.139	0.594	0.262	0.267	0.645	0.066	0.053	0.187	0.035	0.436
TS03-016	ppbv	0.553	1.764	0.136	0.796	0.071	0.593	0.210	0.255	0.451	0.137	0.098	0.442	0.152	0.151	0.944	0.119	0.102	0.363	0.032	0.373
TS03-017	ppbv	0.442	1.793	0.110	0.552	0.041	0.413	0.159	0.204	0.334	0.158	0.090	0.339	0.119	0.117	0.686	0.045	0.036	0.130	0.018	0.333
TS03-018	ppbv	0.515	1.743	0.125	0.723	0.061	1.119	0.447	0.416	0.832	0.175	0.097	0.340	0.173	0.131	0.587	0.059	0.049	0.169	0.023	0.326
TS03-019	ppbv	0.579	1.826	0.214	0.798	0.132	1.968	0.658	0.702	1.386	0.208	0.127	0.288	0.284	0.198	0.646	0.039	0.030	0.113	0.038	0.358
TS03-020	ppbv	0.531	1.779	0.168	0.823	0.119	2.538	0.868	0.855	1.700	0.232	0.145	0.315	0.327	0.226	0.781	0.071	0.060	0.195	0.030	0.392
TS03-021	ppbv	0.634	1.756	0.208	0.564	0.071	0.795	0.234	0.462	0.646	0.230	0.081	0.189	0.172	0.123	0.696	0.068	0.063	0.198	0.021	0.366
TS03-022	ppbv	0.541	1.726	0.187	0.583	0.126	2.456	0.588	1.086	1.918	0.206	0.114	0.264	0.321	0.212	0.620	0.040	0.030	0.111	0.019	0.580
TS03-023	ppbv	0.499	1.713	0.153	0.502	0.098	2.278	0.404	1.114	1.856	0.195	0.100	0.265	0.294	0.199	0.571	0.045	0.033	0.124	0.020	0.514
TS03-024	ppbv	0.542	1.841	0.230	0.940	0.203	4.983	1.856	1.448	3.239	0.259	0.179	0.300	0.460	0.296	0.595	0.047	0.039	0.133	0.031	0.452
TS03-025	ppbv	0.494	1.733	0.174	0.686	0.197	3.952	1.176	1.394	2.839	0.246	0.162	0.295	0.416	0.273	0.697	0.048	0.046	0.148	0.022	0.424
TS03-026	ppbv	0.479	1.718	0.141	0.541	0.114	2.360	0.615	0.859	1.689	0.187	0.106	0.199	0.275	0.182	0.492	0.032	0.025	0.090	0.017	0.389
TS03-027	ppbv	0.420	1.658	0.117	0.488	0.067	1.342	0.401	0.622	0.931	0.169	0.070	0.141	0.170	0.115	0.364	0.022	0.018	0.064	0.009	0.364
TS03-028	ppbv	0.479	1.828	0.170	0.779	0.124	2.674	0.861	0.774	1.505	0.162	0.099	0.192	0.247	0.171	0.700	0.105	0.105	0.333	0.037	0.425
TS03-029	ppbv	0.406	1.739	0.116	0.691	0.058	0.997	0.328	0.428	0.664	0.156	0.054	0.105	0.130	0.087	0.703	0.084	0.082	0.262	0.027	0.403
TS03-030	ppbv	0.531	1.961	0.204	0.742	0.099	2.043	0.627	0.560	1.181	0.218	0.110	0.242	0.233	0.166	0.956	0.059	0.050	0.183	0.022	0.406

Table A8: NMHC isotopic composition (δ^{13}C ‰), York University, May 2003.

Lab #	δ C^{13} ace	δ C^{13} nC3	δ C^{13} propylene	δ C^{13} i-C4	δ C^{13} n-C4	δ C^{13} CH_3Cl	δ C^{13} i-butene	δ C^{13} i-C5	δ C^{13} n-C5	δ C^{13} 2MC5	δ C^{13} MCYC C5	δ C^{13} 3MC5	δ C^{13} n-C6	δ C^{13} Benz	δ C^{13} Tol	δ C^{13} C2Benz	δ C^{13} m,p-xyl	δ C^{13} o-xyl
TS03-001	-15.1	-28.6	LOD	LOD	-31.6	-29.9	-25.9	-29.3	-28.9	LOD	-28.0	-27.1	-26.4	-24.2	-30.3	LOD	-28.2	LOD
TS03-002	-12.6	-28.4	-24.5	LOD	-32.0	LOD	-25.9	-30.6	-29.6	LOD	LOD	LOD	LOD	LOD	-29.1	LOD	LOD	LOD
TS03-003	-18.4	-28.2	LOD	LOD	-31.6	-39.6	LOD	-29.7	LOD	LOD	LOD	LOD	LOD	LOD	-28.0	LOD	-28.5	LOD
TS03-004	-13.0	-28.8	-27.0	-13.5	-31.7	LOD	-22.1	-29.1	-29.0	LOD	-26.8	LOD	LOD	-25.9	-28.5	LOD	-28.4	LOD
TS03-007	-14.3	-28.5	-26.9	LOD	-28.9	LOD	LOD	LOD	-30.4	LOD	LOD	LOD	LOD	-24.7	-26.7	LOD	-27.2	-27.7
TS03-009	-11.8	-29.4	-21.9	-11.1	-31.5	LOD	-24.9	-28.6	-26.2	-30.1	-26.9	-24.7	-25.6	LOD	-27.6	LOD	-28.8	LOD
TS03-010	-5.9	-28.8	-21.9	-16.9	-32.1	-36.6	-26.7	-30.1	-28.9	-25.8	-27.0	-25.5	-24.6	-23.8	-28.3	LOD	-27.5	-23.4
TS03-011	-3.4	-28.8	-25.2	-21.7	-32.0	LOD	-27.3	-30.3	-29.3	-26.2	LOD	LOD	-25.7	LOD	-28.0	LOD	-27.7	LOD
TS03-012	-5.8	-29.3	LOD	-17.2	-31.6	LOD	-27.0	-29.5	-29.2	-26.0	LOD	LOD	LOD	-24.6	-27.6	LOD	-27.2	LOD
TS03-013	-6.2	-29.8	LOD	LOD	-31.3	LOD	LOD	-30.5	-29.0	LOD	LOD	LOD	LOD	-22.8	-27.7	LOD	-26.4	LOD
TS03-015	-10.2	-28.9	LOD	-15.5	-30.6	LOD	-27.7	-30.1	-29.9	LOD	-28.6	-26.6	-29.1	LOD	-26.5	LOD	-26.9	LOD
TS03-016	-4.1	-28.1	LOD	LOD	-32.5	LOD	LOD	-28.6	-28.1	LOD	LOD	LOD	-27.2	-21.5	-29.0	LOD	-27.2	-25.2
TS03-019	-4.5	-28.8	LOD	-21.4	-31.2	LOD	-27.4	-29.8	-28.1	-26.2	-27.9	-26.4	-26.5	-23.2	-27.4	LOD	-25.6	LOD
TS03-022	-6.6	-29.6	LOD	-23.8	-32.4	LOD	-25.7	-30.0	-29.0	-26.0	-28.3	-27.8	-27.9	-20.1	-29.9	LOD	-25.2	LOD
TS03-025	-3.9	-30.6	LOD	-26.3	-31.6	LOD	-26.5	-30.1	-28.9	-26.8	-27.8	-26.9	-26.7	-20.1	-26.4	LOD	-26.5	LOD
TS03-028	-4.9	-30.3	LOD	-24.1	-31.2	LOD	-25.4	-29.7	-28.6	-26.5	-27.2	-25.7	-25.1	-24.8	-29.2	LOD	-26.7	LOD
TS03-029	LOD	-27.9	LOD	LOD	-31.5	LOD	LOD	-29.3	-28.4	LOD	LOD	LOD	LOD	-24.7	-27.1	LOD	-22.8	LOD

Table A9: NMHC isotopic composition ($\delta^{13}C$ ‰), Urban Toronto, June 2003.

Lab #	δ C^{13} ace	δ C^{13} nC3	δ C^{13} propylene	δ C^{13} i-C4	δ C^{13} n-C4	δ C^{13} CH_3Cl	δ C^{13} i-butene	δ C^{13} i-C5	δ C^{13} n-C5	δ C^{13} 2MC5	δ C^{13} MCYCC5	δ C^{13} 3MC5	δ C^{13} n-C6	δ C^{13} n-C7	δ C^{13} Benz	δ C^{13} Tol	δ C^{13} C2Benz	δ C^{13} m,p-xyl	δ C^{13} o-xyl
TS03-031	-12.1	-28.8	-24.6	-14.5	-30.9	-37.3	LOD	-30.0	-29.0	LOD	LOD	LOD	LOD	LOD	-22.4	-28.5	-28.9	-27.4	-27.8
TS03-033	-10.2	-27.7	-21.6	-7.4	-29.5	LOD	-24.3	-27.9	-27.3	LOD	-26.3	-25.8	-25.1	LOD	-22.3	-29.7	LOD	-32.5	LOD
TS03-034	-10.2	-28.9	-25.4	-0.2	-31.4	-34.0	-24.8	-28.6	-27.7	-26.1	-27.5	-26.4	-25.8	LOD	-21.8	-28.1	LOD	-28.1	LOD
TS03-035	-10.3	-28.7	LOD	LOD	-31.5	LOD	-22.4	-29.2	-29.0	LOD	LOD	LOD	LOD	LOD	-22.9	-27.2	LOD	-27.8	LOD
TS03-036	-8.0	-29.1	LOD	LOD	-29.5	LOD	-27.4	-28.7	-27.6	LOD	LOD	LOD	LOD	LOD	-22.9	-28.1	LOD	-28.2	LOD
TS03-037	-10.8	-31.5	LOD	LOD	-31.4	-37.9	LOD	-28.4	-27.2	LOD	-31.3	-27.5	-27.4	LOD	-23.1	LOD	LOD	LOD	LOD
TS03-038	-11.2	-30.4	LOD	-6.4	-29.4	LOD	LOD	-27.7	-26.3	LOD	-25.5	-24.7	-25.1	LOD	-21.7	LOD	LOD	-28.3	-24.1
TS03-039	-12.7	-30.2	LOD	LOD	-30.9	LOD	-26.4	-28.1	-27.2	LOD	-30.6	-28.5	-28.7	LOD	-23.5	-28.9	LOD	-28.1	-23.3
TS03-040	-7.7	-30.7	LOD	LOD	-30.3	-40.5	-26.3	-28.3	-28.0	LOD	LOD	-23.5	-24.9	LOD	-22.6	-28.7	LOD	-28.5	LOD
TS03-041	-7.8	-30.3	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-25.6	LOD	-22.8	-27.0	LOD	-27.9	LOD
TS03-042	-7.9	-29.8	LOD	-9.8	-30.9	-40.4	-24.6	-28.3	-27.0	-28.6	LOD	LOD	-26.0	LOD	-23.9	-27.1	LOD	-28.0	LOD
TS03-043	-12.7	-27.5	-23.4	-17.8	-30.8	-37.5	-25.1	-29.3	-28.3	-19.8	-26.5	-25.3	-24.7	LOD	-23.6	LOD	LOD	-27.1	-23.8
TS03-044	-7.6	-30.3	LOD	-19.0	-31.8	LOD	LOD	-30.1	-28.1	LOD	-27.1	-26.0	-25.6	LOD	-19.7	-29.4	-25.4	-28.3	-22.6
TS03-045	-13.6	-27.2	-24.6	-10.8	-31.0	LOD	-23.6	-29.0	-28.4	LOD	-27.0	-25.5	-24.9	LOD	-19.4	-27.8	-25.9	-27.0	-24.8
TS03-046	-13.0	-31.0	-26.9	LOD	-31.2	-35.9	LOD	-29.1	-28.0	LOD	-27.0	-25.7	-25.4	-21.3	-22.3	-27.5	LOD	-27.2	LOD
TS03-047	-13.7	-31.9	-21.1	LOD	-31.6	LOD	LOD	-29.4	-27.8	LOD	-26.6	-25.5	-25.6	-18.1	-23.0	-25.5	-26.2	-25.6	-23.9
TS03-048	-12.0	-31.7	LOD	LOD	-32.0	LOD	LOD	-29.3	-27.6	LOD	-27.0	-25.4	-24.6	-21.0	-21.0	-27.1	LOD	-25.6	-23.1
TS03-049	-13.8	-29.2	-24.0	LOD	-31.6	LOD	LOD	-28.9	-27.4	LOD	-27.2	-25.7	-25.7	-24.6	-21.2	LOD	-27.5	-27.1	-25.7
TS03-052	LOD	-27.7	LOD	LOD	LOD	-36.8	-24.0	-28.3	-29.4	-25.8	-27.5	-26.1	-26.6	-24.0	-23.4	-27.9	-27.6	LOD	-24.8
TS03-053	-15.6	-29.7	-24.2	-3.2	-30.7	LOD	LOD	-29.8	-28.2	-26.1	-27.0	-25.5	-25.0	LOD	-22.2	-27.3	-27.1	-26.8	-24.9
TS03-054	-12.6	-29.5	-23.4	LOD	-31.6	LOD	-23.4	-29.4	-28.0	-27.4	-26.8	-25.6	-24.7	LOD	-21.1	-27.4	LOD	-26.5	-24.1
TS03-056	LOD	-30.1	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-20.1	-25.9	LOD	-26.6	LOD
TS03-057	-6.8	-30.7	LOD	LOD	-31.3	-36.3	-28.6	-28.7	-28.9	LOD	LOD	LOD	-24.7	LOD	-23.1	-26.8	LOD	-26.8	-21.2
TS03-058	-13.8	-29.8	LOD	LOD	-29.7	-29.1	LOD	-28.9	-27.7	-26.3	-26.5	-25.9	-27.0	LOD	-22.4	-26.3	LOD	-25.6	LOD
TS03-059	-14.3	-29.3	-22.9	LOD	-30.9	LOD	-23.2	-28.9	-27.7	-26.1	-26.8	-25.3	-25.1	LOD	-20.6	-25.4	LOD	LOD	LOD
TS03-060	-13.8	-30.6	-23.4	LOD	-30.6	LOD	LOD	-29.1	-28.3	-25.0	-27.3	-25.5	-26.5	LOD	-18.6	-26.9	LOD	-25.8	-27.6
TS03-061	-12.3	-30.0	LOD	LOD	-30.6	-36.0	LOD	-28.9	-28.7	LOD	-28.7	-27.4	-26.5	LOD	-21.3	-27.8	LOD	-26.9	-24.2
TS03-064	LOD	-30.2	LOD	LOD	LOD	-33.6	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-23.8	LOD	LOD	-27.9	LOD
TS03-067	-14.7	-29.6	LOD	-19.2	-31.1	-38.7	-28.5	-30.0	-28.7	-25.0	-27.4	-26.4	-25.6	LOD	-21.1	-28.5	LOD	-26.0	-24.5
TS03-069	-12.6	-29.4	LOD	LOD	-30.0	LOD	-27.9	-29.2	-28.4	LOD	-26.3	LOD	-25.1	LOD	LOD	-29.6	LOD	-27.2	LOD

Table A10: Sampling Information, York University, June 2003.

Lab #	site	canister	date	time-start	time-end	time [min]	weather	Temp[°C]	humidity	wind direct.	sp.[km/h]	Atmos. Pre.
TS03-070	Petrie roof	Y370	06/24/03	6:30	7:27	57	sunny	PA+18	69%	SW	6	101.72 kPa and driving
TS03-071	Petrie roof	Y408	06/24/03	6:45	6:49	4	sunny	PA+18	69%	SW	6	101.72 kPa and driving
TS03-072	Petrie roof	Y214	06/24/03	7:15	7:19	4	sunny	PA+18	69%	SW	6	101.72 kPa and driving
TS03-073	Petrie roof	Y228	06/24/03	7:30	8:30	60	sunny	PA+21	59%	W	4	101.78 kPa and driving
TS03-074	Petrie roof	Y117	06/24/03	7:48	7:52	4	sunny	PA+21	59%	W	4	101.78 kPa and driving
TS03-075	Petrie roof	Y265	06/24/03	8:19	8:23	4	sunny	PA+21	59%	W	4	101.78 kPa and driving
TS03-076	Petrie roof	Y404	06/24/03	8:32	9:28	56	sunny	PA+25	55%	W	7	101.77 kPA and falling
TS03-077	Petrie roof	Y230	06/24/03	8:45	8:49	4	sunny	PA+25	55%	W	7	101.77 kPA and falling
TS03-078	Petrie roof	Y278	06/24/03	9:15	9:19	3.5	sunny	PA+25	55%	W	7	101.77 kPA and falling
TS03-079	Petrie roof	Y300	06/24/03	10:30	11:26	56	sunny	PA+30	39%	W	15	101.81 kPA and driving
TS03-080	Petrie roof	Y356	06/24/03	10:44	10:48	4	sunny	PA+30	39%	W	15	101.81 kPA and driving
TS03-081	Petrie roof	Y374	06/24/03	11:15	11:19	3.5	sunny	PA+30	39%	W	15	101.81 kPA and driving
TS03-082	Petrie roof	Y206	06/24/03	12:33	13:33	60	mainly sunny	PA+31	39%	SW	11	101.79 kPa and steady
TS03-083	Petrie roof	Y088	06/24/03	12:45	12:50	5	mainly sunny	PA+31	39%	SW	11	101.79 kPa and steady
TS03-084	Petrie roof	Y004	06/24/03	13:15	13:20	5	mainly sunny	PA+31	39%	SW	11	101.79 kPa and steady
TS03-085	Petrie roof	Y441	06/24/03	14:32	15:30	58	mainly sunny	PA+32	37%	SW	19	101.75 kPa and falling
TS03-086	Petrie roof	Y279	06/24/03	14:45	14:50	5	mainly sunny	PA+32	37%	SW	19	101.75 kPa and falling
TS03-087	Petrie roof	Y293	06/24/03	15:15	15:20	5	mainly sunny	PA+32	37%	SW	19	101.75 kPa and falling
TS03-088	Petrie roof	Y280	06/24/03	15:40	16:34	54	mainly sunny	PA+33	36%	SW	15	101.70 kPa and falling
TS03-089	Petrie roof	Y071	06/24/03	15:50	15:55	5	mainly sunny	PA+33	36%	SW	15	101.70 kPa and falling
TS03-090	Petrie roof	Y503	06/24/03	15:15	16:21	6	mainly sunny	PA+33	36%	SW	15	101.70 kPa and falling
TS03-091	Petrie roof	Y435	06/24/03	16:34	17:31	57	mainly sunny	PA+33	34%	SW	22	101.68 kPa and falling
TS03-092	Petrie roof	Y398	06/24/03	15:51	15:56	5	mainly sunny	PA+33	34%	SW	22	101.68 kPa and falling
TS03-093	Petrie roof	Y263	06/24/03	17:15	17:20	5	mainly sunny	PA+33	34%	SW	22	101.68 kPa and falling
TS03-094	Petrie roof	Y204	06/24/03	17:31	18:30	59	sunny	PA+30	46%	SE	17	101.57 kPa and falling
TS03-095	Petrie roof	Y331	06/24/03	17:45	17:50	5	sunny	PA+30	46%	SE	17	101.57 kPa and falling
TS03-096	Petrie roof	Y381	06/24/03	18:15	18:19	4	sunny	PA+30	46%	SE	17	101.57 kPa and falling
TS03-097	Petrie roof	Y229	06/24/03	19:30	20:30	60	sunny	PA+29	47%	SE	13	101.59 kPa and rising
TS03-098	Petrie roof	Y323	06/24/03	19:45	19:49	4.5	sunny	PA+29	47%	SE	13	101.59 kPa and rising
TS03-099	Petrie roof	Y465	06/24/03	20:15	20:20	5	sunny	PA+29	47%	SE	13	101.59 kPa and rising

Table A11: NMHC Mixing Ratio (ppbv), York University, June 2003.

Lab #	ppbV	ace	nC2	propene	nC3	1-butene	iso-butene	nC4	iC4	isoprene	CYC5	nC5	2MC4	Benz	CYCC6	MCYC5	nC6	2MC5	3MC5	23DMC4	Tol	nC7	C2Benz	oXyl	mpXyl	nC8	CH3Cl
TS03-070	ppbv	1.784	3.817	0.980	3.601	0.167	0.344	1.578	0.505	0.092	0.428	1.162	1.955	0.668	0.105	0.251	0.492	0.539	0.365	0.156	2.331	0.154	0.205	0.206	0.661	0.076	0.416
TS03-071	ppbv	1.688	4.090	1.065	3.806	0.180	0.316	1.708	0.544	0.159	0.465	1.266	2.102	0.728	0.119	0.276	0.536	0.586	0.393	0.189	2.526	0.168	0.265	0.279	0.873	0.089	0.488
TS03-072	ppbv	1.640	3.277	1.112	2.319	0.192	0.338	1.707	0.548	0.079	0.348	1.204	2.081	0.750	0.115	0.284	0.536	0.591	0.410	0.173	2.057	0.168	0.253	0.294	0.831	0.081	0.493
TS03-073	ppbv	1.424	2.758	0.577	2.325	0.121	0.225	1.393	0.493	0.154	0.274	0.865	1.545	0.444	0.083	0.186	0.368	0.398	0.276	0.123	1.587	0.155	0.296	0.370	1.267	0.100	0.444
TS03-074	ppbv	2.836	3.346	0.722	4.027	0.189	1.041	2.788	0.801	0.135	0.383	1.605	2.976	0.662	0.131	0.304	0.612	0.650	0.450	0.198	2.220	0.210	0.425	0.362	1.462	0.084	0.477
TS03-075	ppbv	0.938	2.481	0.426	1.667	0.077	0.134	0.818	0.339	0.164	0.208	0.534	0.929	0.337	0.060	0.125	0.248	0.264	0.184	0.081	0.922	0.123	0.169	0.201	0.655	0.098	0.407
TS03-076	ppbv	1.037	2.494	0.454	1.876	0.088	0.193	1.025	0.428	0.188	0.236	0.639	1.126	0.358	0.080	0.154	0.333	0.327	0.237	0.097	1.704	0.160	0.330	0.418	1.462	0.121	0.407
TS03-077	ppbv	0.979	2.662	0.473	1.874	0.086	0.149	1.016	0.505	0.210	0.246	0.635	1.124	0.394	0.094	0.155	0.326	0.320	0.229	0.093	1.496	0.174	0.396	0.502	1.769	0.142	0.488
TS03-078	ppbv	1.292	2.563	0.521	2.217	0.100	0.163	1.298	0.501	0.272	0.303	0.818	1.426	0.449	0.093	0.191	0.437	0.456	0.324	0.131	2.182	0.175	0.269	0.305	1.040	0.119	0.563
TS03-079	ppbv	0.445	2.409	0.106	0.941	0.031	0.089	0.608	0.215	0.152	0.177	0.271	0.497	0.147	0.020	0.042	0.095	0.107	0.073	0.035	0.547	0.029	0.118	0.137	0.420	0.023	0.514
TS03-080	ppbv	0.386	1.756	0.028	0.901	0.012	0.024	0.519	0.182	0.073	0.142	0.232	0.437	0.176	0.014	0.033	0.072	0.085	0.056	0.028	0.288	0.021	0.069	0.061	0.215	0.012	0.399
TS03-081	ppbv	0.339	1.712	0.063	0.666	0.021	0.047	0.399	0.138	0.174	0.234	0.180	0.328	0.170	0.018	0.053	0.299	0.063	0.046	0.022	1.070	0.042	0.063	0.069	0.211	0.011	0.373
TS03-082	ppbv	0.318	0.978	0.072	0.512	0.025	0.061	0.431	0.127	0.127	0.239	0.170	0.295	0.095	0.009	0.033	0.141	0.051	0.037	0.015	0.219	0.016	0.033	0.029	0.104	0.010	0.418
TS03-083	ppbv	0.313	1.520	0.049	0.482	0.019	0.076	0.373	0.118	0.133	0.212	0.162	0.283	0.136	0.009	0.047	0.217	0.053	0.037	0.018	0.200	0.015	0.029	0.027	0.092	0.009	0.380
TS03-084	ppbv	0.279	0.898	0.041	0.386	0.015	0.041	0.282	0.087	0.079	0.201	0.193	0.223	0.125	0.007	0.018	0.070	0.038	0.026	0.012	0.222	0.012	0.019	0.019	0.055	0.006	0.533
TS03-085	ppbv	0.383	1.576	0.083	0.581	0.029	0.077	0.438	0.140	0.113	0.333	0.204	0.343	0.106	0.012	0.029	0.091	0.067	0.044	0.024	0.521	0.023	0.152	0.122	0.465	0.023	0.019
TS03-086	ppbv	0.404	1.662	0.165	0.621	0.068	0.088	0.511	0.163	0.230	0.377	0.211	0.368	0.189	0.013	0.027	0.086	0.080	0.048	0.023	0.767	0.029	0.430	0.153	1.263	0.031	0.547
TS03-087	ppbv	0.328	1.568	0.048	0.549	0.017	0.045	0.342	0.110	0.112	0.271	0.176	0.275	0.130	0.012	0.025	0.079	0.051	0.035	0.024	0.208	0.016	0.055	0.053	0.171	0.011	0.425
TS03-088	ppbv	0.387	1.559	0.117	0.583	0.031	0.109	0.483	0.153	0.197	0.364	0.290	0.420	0.170	0.014	0.047	0.165	0.083	0.057	0.031	0.709	0.025	0.074	0.081	0.249	0.015	0.458
TS03-089	ppbv	0.364	1.479	0.082	0.581	0.030	0.126	0.552	0.165	0.216	0.427	0.284	0.447	0.165	0.015	0.041	0.133	0.085	0.056	0.029	0.537	0.022	0.079	0.092	0.263	0.014	0.511
TS03-090	ppbv	0.340	1.427	0.081	0.553	0.022	0.045	0.434	0.134	0.111	0.257	0.228	0.393	0.173	0.012	0.031	0.076	0.077	0.050	0.027	0.457	0.020	0.034	0.026	0.097	0.011	0.425
TS03-091	ppbv	0.321	1.405	0.080	0.487	0.023	0.085	0.340	0.106	0.173	0.218	0.267	0.329	0.116	0.010	0.049	0.201	0.064	0.043	0.023	0.260	0.015	0.029	0.027	0.096	0.009	0.399
TS03-092	ppbv	0.280	1.403	0.058	0.450	0.016	0.037	0.307	0.094	0.073	0.173	0.148	0.267	0.141	0.008	0.051	0.243	0.051	0.035	0.019	0.165	0.013	0.011	0.008	0.027	0.007	0.524
TS03-093	ppbv	0.348	1.474	0.100	0.495	0.027	0.055	0.457	0.152	0.220	0.243	0.242	0.458	0.169	0.016	0.037	0.087	0.088	0.057	0.030	0.267	0.024	0.032	0.027	0.107	0.010	0.428
TS03-094	ppbv	0.505	1.692	0.193	0.659	0.051	0.151	0.779	0.231	0.337	0.321	1.616	0.677	0.171	0.027	0.060	0.147	0.137	0.088	0.044	0.882	0.051	0.159	0.180	0.556	0.025	0.431
TS03-095	ppbv	0.354	1.514	0.101	0.499	0.027	0.058	0.458	0.150	0.216	0.311	2.258	0.418	0.167	0.015	0.037	0.118	0.084	0.054	0.025	0.346	0.025	0.182	0.124	0.641	0.010	0.327
TS03-096	ppbv	0.768	2.762	0.175	1.379	0.045	0.066	1.192	0.441	0.291	0.270	0.613	1.047	0.308	0.048	0.098	0.188	0.237	0.157	0.071	0.705	0.106	0.153	0.171	0.504	0.076	0.022
TS03-097	ppbv	0.820	2.438	0.347	1.673	0.074	0.146	1.659	0.470	0.390	0.287	0.728	1.218	0.310	0.065	0.131	0.245	0.291	0.192	0.089	1.022	0.096	0.238	0.301	0.810	0.040	0.404
TS03-098	ppbv	0.967	1.714	0.390	1.815	0.079	0.141	1.880	0.535	0.387	0.331	0.734	1.355	0.338	0.070	0.136	0.246	0.307	0.202	0.098	0.821	0.098	0.250	0.304	0.843	0.038	0.415
TS03-099	ppbv	1.305	3.013	0.623	2.781	0.120	0.190	2.162	0.689	0.451	0.368	0.990	1.785	0.502	0.136	0.238	0.426	0.475	0.317	0.131	1.286	0.165	0.322	0.383	1.094	0.070	0.025

Table A12: NMHC isotopic composition (δ^{13}C ‰), York University, June 2003.

Lab #	δ C^{13} ace	δ C^{13} nC3	δ C^{13} propylene	δ C^{13} i-C4	δ C^{13} n-C4	δ C^{13} CH$_3$Cl	δ C^{13} i-butene	δ C^{13} i-C5	δ C^{13} n-C5	δ C^{13} 2MC5	δ C^{13} MCYCC5	δ C^{13} 3MC5	δ C^{13} n-C6	δ C^{13} Benz	δ C^{13} Tol	δ C^{13} C2Benz	δ C^{13} m,p-xyl	δ C^{13} o-xyl
TS03-070	-15.6	-28.9	-25.2	LOD	-31.2	-32.8	-24.2	-29.6	-28.3	-27.9	-26.0	-26.4	-27.1	-23.8	-26.1	LOD	-26.0	LOD
TS03-071	-15.1	-28.7	-23.9	LOD	-29.6	LOD	LOD	-28.7	-26.9	-29.5	-25.8	-23.8	-22.1	-23.6	-28.0	LOD	-26.5	LOD
TS03-073	-18.7	-29.0	-25.0	-11.1	-33.2	-33.2	LOD	-29.2	-28.2	-29.3	-27.9	-26.8	-27.2	LOD	-26.6	-27.8	-28.0	LOD
TS03-074	-28.1	-28.6	-23.0	LOD	-30.2	LOD	LOD	LOD	-28.3	LOD	LOD	LOD	-24.0	-25.8	LOD	LOD	-26.9	LOD
TS03-075	-13.3	-27.8	LOD	LOD	-29.2	LOD	LOD	-27.2	-26.6	LOD	LOD	LOD	LOD	-22.3	-25.3	LOD	-22.3	LOD
TS03-076	-13.9	-28.6	-24.3	-16.0	-30.8	-36.3	LOD	-29.7	-28.6	LOD	LOD	LOD	LOD	-22.5	-27.9	-27.5	-27.4	-26.2
TS03-077	-12.6	-29.0	-24.2	-15.3	-30.6	LOD	LOD	-28.3	26.1	LOD	LOD	LOD	LOD	-26.2	-25.2	-27.1	-24.6	-25.2
TS03-078	-14.8	-28.4	-24.0	-9.6	-29.7	LOD	LOD	-28.6	-27.0	LOD	-27.9	-25.0	-24.0	LOD	-27.9	LOD	-25.8	-24.0
TS03-079	-8.3	-29.6	LOD	LOD	-31.7	LOD	-24.3	-28.6	-27.5	-28.1	LOD	LOD	-27.8	-22.7	-25.8	LOD	-27.5	LOD
TS03-080	LOD	-29.4	LOD	LOD	-28.2	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-24.2	LOD	LOD	-26.8	LOD
TS03-082	-5.2	-29.1	LOD	LOD	-32.1	LOD	-28.4	-28.4	-26.6	-29.6	LOD	LOD	-28.0	-25.6	LOD	LOD	-27.7	LOD
TS03-085	-3.6	-28.4	LOD	LOD	LOD	-36.1	-28.2	-28.1	-28.4	LOD	LOD	LOD	LOD	-25.2	-27.1	LOD	-27.1	LOD
TS03-088	-5.9	-27.8	LOD	LOD	-30.9	-31.6	-27.2	-29.3	-28.7	LOD	LOD	LOD	LOD	-25.2	-29.9	LOD	-31.1	LOD
TS03-091	-2.3	-27.3	LOD	LOD	-32.9	-30.8	-27.7	-28.5	-27.2	LOD	LOD	LOD	LOD	-18.3	-26.8	-26.1	-28.5	LOD
TS03-094	-7.3	-29.5	LOD	-23.7	-31.2	-34.2	LOD	-28.5	-27.2	LOD	-26.9	LOD	LOD	-22.4	-28.5	-24.3	-27.4	-24.0
TS03-095	-11.8	-29.6	LOD	LOD	-28.4	-30.9	-26.6	-30.1	-28.9	-27.1	-27.2	LOD	-27.4	-21.9	-29.6	-26.8	-25.4	LOD
TS03-096	-8.4	-28.8	LOD	-9.7	-28.7	LOD	LOD	-27.5	-26.6	LOD	LOD	LOD	LOD	-22.8	-28.0	LOD	-25.7	LOD
TS03-098	-10.8	-28.8	LOD	-6.0	-28.9	LOD	LOD	-29.2	-27.5	LOD	LOD	LOD	LOD	-20.7	-27.8	LOD	-27.0	-25.5
TS03-099	-10.7	-29.1	-20.0	-5.2	-28.8	LOD	LOD	-29.6	-27.1	LOD	LOD	-27.1	-26.7	-23.1	-28.6	LOD	-27.4	-25.3

Table A13: Sampling Information, Suburban/Rural (GTA), July 2003.

Lab #	site	canister	date	time-start	time-end	time [min]	weather	temp[°C]	humidity	wind direct.	sp.[km/h]
TS03-100	#14	Y358	14/07/2003	12:00	12:56	0:56	mainly clear	26.9	46%	17-18	18.5
TS03-101	#14	Y371	14/07/2003	12:15	12:20	0:05	mainly clear	26.4	48%	17	20
TS03-102	#14	Y511	14/07/2003	12:46	12:53	0:07	mainly clear	27.4	44%	18	17
TS03-103	#15	Y366	14/07/2003	13:20	14:15	0:55	mainly clear	27.35	43.5%	18	20.5
TS03-104	#15	Y521	14/07/2003	13:37	13:43	0:06	mainly clear	27.4	44%	18	17
TS03-105	#15	Y213	14/07/2003	14:00	14:07	0:07	mainly clear	27.3	43%	18	24
TS03-106	#16	Y289	14/07/2003	15:04	15:54	0:50	mostly cloudy	26.6	42%	20-19	19
TS03-107	#16	Y352	14/07/2003	15:20	15:26	0:06	mostly cloudy	26.8	41%	20	19
TS03-108	#16	Y208	14/07/2003	15:43	15:50	0:07	mostly cloudy	26.4	43%	19	19
TS03-109	#17	Y426	14/07/2003	16:30	17:20	0:50	mostly cloudy	26.8	41.5%	19-20	19
TS03-110	#17	Y399	14/07/2003	16:46	16:54	0:08	mostly cloudy	27.2	40%	20	19
TS03-111	#17	Y363	14/07/2003	17:08	17:19	0:11	mostly cloudy	27.2	40%	20	19
TS03-112	#18	Y378	14/07/2003	18:05	18:55	0:50	mainly clear	26.3	44%	19	17.5
TS03-113	#18	Y271	14/07/2003	18:21	18:30	0:09	mainly clear	26.8	44%	19	20
TS03-114	#18	Y409	14/07/2003	18:44	18:47	0:03	mainly clear	25.8	44%	19	15
TS03-115	#19	Y480	14/07/2003	19:20	20:10	0:50	mainly clear	25.0	46.5%	19-17	14
TS03-116	#19	Y522	14/07/2003	19:39	19:43	0:04	mainly clear	25.8	44	19	15
TS03-117	#19	Y526	14/07/2003	20:00	20:04	0:04	mainly clear	24.3	49%	17	13

Table A14: NMHC Mixing Ratio (ppbv), Suburban/Rural (GTA), July 2003.

Lab #	ppbV	ace	nC2	propene	nC3	1-butene	iso-butene	nC4	iC4	isoprene	CYC5	nC5	2MC4	Benz	nC6	2MC5	3MC5	23DMC4	Tol	nC7	C2Benz	oXyl	mpXyl	nC8	CH3Cl
TS03-100	ppbv	0.357	1.563	0.060	0.515	0.017	0.086	0.237	0.107	0.513	0.049	0.125	0.231	0.111	0.042	0.048	0.031	0.014	0.393	0.015	0.015	0.011	0.034	0.010	0.356
TS03-101	ppbv	0.304	1.342	0.067	0.511	0.024	0.121	0.240	0.112	0.752	0.242	0.128	0.050	0.127	0.044	0.049	0.031	0.015	0.108	0.015	0.009	0.004	0.016	0.010	0.548
TS03-102	ppbv	0.259	1.478	0.052	0.745	0.026	0.045	0.215	0.096	0.632	0.209	0.112	0.046	0.110	0.034	0.041	0.025	0.012	0.167	0.012	0.012	0.006	0.022	0.009	0.460
TS03-103	ppbv	0.241	1.263	0.040	0.797	0.015	0.088	0.180	0.074	0.451	0.049	0.096	0.173	0.082	0.033	0.036	0.023	0.012	0.353	0.011	0.014	0.010	0.028	0.006	0.377
TS03-104	ppbv	0.230	1.392	0.051	0.954	0.007	0.032	0.179	0.075	0.485	0.045	0.095	0.170	0.079	0.028	0.033	0.021	0.012	0.239	0.009	0.013	0.011	0.031	0.006	0.384
TS03-105	ppbv	0.259	1.418	0.112	0.864	0.018	0.035	0.188	0.076	1.006	0.045	0.105	0.185	0.088	0.031	0.038	0.023	0.013	0.108	0.010	0.009	0.004	0.013	0.007	0.365
TS03-106	ppbv	0.269	1.398	0.051	0.595	0.004	0.043	0.205	0.106	1.098	0.047	0.113	0.184	0.081	0.036	0.040	0.025	0.015	0.287	0.012	0.016	0.010	0.034	0.007	0.419
TS03-107	ppbv	0.207	1.327	0.054	0.474	0.005	0.025	0.127	0.058	0.914	0.040	0.061	0.109	0.068	0.016	0.021	0.013	0.008	0.136	0.005	0.006	0.004	0.011	0.003	0.350
TS03-108	ppbv	0.569	1.711	0.127	1.075	0.018	0.033	0.599	0.361	0.943	0.084	0.388	0.580	0.184	0.139	0.138	0.096	0.039	0.572	0.047	0.062	0.040	0.116	0.020	0.344
TS03-109	ppbv	0.502	1.613	0.170	1.062	0.014	0.066	0.610	0.326	1.493	0.126	0.372	0.632	0.187	0.196	0.162	0.123	0.060	0.737	0.059	0.087	0.065	0.236	0.025	0.384
TS03-110	ppbv	0.507	1.627	0.173	1.004	0.014	0.063	0.599	0.309	1.623	0.113	0.372	0.647	0.202	0.199	0.169	0.126	0.057	0.706	0.062	0.084	0.065	0.240	0.024	0.348
TS03-111	ppbv	0.500	1.567	0.139	0.864	0.026	0.058	0.600	0.279	1.383	0.123	0.314	0.571	0.187	0.143	0.134	0.095	0.041	0.537	0.051	0.051	0.033	0.121	0.024	0.511
TS03-112	ppbv	0.316	1.345	0.082	0.443	0.021	0.039	0.418	0.144	0.158	0.071	0.245	0.452	0.107	0.111	0.104	0.069	0.031	0.394	0.047	0.038	0.025	0.089	0.025	0.537
TS03-113	ppbv	0.310	1.397	0.069	0.455	0.019	0.041	0.429	0.148	0.162	0.070	0.248	0.468	0.173	0.116	0.104	0.070	0.031	0.438	0.055	0.029	0.020	0.069	0.029	0.442
TS03-114	ppbv	0.361	1.297	0.085	0.435	0.019	0.035	0.376	0.127	0.443	0.064	0.216	0.414	0.125	0.116	0.099	0.066	0.030	0.424	0.037	0.048	0.038	0.133	0.015	0.380
TS03-115	ppbv	0.290	1.320	0.091	0.400	0.018	0.067	0.255	0.086	2.048	0.050	0.144	0.256	0.089	0.045	0.058	0.037	0.017	0.230	0.019	0.017	0.015	0.149	0.010	0.378
TS03-116	ppbv	0.314	1.305	0.153	0.399	0.029	0.057	0.249	0.082	2.279	0.052	0.152	0.264	0.131	0.049	0.064	0.041	0.021	0.206	0.019	0.016	0.019	0.181	0.009	0.361
TS03-117	ppbv	0.393	1.397	0.133	0.551	0.020	0.039	0.465	0.189	1.451	0.053	0.276	0.521	0.152	0.128	0.120	0.083	0.038	0.458	0.048	0.048	0.038	0.182	0.021	0.400

Table A15: NMHC isotopic composition ($\delta^{13}C$ ‰), Suburban/Rural (GTA), July 2003.

Lab #	δ C^{13} acetylene	δ C^{13} propane	δ C^{13} iso-butane	δ C^{13} n-butane	δ C^{13} cyclopropane	δ C^{13} CH3Cl	δ C^{13} i-butene	δ C^{13} iso-pentane	δ C^{13} n-pentane	δ C^{13} cyclopentane	δ C^{13} 2-methylpentane	δ C^{13} isoprene	δ C^{13} benzene	δ C^{13} toluene	δ C^{13} ethyl benzene	δ C^{13} m,p-xylene	δ C^{13} o-xylene
TS03-100	-8.0	-29.0	LOD	LOD	LOD	-36.5	LOD	LOD	LOD	LOD	LOD	-29.3	-20.6	LOD	LOD	-26.8	LOD
TS03-101	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-28.8	-22.2	LOD	-28.8	-20.9	LOD	LOD	-28.2	LOD
TS03-102	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-28.9	-20.6	LOD	LOD	-24.6	LOD
TS03-104	LOD	-26.4	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-24.5	-23.9	-25.8	LOD	-23.0	LOD
TS03-106	-8.7	-29.6	LOD	LOD	-27.3	LOD	-29.4	LOD	LOD	LOD	LOD	-27.7	-28.5	-30.5	LOD	-27.1	LOD
TS03-108	LOD	-28.8	LOD	-30.7	LOD	LOD	-26.6	-27.2	-27.3	LOD	LOD	-26.1	-25.0	-28.2	LOD	-26.4	LOD
TS03-109	-11.5	-28.1	LOD	-30.8	-26.6	-38.0	LOD	-28.0	-27.8	LOD	LOD	-27.6	-22.1	-29.0	LOD	-25.5	-24.9
TS03-112	-9.1	-28.2	LOD	-31.2	LOD	-38.0	LOD	-27.1	-24.2	LOD	LOD	LOD	-22.6	-29.1	LOD	-25.4	LOD
TS03-114	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-26.6	-22.5	-29.0	LOD	-25.8	LOD
TS03-115	-8.6	-28.7	LOD	LOD	LOD	-36.5	LOD	-28.6	-27.0	LOD	-27.5	-27.8	-22.5	-28.9	LOD	-25.6	LOD
TS03-117	LOD	-28.9	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-28.8	-24.2	LOD	LOD	-26.4	LOD

Table A16: Sampling Information, Urban Toronto, July 2003.

Lab #	site	canister	date	time-start	time-end	time [min]	weather	temp[°C]	humidity	wind direct.	sp.[km/h]	Atmos. Pre.
TS03-118	#9	Y427	07/15/03	9:46	10:40	0:54	mainly sunny at PA	21	74%	SE	11	101.65 kPa and falling
TS03-119	#9	Y423	07/15/03	10:00	10:04	0:04						
TS03-120	#9	Y469	07/15/03	10:25	10:28	0:03						
TS03-121	#8	Y245	07/15/03	10:53	11:46	0:53	partly cloudy at PA	24	70%	SE	15	101.51 kPa and falling
TS03-122	#8	Y296	07/15/03	11:12	11:16	0:04						
TS03-123	#8	Y301	07/15/03	11:35	11:39	0:04						
TS03-124	#11	Y285	07/15/03	12:28	13:28	1:00	partly cloudy at PA	25	64%	SE	20	101.36 kPa and falling
TS03-125	#11	Y234	07/15/03	12:46	12:50	0:04						
TS03-126	#11	Y302	07/15/03	13:05	13:09	0:04						
TS03-127	#10	Y483	07/15/03	13:43	14:40	0:57	mainly cloudy at PA	26	61%	SE	22	101.26 kPa and falling
TS03-128	#10	Y504	07/15/03	14:00	14:04	0:04						
TS03-129	#10	Y232	07/15/03	14:24	14:28	0:04						
TS03-130	#13	Y402	07/15/03	15:02	15:35	0:33	cloudy at PA	25	54%	SE	19	101.20 kPa and falling
TS03-131	#13	Y482	07/15/03	15:19	15:24	0:05						
TS03-132	#13	Y422	07/15/03	15:30	15:35	0:05						
TS03-133	#6	Y524	07/15/03	16:38	17:22	0:44	overcast at PA	25	56%	SE	15	100.96 kPa and falling
TS03-134	#6	Y394	07/15/03	16:51	16:56	0:05						
TS03-135	#6	Y032	07/15/03	17:11	17:16	0:05						

Table A17: NMHC Mixing Ratio (ppbv), Urban Toronto, July 2003.

Lab #	ppbV	ace	nC2	propene	nC3	1-butene	iso-butene	nC4	iC4	isoprene	CYC5	nC5	2MC4	Benz	MCYC5	nC6	2MC5	3MC5	23DMC4	Tol	nC7	C2Benz	oXyl	mpXyl	nC8	CH3Cl
TS03-118	ppbv	0.852	4.881	0.356	2.584	0.060	0.090	1.120	0.492	0.061	0.122	0.592	1.007	0.244	0.098	0.198	0.242	0.161	0.075	1.671	0.107	0.321	0.213	1.152	0.048	0.399
TS03-119	ppbv	0.729	5.014	0.346	2.650	0.059	0.074	1.073	0.492	0.076	0.128	0.595	0.985	0.248	0.099	0.197	0.241	0.160	0.074	2.031	0.110	0.213	0.174	0.738	0.062	0.488
TS03-120	ppbv	2.623	5.099	0.738	2.572	0.071	0.167	1.543	0.526	0.046	0.118	0.619	1.066	0.595	0.096	0.186	0.236	0.155	0.071	1.690	0.083	0.351	0.266	1.378	0.035	0.510
TS03-121	ppbv	0.836	4.508	0.436	3.337	0.112	0.149	1.909	0.680	0.125	0.141	0.982	1.760	0.343	0.193	0.606	0.415	0.274	0.115	1.519	0.100	0.110	0.096	0.318	0.039	0.643
TS03-122	ppbv	0.876	4.667	0.438	3.383	0.261	0.284	5.199	1.460	0.130	0.225	2.518	4.678	0.423	0.267	0.543	0.848	0.550	0.223	1.650	0.132	0.128	0.120	0.381	0.052	0.410
TS03-123	ppbv	0.975	4.379	0.316	3.558	0.050	0.068	0.837	0.401	0.052	0.101	0.458	0.782	0.231	0.069	0.147	0.192	0.121	0.054	0.664	0.059	0.053	0.040	0.141	0.039	0.439
TS03-124	ppbv	0.753	3.973	0.258	2.748	0.052	0.091	0.730	0.592	0.111	0.125	0.679	0.721	0.263	0.116	0.381	0.242	0.216	0.051	1.354	0.379	0.064	0.050	0.168	0.032	0.589
TS03-125	ppbv	0.659	3.940	0.230	2.960	0.049	0.084	0.782	0.808	0.107	0.105	0.882	0.727	0.296	0.109	0.312	0.232	0.198	0.063	1.258	0.214	0.063	0.055	0.166	0.046	0.523
TS03-126	ppbv	0.580	3.727	0.167	1.628	0.036	0.067	0.612	0.290	0.096	0.106	0.733	0.611	0.246	0.080	0.218	0.176	0.141	0.050	1.349	0.097	0.086	0.086	0.237	0.027	0.455
TS03-127	ppbv	0.572	2.112	0.159	1.307	0.033	0.089	0.633	0.289	0.522	0.113	0.353	0.626	0.164	0.177	1.009	0.163	0.126	0.051	0.570	0.043	0.097	0.158	0.406	0.038	0.424
TS03-128	ppbv	0.549	3.522	0.109	1.214	0.028	0.054	0.559	0.280	0.372	0.104	0.322	0.586	0.205	0.254	1.641	0.164	0.147	0.049	0.852	0.043	0.111	0.136	0.386	0.032	0.418
TS03-129	ppbv	0.498	3.419	0.195	1.174	0.028	0.049	0.577	0.240	0.460	0.107	0.305	0.547	0.176	0.085	0.345	0.137	0.095	0.041	0.784	0.040	0.074	0.099	0.262	0.032	0.410
TS03-130	ppbv	0.778	3.465	0.348	2.020	0.061	0.155	1.079	0.323	0.178	1.866	0.494	0.877	0.254	0.124	0.341	0.239	0.172	0.056	1.509	0.357	0.209	0.201	0.695	0.363	0.352
TS03-131	ppbv	0.853	4.155	0.624	2.713	0.165	0.168	1.103	0.353	0.181	6.392	0.549	1.048	0.298	0.139	0.313	0.293	0.207	0.078	2.881	0.450	0.364	0.353	1.211	0.366	0.603
TS03-132	ppbv	0.876	3.624	0.458	1.599	0.071	0.119	0.859	0.363	0.141	29.572	0.561	1.579	0.321	0.207	0.407	0.382	0.288	0.101	2.095	0.191	0.310	0.294	1.033	0.067	0.475
TS03-133	ppbv	0.884	4.177	0.335	1.749	0.150	0.234	3.467	1.009	0.097	0.192	1.545	3.215	0.332	0.245	0.551	0.589	0.402	0.190	2.429	0.142	0.160	0.133	0.389	0.058	0.355
TS03-134	ppbv	0.922	4.156	0.298	1.653	0.156	0.157	4.234	1.293	0.069	0.178	1.817	3.816	0.321	0.279	0.707	0.665	0.470	0.209	2.114	0.152	0.131	0.141	0.395	0.060	0.339
TS03-135	ppbv	0.839	3.035	0.314	1.831	0.179	0.249	4.729	1.550	0.058	0.162	1.940	4.162	0.308	0.257	0.508	0.649	0.425	0.212	1.894	0.146	0.142	0.142	0.436	0.001	0.339

Table A19: NMHC isotopic composition ($\delta^{13}C$ ‰), Urban Toronto, July 2003.

Lab #	δC^{13} ace	δC^{13} nC3	δC^{13} propylene	δC^{13} i-C4	δC^{13} n-C4	δC^{13} CH_3Cl	δC^{13} i-C5	δC^{13} n-C5	δC^{13} 2MC5	δC^{13} MCYCC5	δC^{13} 3MC5	δC^{13} n-C6	δC^{13} Benz	δC^{13} Tol	δC^{13} C2Benz	δC^{13} m,p-xyl	δC^{13} o-xyl
TS03-118	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-22.6	LOD	LOD	LOD	LOD
TS03-119	LOD	-30.5	LOD	LOD	-29.6	LOD	-29.1	-27.8	LOD	LOD	LOD	LOD	-24.8	-28.3	LOD	-24.8	-24.5
TS03-120	-13.1	-30.8	-25.8	LOD	-28.2	LOD	-28.8	-26.7	LOD	LOD	LOD	LOD	-22.8	LOD	-28.0	-25.5	-26.5
TS03-121	-14.5	-29.9	-21.3	-15.7	-30.3	-35.1	-29.6	-28.6	-27.9	-28.3	-25.8	-27.3	-23.5	-28.7	LOD	-26.9	-24.3
TS03-122	-11.9	-29.6	-21.2	-24.9	-30.2	LOD	-29.6	-28.6	-27.8	-29.2	-26.2	-25.4	-24.0	-28.6	LOD	LOD	LOD
TS03-123	-12.0	-29.2	LOD	-15.6	-29.0	LOD	-28.5	-26.1	LOD	LOD	LOD	LOD	-24.3	-26.2	LOD	-25.3	LOD
TS03-124	-9.8	-29.8	LOD	LOD	-30.1	-32.2	-28.5	-27.0	LOD	LOD	LOD	LOD	-21.9	-26.8	LOD	-26.1	LOD
TS03-125	-9.8	-30.2	-22.2	LOD	-29.4	LOD	-28.5	-26.7	LOD	LOD	LOD	LOD	-26.3	-27.3	LOD	-26.6	-25.8
TS03-127	-11.9	-29.3	LOD	LOD	-30.5	-35.9	-28.9	-26.5	LOD	-25.8	LOD	-27.9	-23.0	-28.9	-28.4	-27.5	LOD
TS03-128	-9.5	-29.7	LOD	LOD	-29.9	LOD	-27.9	-26.0	LOD	LOD	LOD	-26.7	-24.0	-27.7	LOD	-26.4	LOD
TS03-129	-9.0	-29.6	LOD	LOD	LOD	LOD	-27.7	-24.3	LOD	-27.4	LOD	-28.2	-24.4	-25.6	LOD	LOD	LOD
TS03-130	-13.2	-29.8	LOD	LOD	-29.8	LOD	-27.6	-27.3	LOD	LOD	LOD	LOD	-23.8	-28.1	LOD	-24.7	-23.2
TS03-131	-11.3	-28.2	LOD	LOD	-28.3	LOD	-28.9	-27.8	LOD	LOD	LOD	LOD	-25.3	-26.6	-27.6	-27.1	-24.5
TS03-132	-14.0	-27.2	LOD	LOD	-33.3	LOD	-29.1	-27.6	LOD	-27.5	-25.7	-25.3	-25.4	-25.7	-27.3	-26.9	-25.3
TS03-133	-13.8	-29.4	LOD	-22.5	-31.1	LOD	-29.9	-28.6	-27.1	-27.7	-26.6	-26.7	-25.6	-28.7	-28.4	-26.7	-24.6
TS03-134	-14.1	-29.5	LOD	-25.4	-31.3	LOD	-29.9	-28.0	LOD	-28.4	-26.4	-26.7	-25.4	-28.0	LOD	-26.3	-24.7
TS03-135	-14.6	-29.3	LOD	-27.4	-31.5	LOD	-30.2	-29.1	-26.0	-28.1	-26.5	-26.4	-22.7	-28.4	LOD	-26.0	LOD

Table A20: NMHC Mixing Ratio (ppbv), York University, July 2003.

Lab #	ppbV	ace	nC2	propene	nC3	1-butene	iso-butene	nC4	iC4	isoprene	CYC5	nC5	2MC4	Benz	MCYC5	nC6	2MC5	3MC5	23DMC4	Tol	nC7	C2Benz	oXyl	mpXyl	nC8	CH3Cl
TS03-136	ppbv	0.742	1.593	0.590	2.500	0.090	0.273	0.522	0.162	0.018	0.212	0.510	0.812	0.356	0.102	0.195	0.288	0.169	0.188	0.849	0.070	0.013	0.002	0.015	0.016	0.234
TS03-137	ppbv	0.849	1.311	0.638	6.355	0.112	0.221	0.630	0.203	0.067	0.295	0.672	1.036	0.490	0.150	0.280	0.418	0.247	0.199	0.973	0.124	0.151	0.103	0.313	0.038	0.295
TS03-138	ppbv	1.091	1.888	0.743	2.076	0.095	0.197	0.530	0.169	0.098	0.274	0.497	0.792	0.379	0.098	0.191	0.284	0.165	0.094	0.615	0.070	0.076	0.052	0.158	0.029	0.288
TS03-139	ppbv	0.804	1.753	0.578	1.328	0.090	0.223	0.548	0.186	0.102	0.229	0.760	0.843	0.372	0.113	0.229	0.308	0.184	0.183	1.214	0.070	0.066	0.034	0.130	0.024	0.279
TS03-140	ppbv	0.999	2.010	0.739	2.274	0.096	0.200	0.652	0.219	0.016	0.221	1.037	1.071	0.411	0.147	0.273	0.333	0.224	0.348	0.849	0.091	0.135	0.138	0.441	0.040	0.442
TS03-141	ppbv	0.729	1.646	0.438	1.052	0.063	0.158	0.535	0.202	0.139	0.152	0.488	0.834	0.265	0.092	0.166	0.230	0.153	0.074	0.543	0.063	0.068	0.069	0.211	0.026	0.469
TS03-142	ppbv	0.371	1.390	0.227	0.625	0.043	0.128	0.327	0.143	0.139	0.198	0.250	0.425	0.171	0.054	0.111	0.148	0.089	0.043	0.551	0.049	0.043	0.034	0.089	0.021	0.443
TS03-143	ppbv	0.411	1.413	0.358	0.686	0.041	0.073	0.361	0.148	0.115	0.119	0.299	0.508	0.187	0.064	0.118	0.145	0.096	0.059	0.386	0.055	0.030	0.024	0.085	0.023	0.354
TS03-144	ppbv	0.447	1.370	0.486	1.135	0.038	0.077	0.309	0.161	0.162	0.122	0.243	0.428	0.175	0.049	0.097	0.114	0.079	0.044	0.311	0.037	0.028	0.028	0.087	0.018	0.332
TS03-145	ppbv	0.218	1.060	0.165	0.249	0.035	0.084	0.176	0.070	0.095	0.733	0.098	0.179	1.298	0.039	0.285	0.053	0.043	0.016	0.497	0.357	5.709	0.063	0.149	0.598	0.481
TS03-146	ppbv	0.001	1.019	0.097	0.169	0.023	0.042	0.106	0.038	0.120	0.170	0.071	0.119	0.087	0.014	0.039	0.040	0.025	0.012	0.240	0.014	0.040	0.018	0.042	0.017	0.385
TS03-147	ppbv	0.165	1.024	0.105	0.284	0.025	0.131	0.189	0.084	0.095	3.028	0.115	0.230	0.102	0.026	0.081	0.071	0.044	0.021	0.439	0.021	0.036	0.027	0.074	0.017	0.464
TS03-148	ppbv	0.266	0.933	0.143	0.311	0.022	0.073	0.174	0.065	0.096	0.289	0.112	0.198	0.076	0.023	0.058	0.052	0.037	0.019	0.343	0.024	0.036	0.032	0.111	0.010	0.353
TS03-149	ppbv	0.283	1.261	0.438	0.405	0.029	0.109	0.234	0.082	0.105	0.273	0.159	0.276	0.103	0.036	0.095	0.081	0.060	0.023	0.304	0.030	0.032	0.032	0.095	0.017	0.352
TS03-150	ppbv	0.203	1.192	0.130	0.285	0.017	0.058	0.137	0.045	0.088	0.234	0.088	0.154	0.094	0.014	0.042	0.035	0.025	0.013	0.166	0.017	0.016	0.017	0.061	0.011	0.343
TS03-151	ppbv	0.412	0.994	0.171	0.576	0.036	0.124	0.387	0.200	0.193	0.263	0.238	0.387	0.134	0.049	0.122	0.126	0.080	0.030	0.483	0.051	0.100	0.094	0.213	0.036	0.371
TS03-152	ppbv	0.505	1.457	0.218	0.841	0.031	0.066	0.516	0.244	0.246	0.177	0.333	0.571	0.148	0.066	0.157	0.148	0.106	0.043	0.566	0.058	0.087	0.083	0.249	0.032	0.404
TS03-153	ppbv	0.455	1.103	0.201	0.495	0.044	0.126	0.441	0.214	0.240	0.201	0.272	0.467	0.159	0.060	0.145	0.153	0.097	0.036	0.455	0.052	0.101	0.089	0.206	0.032	0.367
TS03-154	ppbv	0.302	1.071	0.143	0.384	0.036	0.178	0.372	0.137	0.146	0.332	0.225	0.400	0.141	0.051	0.189	0.108	0.070	0.028	0.420	0.040	0.066	0.043	0.132	0.023	0.536
TS03-155	ppbv	0.140	0.704	0.141	0.221	0.037	0.087	0.119	0.050	0.102	0.317	0.078	0.126	0.100	0.045	0.264	0.039	0.029	0.011	0.153	0.017	0.020	0.015	0.039	0.020	0.504
TS03-156	ppbv	0.283	1.717	0.401	0.496	0.050	0.081	0.274	0.075	0.185	0.312	0.158	0.288	0.106	0.046	0.188	0.066	0.051	0.019	0.281	0.028	0.051	0.054	0.166	0.025	0.345
TS03-157	ppbv	0.259	1.294	0.235	0.318	0.039	0.089	0.231	0.071	0.135	0.208	0.155	0.268	0.099	0.049	0.207	0.070	0.054	0.021	0.380	0.027	0.048	0.049	0.159	0.013	0.417
TS03-158	ppbv	0.274	1.261	0.227	0.313	0.024	0.209	0.242	0.085	0.147	0.240	0.174	0.302	0.120	0.066	0.306	0.088	0.067	0.024	0.342	0.044	0.051	0.035	0.129	0.022	0.370
TS03-159	ppbv	0.300	1.221	0.250	0.263	0.027	0.119	0.190	0.064	0.148	0.225	0.138	0.245	0.106	0.029	0.080	0.064	0.047	0.018	0.189	0.021	0.027	0.025	0.089	0.014	0.349
TS03-160	ppbv	0.240	0.657	0.124	0.259	0.015	0.026	0.201	0.081	0.177	0.321	0.134	0.230	0.138	0.027	0.068	0.076	0.046	0.021	0.273	0.021	0.120	0.081	0.278	0.013	0.812
TS03-161	ppbv	0.253	1.081	0.122	0.325	0.026	0.055	0.189	0.090	0.161	0.272	0.119	0.205	0.104	0.027	0.072	0.066	0.042	0.018	0.258	0.022	0.180	0.116	0.439	0.016	0.521
TS03-162	ppbv	0.300	0.966	0.175	0.370	0.036	0.129	0.240	0.117	0.153	0.288	0.173	0.292	0.147	0.037	0.081	0.102	0.061	0.025	0.360	0.035	0.115	0.066	0.265	0.016	0.466
TS03-163	ppbv	0.327	1.581	0.435	1.507	0.024	0.052	0.233	0.123	0.125	0.160	0.192	0.282	0.127	0.031	0.076	0.082	0.057	0.026	0.321	0.035	0.036	0.031	0.121	0.018	0.582
TS03-164	ppbv	0.321	1.474	0.283	0.752	0.028	0.039	0.290	0.127	0.120	0.198	0.436	0.386	0.113	0.070	0.217	0.201	0.153	0.046	0.296	0.047	0.030	0.027	0.100	0.029	0.499
TS03-165	ppbv	0.336	1.406	0.210	0.463	0.026	0.046	0.261	0.089	0.187	0.146	0.204	0.345	0.130	0.038	0.076	0.090	0.059	0.053	0.338	0.026	0.024	0.019	0.072	0.013	0.410

Table A21: NMHC isotopic composition (δ^{13}C ‰), York University, July 2003.

Lab #	δC^{13} ace	δC^{13} nC3	δC^{13} propylene	δC^{13} i-C4	δC^{13} n-C4	δC^{13} CH_3Cl	δC^{13} 1- butene	δC^{13} i-butene	δC^{13} i-C5	δC^{13} n-C5	δC^{13} 2MC5	δC^{13} 3MC5	δC^{13} n-C6	δC^{13} Benz	δC^{13} Tol	δC^{13} C2Benz	δC^{13} m,p-xyl	δC^{13} o-xyl
TS03-136	-12.2	-29.0	LOD	LOD	LOD	-40.8	LOD	-24.6	-28.3	-26.8	LOD	LOD	LOD	-21.5	-27.4	LOD	-25.5	LOD
TS03-137	-13.2	-28.4	-21.7	LOD	-26.8	LOD	LOD	-24.2	-28.2	-26.6	LOD	LOD	LOD	-23.0	-26.7	LOD	-24.5	LOD
TS03-138	-20.2	-28.9	-24.4	LOD	-30.7	LOD	LOD	-25.5	-30.8	-27.9	LOD	LOD	LOD	-25.2	-26.6	LOD	-24.9	LOD
TS03-140	-11.0	-27.8	-25.4	LOD	-31.4	LOD	LOD	LOD	-28.9	-27.0	-27.1	-25.6	-25.3	-24.5	-28.5	LOD	-26.5	-24.0
TS03-141	-11.6	-27.1	-27.0	LOD	-30.1	LOD	LOD	LOD	-29.2	-27.8	-26.7	-25.1	-24.5	-17.9	-25.5	LOD	-24.7	LOD
TS03-142	-10.8	-28.8	LOD	LOD	LOD	LOD	-29.7	LOD	-29.2	-27.3	LOD	LOD	LOD	-24.2	-30.1	LOD	-25.7	LOD
TS03-143	LOD	-28.3	LOD	LOD	LOD	LOD	LOD	LOD	-28.7	-26.9	LOD	LOD	LOD	-20.0	-26.8	LOD	-26.0	LOD
TS03-144	LOD	-28.2	LOD	LOD	LOD	LOD	LOD	LOD	-29.0	LOD	LOD	LOD	LOD	-21.7	-26.8	LOD	-26.4	LOD
TS03-145	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-21.4	-31.0	LOD	-25.8	LOD
TS03-146	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-22.2	-29.8	LOD	-24.6	LOD
TS03-147	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-22.0	-29.3	LOD	-24.9	LOD
TS03-148	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-24.7	LOD	LOD	-26.1	LOD
TS03-149	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-21.5	-28.4	LOD	LOD	LOD
TS03-151	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-25.2	-27.4	LOD	LOD	LOD
TS03-152	LOD	-28.6	LOD	LOD	-33.0	LOD	LOD	LOD	-28.8	-28.7	LOD	LOD	LOD	-25.8	-27.0	LOD	-26.1	LOD
TS03-153	LOD	LOD	LOD	LOD	-29.7	LOD	LOD	LOD	-29.1	-27.3	LOD	LOD	LOD	-23.3	-26.5	LOD	-25.6	LOD
TS03-154	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-21.3	-25.6	LOD	-23.4	LOD
TS03-155	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-27.5	LOD	LOD	LOD	-22.3	-27.9	LOD	-26.1	LOD
TS03-157	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-22.3	-27.3	LOD	-24.7	LOD
TS03-158	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-28.0	LOD	LOD	LOD	-21.9	LOD	LOD	-25.1	LOD
TS03-160	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-21.0	LOD	LOD	-24.0	LOD
TS03-163	LOD	-28.0	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-18.2	-28.6	LOD	-26.4	LOD
TS03-164	LOD	-27.5	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-19.0	-25.5	LOD	-24.1	LOD
TS03-165	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-28.4	-26.4	LOD	LOD	LOD	-19.5	-27.2	LOD	-24.7	LOD

Table A22: Sampling Information, York University, August 2003.

Lab #	site	canister	date	time-start	time-end	time [min]	weather	temp[°C]	humidity	wind direct.	sp.[km/h]	Atmos. Pre.
TS03-166	Petrie roof	Y247	08/14/03	7:35	8:35	1:00	sunny	22	77%	W	7	102.93 kPa and rising
TS03-167	Petrie roof	Y282	08/14/03	7:52	7:56	0:04	sunny	22	77%	W	7	102.93 kPa and rising
TS03-168	Petrie roof	Y456	08/14/03	8:15	8:19	0:04	sunny	22	77%	W	7	102.93 kPa and rising
TS03-169	Petrie roof	Y316	08/14/03	8:35	9:35	1:00	sunny	25	62	NW	15	102.96 kPa and rising
TS03-170	Petrie roof	Y349	08/14/03	8:47	8:51	0:04	sunny	25	62	NW	15	102.96 kPa and rising
TS03-171	Petrie roof	Y458	08/14/03	9:16	9:19	0:03	sunny	25	62	NW	15	102.96 kPa and rising
TS03-172	Petrie roof	Y468	08/14/03	16:30	17:30	1:00	N/A	N/A	N/A	N/A	N/A	
TS03-173	Petrie roof	Y252	08/14/03	16:45	16:49	0:04	N/A	N/A	N/A	N/A	N/A	
TS03-174	Petrie roof	Y054	08/14/03	17:15	17:19	0:04	N/A	N/A	N/A	N/A	N/A	
TS03-175	Petrie roof	Y207	08/14/03	17:30	18:30	1:00	N/A	N/A	N/A	N/A	N/A	
TS03-176	Petrie roof	Y014	08/14/03	17:45	17:49	0:04	N/A	N/A	N/A	N/A	N/A	
TS03-177	Petrie roof	Y269	08/14/03	18:15	18:19	0:04	N/A	N/A	N/A	N/A	N/A	

Table A23: NMHC Mixing Ratio (ppbv), York University, August 2003.

Lab #	ppbV	ace	nC2	propene	nC3	1-butene	iso-butene	nC4	iC4	isoprene	CYC5	nC5	2MC4	Benz	MCYC5	nC6	2MC5	3MC5	23DMC4	Tol	nC7	C2Benz	oXyl	mpXyl	nC8	CH3Cl
TS03-166	ppbv	1.118	1.798	0.852	2.161	0.146	0.250	1.003	0.363	0.203	0.368	0.903	1.499	0.578	0.177	0.405	0.488	0.299	0.164	1.289	0.108	0.094	0.049	0.176	0.037	0.435
TS03-167	ppbv	1.023	1.713	2.183	2.029	0.660	0.491	0.990	0.346	0.259	0.320	0.863	1.463	0.584	0.168	0.414	0.463	0.284	0.135	0.706	0.097	0.056	0.027	0.094	0.036	0.426
TS03-168	ppbv	0.972	1.478	0.637	1.246	0.121	0.204	0.844	0.299	0.170	0.344	0.751	1.328	0.481	0.226	0.674	0.475	0.341	0.107	1.199	0.099	0.158	0.136	0.385	0.042	0.406
TS03-169	ppbv	0.505	1.849	0.571	4.740	0.083	0.112	0.935	0.460	0.129	0.182	0.685	1.280	0.203	0.205	0.835	0.459	0.419	0.082	2.317	0.165	0.769	0.786	2.138	0.239	0.180
TS03-170	ppbv	0.537	2.959	0.388	7.867	0.145	0.164	1.734	0.728	0.165	0.042	1.286	2.625	0.324	0.194	0.691	0.574	0.415	0.111	0.314	0.119	0.010	0.008	0.018	0.047	0.233
TS03-171	ppbv	0.441	1.149	0.479	1.754	0.067	0.194	0.455	0.385	0.175	0.044	0.320	0.689	0.268	0.180	0.674	0.301	0.292	0.052	0.347	0.127	0.005	0.006	0.002	0.023	0.282
TS03-172	ppbv	0.261	0.994	0.157	0.321	0.038	0.088	0.269	0.087	0.159	0.336	0.211	0.394	0.148	0.035	0.082	0.107	0.065	0.026	0.534	0.025	0.114	0.108	0.311	0.017	0.352
TS03-173	ppbv	0.249	0.947	0.118	0.258	0.029	0.065	0.278	0.086	0.229	0.251	0.208	0.399	0.156	0.031	0.069	0.099	0.058	0.023	0.332	0.020	0.033	0.021	0.059	0.011	0.285
TS03-174	ppbv	0.337	1.040	0.222	0.356	0.051	0.099	0.492	0.144	0.223	0.267	0.347	0.685	0.193	0.045	0.099	0.152	0.090	0.037	0.303	0.030	0.049	0.032	0.088	0.013	0.285
TS03-175	ppbv	0.465	1.084	0.248	0.416	0.063	0.128	0.710	0.236	0.166	0.376	0.420	0.828	0.187	0.062	0.129	0.206	0.119	0.047	0.535	0.050	0.072	0.051	0.136	0.019	0.268
TS03-176	ppbv	0.351	0.987	0.211	0.509	0.052	0.145	0.640	0.214	0.126	0.248	0.369	0.739	0.206	0.052	0.109	0.172	0.101	0.041	0.425	0.054	0.040	0.029	0.031	0.014	0.241
TS03-177	ppbv	0.247	1.077	0.171	0.328	0.041	0.078	0.475	0.128	0.168	0.338	0.283	0.538	0.179	0.040	0.089	0.132	0.078	0.032	0.386	0.036	0.045	0.028	0.083	0.015	0.482

Table A24: NMHC isotopic composition (δ^{13}C ‰), York University, August 2003.

Lab #	δ C^{13} ace	δ C^{13} nC3	δ C^{13} propylene	δ C^{13} i-C4	δ C^{13} n-C4	δ C^{13} CH_3Cl	δ C^{13} i-butene	δ C^{13} i-C5	δ C^{13} n-C5	δ C^{13} 2MC5	δ C^{13} MCYCC5	δ C^{13} 3MC5	δ C^{13} n-C6	δ C^{13} Benz	δ C^{13} Tol	δ C^{13} C2Benz	δ C^{13} m,p-xyl	δ C^{13} o-xyl
TS03-166	-13.9	-28.9	-25.8	LOD	-31.0	-38.8	-29.4	-29.6	-28.0	LOD	LOD	LOD	LOD	-21.4	-27.5	LOD	-25.7	LOD
TS03-167	-12.9	-28.9	-23.9	LOD	-31.0	-32.4	LOD	-29.8	-27.3	LOD	LOD	LOD	-28.6	-18.9	-25.9	LOD	-25.3	LOD
TS03-168	-13.2	-28.9	LOD	LOD	-31.2	LOD	LOD	-30.1	-27.9	LOD	-26.1	-25.4	-26.2	-17.4	-27.5	LOD	-25.1	LOD
TS03-169	LOD	-29.4	LOD	LOD	LOD	LOD	LOD	-29.6	-27.9	LOD	-28.6	-27.6	-27.2	-21.1	-26.9	LOD	-26.0	-25.5
TS03-170	LOD	-29.4	LOD	LOD	-29.2	LOD	LOD	-29.7	-27.9	LOD	-29.4	-30.0	-31.0	-23.3	-27.5	LOD	-25.6	-25.8
TS03-171	LOD	-28.0	LOD	LOD	-31.1	LOD	LOD	-28.9	-27.1	-31.1	LOD	-26.6	-27.0	-26.1	-26.4	LOD	-25.8	-25.6
TS03-173	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-28.8	-26.5	LOD	LOD	LOD	LOD	-25.0	LOD	LOD	-24.0	LOD
TS03-174	LOD	LOD	LOD	LOD	-30.3	LOD	LOD	-28.3	-25.9	LOD	LOD	LOD	LOD	-26.0	LOD	LOD	-24.7	LOD
TS03-175	LOD	LOD	LOD	LOD	-31.3	LOD	-27.0	-28.6	-26.8	LOD	LOD	LOD	LOD	-20.7	LOD	LOD	-26.7	LOD
TS03-176	LOD	-27.5	LOD	LOD	-30.6	LOD	LOD	-29.2	-27.1	LOD	LOD	LOD	LOD	-19.5	-24.0	LOD	-24.9	LOD
TS03-177	-16.9	LOD	LOD	LOD	LOD	LOD	LOD	-28.5	-29.1	LOD	LOD	LOD	LOD	-19.2	-27.2	LOD	-25.2	LOD

Table A25: NMHC isotopic composition ($\delta^{13}C$ ‰), Suburban/Rural (GTA), August 2003.

Lab #	δ C^{13} ace	δ C^{13} nC3	δ C^{13} i-C4	δ C^{13} n-C4	δ C^{13} 1-butene	δ C^{13} i-butene	δ C^{13} i-C5	δ C^{13} n-C5	δ C^{13} isoprene	δ C^{13} Benz	δ C^{13} Tol	δ C^{13} C2Benz	δ C^{13} m,p-xyl	δ C^{13} o-xyl
TS03-178	LOD	-28.5	LOD	LOD	LOD	-29.5	LOD	LOD	-28.0	-24.0	-28.7	LOD	-25.1	LOD
TS03-179	LOD	-28.5	LOD	LOD	LOD	LOD	-26.4	LOD	-26.3	-25.5	LOD	LOD	-25.7	LOD
TS03-181	LOD	LOD	LOD	LOD	-26.1	LOD	LOD	LOD	-27.1	LOD	-28.2	LOD	-25.0	LOD
TS03-182	LOD	-28.3	LOD	LOD	LOD	LOD	LOD	LOD	-26.8	-27.7	LOD	LOD	-25.3	LOD
TS03-184	LOD	-29.6	LOD	LOD	-27.2	LOD	LOD	LOD	LOD	-25.8	LOD	LOD	-26.5	LOD
TS03-187	LOD	LOD	LOD	LOD	-27.0	LOD	LOD	LOD	LOD	-25.9	LOD	LOD	-25.8	LOD
TS03-189	LOD	-28.1	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-24.9	LOD	LOD	-25.1	LOD
TS03-190	LOD	-28.3	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-23.3	LOD	LOD	-25.6	LOD
TS03-191	LOD	-28.0	LOD	LOD	LOD	LOD	LOD	LOD	-28.3	-23.0	LOD	-23.1	-27.9	LOD
TS03-192	LOD	-29.4	LOD	LOD	LOD	LOD	LOD	LOD	-28.5	LOD	LOD	LOD	-25.9	LOD
TS03-193	LOD	-28.4	LOD	LOD	LOD	LOD	-28.4	LOD	-27.0	-17.5	LOD	LOD	-26.1	LOD
TS03-196	LOD	-28.4	LOD	LOD	LOD	-32.4	LOD	LOD	-27.8	-25.5	-27.9	LOD	-26.4	LOD
TS03-197	LOD	-28.4	LOD	-30.5	LOD	LOD	-29.3	-28.5	LOD	-28.6	LOD	LOD	-25.7	LOD
TS03-199	-13.5	-29.1	LOD	LOD	LOD	-33.3	LOD	LOD	-25.2	-27.3	LOD	LOD	-26.8	LOD
TS03-201	LOD	-28.7	LOD	LOD	LOD	LOD	LOD	LOD	-25.2	-27.9	-26.1	LOD	-25.9	LOD
TS03-202	LOD	-28.2	LOD	LOD	LOD	LOD	-29.6	LOD	-28.3	-26.5	LOD	LOD	-25.9	LOD
TS03-204	LOD	-27.7	LOD	LOD	LOD	LOD	LOD	LOD	-26.0	-26.3	LOD	LOD	-26.1	LOD
TS03-205	LOD	LOD	LOD	LOD	LOD	-29.6	-29.9	LOD	LOD	-25.3	LOD	LOD	-25.7	LOD
TS03-207	LOD	-27.5	LOD	LOD	LOD	LOD	LOD	LOD	LOD	-27.6	LOD	LOD	-27.4	LOD
TS03-208	-18.0	-30.3	LOD	-27.9	LOD	-29.2	-29.1	-27.4	-27.0	-19.8	-27.5	LOD	-26.5	LOD
TS03-209	LOD	-29.5	LOD	-31.0	LOD	LOD	-27.9	LOD	LOD	-27.0	-27.5	LOD	-27.0	LOD
TS03-210	-13.4	-29.1	LOD	-30.9	LOD	LOD	-28.0	-27.6	LOD	-25.7	-25.8	LOD	-28.1	-33.0
TS03-211	-14.3	-29.0	LOD	-30.0	LOD	-26.2	-28.2	-26.7	-28.6	-22.6	-26.7	LOD	-26.6	LOD
TS03-212	-13.4	-28.3	LOD	-30.7	LOD	LOD	-29.2	-29.5	LOD	-24.6	-27.1	LOD	-27.2	LOD
TS03-213	-15.6	-29.0	LOD	-30.1	LOD	LOD	-28.6	-27.9	-28.4	-24.8	-28.5	LOD	-26.9	LOD

Table A26: Sampling Information, Urban Toronto, August 2003.

Lab #	site	canister	date	time-start	time-end	time [min]	weather	temp[°C]	humidity	wind direct.	sp.[km/h]
TS03-214	2	Y507	08/21/03	10:04	10:50	0:46	maily clear	28.5	59%	26	24
TS03-215	2	Y284	08/21/03	10:19	10:23	0:04	maily clear	27.8	63%	24	24
TS03-216	2	Y065	08/21/03	10:34	10:38	0:04	maily clear	27.8	63%	24	24
TS03-217	1	Y264	08/21/03	11:14	12:00	0:46	clear	29.7	50%	25	26
TS03-218	1	Y099	08/21/03	11:31	11:35	0:04	clear	29.7	50%	25	26
TS03-219	1	Y068	08/21/03	11:44	11:48	0:04	clear	29.7	50%	25	26
TS03-220	3	Y361	08/21/03	12:37	13:22	0:45	clear	31	49%	19	20
TS03-221	3	Y091	08/21/03	12:52	12:56	0:04	clear	31	49%	19	20
TS03-222	3	Y439	08/21/03	13:10	13:14	0:04	clear	31	49%	19	20
TS03-223	5	Y415	08/21/03	14:04	14:50	0:46	maily clear	31.7	47%	21	29
TS03-224	5	Y377	08/21/03	14:20	14:25	0:05	maily clear	31.7	47%	21	29
TS03-225	5	Y505	08/21/03	14:36	14:40	0:04	maily clear	31.7	47%	21	29
TS03-226	4	Y205	08/21/03	15:46	16:31	0:45	maily clear	31.7	48%	21	28
TS03-227	4	Y115	08/21/03	16:01	16:05	0:04	maily clear	31.7	48%	21	28
TS03-228	4	Y110	08/21/03	16:17	16:21	0:04	maily clear	31.7	48%	21	28
TS03-229	7	Y262	08/21/03	16:43	17:30	0:47	maily clear	30.4	43%	21	30
TS03-230	7	Y210	08/21/03	17:00	17:04	0:04	maily clear	30.4	43%	21	30
TS03-231	7	Y024	08/21/03	17:17	17:21	0:04	maily clear	30.4	43%	21	30
TS03-232	12	Y391	08/21/03	18:23	19:18	0:55	clear	28.7	46%	21	19
TS03-233	12	Y101	08/21/03	18:38	18:42	0:04	clear	28.7	46%	21	19
TS03-234	12	Y306	08/21/03	19:05	19:09	0:04	clear	28.7	46%	21	19

Table A27: NMHC Mixing Ratio (ppbv), Urban Toronto, August 2003.

Lab #	ppbV	ace	nC2	propene	nC3	1-butene	iso-butene	nC4	iC4	isoprene	CYC5	nC5	2MC4	Benz	MCYC5	nC6	2MC5	3MC5	23DMC4	Tol	nC7	C2Benz	oXyl	mpXyl	nC8	CH3Cl
TS03-214	ppbv	1.147	5.398	0.652	2.624	0.075	0.121	1.849	0.698	0.643	0.171	1.312	1.474	0.618	0.185	0.481	0.409	0.279	0.112	1.542	0.154	0.073	0.053	0.192	0.037	0.543
TS03-215	ppbv	0.976	4.459	0.455	2.045	0.063	0.072	1.578	0.561	0.598	0.043	1.010	1.266	0.397	0.148	0.410	0.379	0.240	0.088	1.523	0.148	0.183	0.153	0.365	0.064	0.385
TS03-216	ppbv	1.187	5.709	0.673	2.775	0.073	0.103	1.755	0.750	0.697	0.174	1.312	1.521	0.496	0.186	0.494	0.400	0.282	0.111	8.439	0.164	0.163	0.139	0.453	0.075	0.475
TS03-217	ppbv	1.628	6.928	0.933	5.280	0.118	0.149	2.080	0.993	0.222	0.306	1.169	1.885	0.733	0.216	0.628	0.584	0.386	0.131	2.014	0.511	0.390	0.314	0.787	0.068	0.451
TS03-218	ppbv	1.939	6.848	1.043	5.260	0.116	0.137	2.837	1.350	0.240	0.270	1.410	2.281	0.689	0.232	0.604	0.558	0.394	0.164	11.908	0.676	0.548	0.265	0.811	0.097	0.427
TS03-219	ppbv	1.907	6.990	1.358	4.911	0.103	0.114	2.716	1.538	0.254	0.240	1.494	2.455	0.622	0.248	0.622	0.596	0.407	0.171	8.569	0.214	0.203	0.148	0.512	0.078	0.390
TS03-220	ppbv	1.015	5.167	0.281	2.155	0.052	0.081	1.420	0.548	0.624	0.183	0.739	1.158	0.521	0.101	0.283	0.313	0.194	0.070	0.932	0.093	0.206	0.188	0.469	0.038	0.331
TS03-221	ppbv	0.998	5.144	0.284	2.051	0.056	0.075	1.303	0.500	0.544	0.044	0.669	1.128	0.580	0.104	0.282	0.313	0.195	0.072	8.156	0.093	0.197	0.161	0.427	0.042	0.453
TS03-222	ppbv	1.018	4.828	0.241	1.859	0.050	0.109	0.982	0.388	0.641	0.041	0.467	0.912	0.359	0.087	0.216	0.259	0.158	0.058	5.162	0.068	0.096	0.073	0.174	0.030	0.431
TS03-223	ppbv	0.687	5.691	0.087	1.688	0.019	0.060	0.953	0.253	0.479	0.020	0.208	0.425	0.192	0.024	0.084	0.095	0.055	0.024	0.323	0.024	0.018	0.006	0.013	0.008	0.411
TS03-224	ppbv	0.742	6.022	0.058	1.624	0.015	0.047	0.822	0.261	0.433	0.023	0.197	0.416	0.206	0.023	0.082	0.093	0.055	0.022	4.539	0.035	0.016	0.006	0.011	0.035	0.386
TS03-225	ppbv	0.521	4.948	0.170	1.464	0.020	0.061	0.451	0.207	0.393	0.133	0.146	0.255	0.223	0.015	0.054	0.062	0.036	0.017	4.502	0.022	0.017	0.008	0.016	0.019	0.507
TS03-226	ppbv	1.374	5.515	0.827	2.183	0.125	0.210	1.311	0.529	0.259	0.159	0.941	1.671	0.571	0.167	0.328	0.447	0.304	0.123	1.207	0.171	0.218	0.221	0.644	0.063	0.356
TS03-227	ppbv	1.558	5.479	1.081	2.115	0.128	0.331	1.310	0.477	0.325	0.159	0.977	1.720	0.583	0.182	0.356	0.477	0.319	0.137	5.584	0.132	0.118	0.083	0.295	0.070	0.400
TS03-228	ppbv	1.037	5.861	0.909	2.219	0.160	0.232	1.549	0.497	0.301	0.106	1.014	1.979	0.510	0.190	0.361	0.506	0.326	0.137	3.370	0.166	0.091	0.082	0.239	0.058	0.406
TS03-229	ppbv	1.107	6.684	0.508	2.379	0.108	0.181	1.403	0.559	0.221	0.156	0.888	1.401	0.363	0.168	0.624	0.410	0.366	0.100	2.608	0.119	0.221	0.292	0.653	0.070	0.377
TS03-230	ppbv	1.076	6.872	0.477	2.433	0.063	0.121	1.229	0.507	0.188	0.172	0.782	1.210	0.346	0.108	0.301	0.291	0.198	0.075	4.123	0.096	0.138	0.126	0.393	0.047	0.401
TS03-231	ppbv	1.053	6.655	0.747	2.563	0.070	0.105	1.311	0.536	0.255	0.197	0.833	1.325	0.333	0.176	0.495	0.384	0.295	0.101	3.866	0.109	0.149	0.141	0.470	0.050	0.506
TS03-232	ppbv	0.350	2.261	0.233	0.804	0.044	0.103	0.460	0.221	0.279	0.272	0.286	0.497	0.227	0.045	0.108	0.138	0.083	0.033	1.820	0.070	0.033	0.015	0.057	0.058	0.420
TS03-233	ppbv	0.383	2.154	0.190	0.766	0.036	0.083	0.372	0.194	0.260	0.276	0.236	0.403	0.239	0.035	0.089	0.110	0.068	0.029	2.622	0.132	0.036	0.032	0.078	0.081	0.396
TS03-234	ppbv	0.346	2.061	0.219	0.741	0.035	0.069	0.380	0.166	0.143	0.279	0.238	0.410	0.171	0.037	0.092	0.114	0.066	0.027	2.154	0.050	0.014	0.007	0.018	0.025	0.350

Table A28: NMHC isotopic composition (δ^{13}C ‰), Urban Toronto, August 2003.

Lab #	δ C^{13} ace	δ C^{13} nC3	δ C^{13} propylene	δ C^{13} i-C4	δ C^{13} n-C4	δ C^{13} CH$_3$Cl	δ C^{13} i-butene	δ C^{13} i-C5	δ C^{13} n-C5	δ C^{13} 2-MC5	δ C^{13} 3-MC5	δ C^{13} isoprene	δ C^{13} nC6	δ C^{13} Benz	δ C^{13} Tol	δ C^{13} C2Benz	δ C^{13} m,p-xyl	δ C^{13} o-xyl
TS03-214	-6.0	-30.0	-21.6	-15.2	-30.9	-40.8	LOD	-29.5	-27.9	LOD	LOD	LOD	-26.7	-19.4	-28.4	LOD	-26.4	-25.7
TS03-216	-15.6	-29.9	-21.8	-16.4	-31.7	LOD	LOD	-29.2	-27.6	LOD	LOD	LOD	-26.5	-22.2	-28.1	LOD	-26.5	-24.4
TS03-218	-17.8	-29.9	-22.1	LOD	-32.7	LOD	LOD	-29.5	-28.5	-28.4	-28.3	-26.1	-27.2	-21.7	-27.1	-27.3	-24.3	-22.5
TS03-219	-17.2	-29.9	-21.7	-21.1	-30.2	LOD	LOD	-28.8	-27.5	LOD	-27.7	-26.1	-26.3	-17.5	-27.7	LOD	-26.2	-23.2
TS03-225	-15.3	-30.5	LOD	LOD	-28.7	-28.6	LOD	-27.6	-21.8	LOD	LOD	LOD	LOD	-23.0	-25.2	-27.7	-26.9	-23.0
TS03-226	-16.1	-29.2	-24.2	-16.1	-30.2	-33.4	LOD	-28.5	-27.3	LOD	-26.2	-25.7	-24.8	-21.0	-28.1	LOD	-25.8	LOD
TS03-227	-14.4	-29.1	-23.5	LOD	-31.2	LOD	-25.1	-29.0	-27.9	LOD	-26.6	-25.7	-25.5	-19.8	-27.7	LOD	-26.1	-24.4
TS03-229	-13.8	-29.8	-10.2	LOD	-30.3	LOD	LOD	-28.5	-26.7	LOD	LOD	LOD	-26.4	-21.1	-28.1	LOD	-26.8	-25.7
TS03-231	LOD	-29.3	LOD	LOD	-29.1	LOD	LOD	-28.8	-27.8	LOD	-27.2	-25.8	-25.7	-22.2	-27.6	LOD	-25.9	LOD
TS03-232	-8.4	-30.2	LOD	LOD	-31.3	-39.0	LOD	-27.5	-28.4	LOD	LOD	LOD	LOD	LOD	-27.6	LOD	-25.6	LOD
TS03-233	-9.0	-29.8	LOD	-32.5	-30.7	LOD	LOD	-28.6	-26.1	LOD	LOD	LOD	LOD	-22.6	-27.3	LOD	-25.8	LOD

Table A29: Sampling Information, Urban Toronto, June 2003.

Lab #	site	canister	date	time-start	time-end	time [min]	weather	temp[°C]	humidity	wind direct.	sp.[km/h]	Atmos. Pre.
TS03-031	8	Y217	06/17/03	10:33	11:30	57	sunny	22	65%	SE	11	102.5 and falling
TS03-032	8	Y227	06/17/03	10:50	10:54	4		20				
TS03-033	8	Y341	06/17/03	11:15	11:19	4						
TS03-034	9	Y318	06/17/03	12:34	13:30	56	sunny	24	63%	S	7	101.96 and falling
TS03-035	9	Y320	06/17/03	12:50	12:54	4		22				
TS03-036	9	Y528	06/17/03	13:16	13:20	4						
TS03-037	11	Y277	06/17/03	14:18	15:15	57	sunny (PA at 3 PM)	24	64%	SE	17	101.84 and falling
TS03-038	11	Y221	06/17/03	14:40	14:43	3.5	(DT)	25				
TS03-039	11	Y288	06/17/03	15:00	15:04	4						
TS03-040	10	Y365	06/17/03	15:42	16:30	52	sunny (PA at 4 PM)	25	63%	SE	11	101.78 and falling
TS03-041	10	Y340	06/17/03	16:00	16:06	6	(DT)	24				
TS03-042	10	Y457	06/17/03	16:20	16:25	5						
TS03-043	6	Y240	06/17/03	17:19	18:15	56	partly cloudy (PA at 6 PM)	22	66%	SE	15	101.69 and falling
TS03-044	6	Y514	06/17/03	17:40	17:43	3.5	(DT)	23				
TS03-045	6	Y050	06/17/03	18:05	18:11	6						
TS03-046	7	Y359	06/17/03	18:34	19:24	50	mainly cloudy (PA at 7 PM)	20	71%	SE	9	101.62 and falling
TS03-047	7	Y479	06/17/03	18:50	18:54	4	(DT)	21				
TS03-048	7	Y330	06/17/03	19:10	19:13	3						
TS03-049	12	Y219	06/18/03	8:04	9:03	59	cloudy (PA at 8 AM)	18	81%	S	7	101.39 and steady
TS03-050	12	Y390	06/18/03	8:18	8:22	4	(DT)					
TS03-051	12	Y250	06/18/03	8:46	8:50	4						
TS03-052	4	Y519	06/18/03	9:51	10:45	54	mainly cloudy (PA at 9 AM)	20	74%	S	7	101.33 and falling
TS03-053	4	Y336	06/18/03	10:11	10:14	3.5	(DT)	18				
TS03-054	4	Y336	06/18/03	10:36	10:39	3						
TS03-055	2	Y291	06/18/03	11:22	12:15	53	partly cloudy (PA at 12 PM)	21	69%	W	6	101.28 and falling
TS03-056	2	Y345	06/18/03	11:40	11:43	3	(DT)	21				
TS03-057	2	Y201	06/18/03	12:05	12:09	3.5						
TS03-058	1	Y257	06/18/03	12:50	13:42	52	sunny (PA at 1 PM)	22	64%	SE	15	101.22 and falling
TS03-059	1	Y517	06/18/03	13:06	13:10	4	(DT)	21				
TS03-060	1	Y478	06/18/03	13:27	13:31	4						
TS03-061	3	Y348	06/18/03	14:15	15:10	55	sunny (PA at 3 PM)	22	70%	SE	15	101.15 and falling
TS03-062	3	Y215	06/18/03	14:30	14:34	4	(DT)	22				
TS03-063	3	Y267	06/18/03	14:50	14:54	4						
TS03-064	5	Y225	06/18/03	15:53	16:45	52	sunny (PA at 4 PM)	23	66	SE	22	101.10 and falling
TS03-065	5	Y458	06/18/03	16:12	16:18	6	(DT)	23				
TS03-066	5	Y428	06/18/03	16:30	16:34	4						
TS03-067	13	Y373	06/18/03	18:08	19:03	55	sunny (PA at 7 PM)	22	71	SE	19	100.90
TS03-068	13	Y220	06/18/03	18:25	18:29	4	(DT)	22				
TS03-069	13	Y309	06/18/03	18:45	18:49	4						

Table A30: NMHC Mixing Ratio (ppbv), Urban Toronto, June 2003.

Lab #	ppbV	ace	NC2	propene	nC3	1-butene	iso-butene	nC4	iC4	isoprene	CYC5	nC5	2MC4	Benz	CYCC6	MCYC5	nC6	2MC5	3MC5	23DMC4	Tol	nC7	C2Benz	oXyl	mpXyl	nC8	CH3Cl
TS03-031	ppbv	1.275	2.473	0.774	2.803	0.151	0.279	1.850	0.571	0.104	0.185	1.025	1.789	0.459	0.091	0.204	0.400	0.485	0.325	0.146	7.813	0.149	0.667	0.649	2.309	0.115	0.440
TS03-032	ppbv	0.963	2.257	0.467	2.631	0.093	0.137	1.489	0.435	0.060	0.148	0.670	1.090	0.362	0.064	0.135	0.255	0.308	0.208	0.089	4.410	0.097	0.405	0.494	1.405	0.098	0.451
TS03-033	ppbv	0.778	2.415	0.454	2.205	0.046	0.110	1.113	0.356	0.065	0.122	0.561	1.014	0.382	0.052	0.116	0.235	0.279	0.187	0.084	6.096	0.098	0.747	0.764	2.605	0.068	0.509
TS03-034	ppbv	1.776	2.472	0.488	1.765	0.104	0.174	0.815	0.261	0.053	0.126	0.532	0.883	0.275	0.036	0.087	0.182	0.239	0.157	0.076	1.166	0.149	0.556	0.592	2.593	0.051	0.499
TS03-035	ppbv	0.925	2.284	0.246	1.307	0.063	0.083	0.711	0.247	0.038	0.117	0.362	0.615	0.223	0.029	0.058	0.120	0.150	0.096	0.048	0.557	0.167	0.182	0.201	0.699	0.037	0.459
TS03-036	ppbv	0.642	2.716	0.259	1.905	0.057	0.102	0.907	0.271	0.031	0.103	0.336	0.606	0.237	0.029	0.058	0.104	0.146	0.093	0.048	0.559	0.074	0.583	0.651	2.781	0.038	0.467
TS03-037	ppbv	0.847	2.927	0.262	2.753	0.050	0.129	1.051	0.635	0.074	0.186	1.252	0.831	0.257	0.607	4.458	18.858	5.884	9.057	0.868	98.055	1.256	0.273	0.266	0.751	0.041	0.505
TS03-038	ppbv	0.945	3.162	0.226	2.073	0.051	0.084	1.039	0.439	0.047	0.183	0.835	0.837	0.246	0.071	0.330	1.226	0.526	0.634	0.106	19.070	0.160	0.234	0.189	0.644	0.039	0.618
TS03-039	ppbv	0.807	3.371	0.238	3.070	0.045	0.079	1.651	0.417	0.055	0.228	0.784	0.855	0.240	0.185	1.247	5.218	1.766	2.571	0.283	10.115	0.361	0.290	0.254	0.808	0.040	0.446
TS03-040	ppbv	0.632	3.214	0.153	1.443	0.038	0.122	0.905	0.283	0.235	0.109	0.328	0.568	0.203	0.033	0.108	0.377	0.157	0.113	0.040	0.704	0.084	0.133	0.166	0.555	0.091	0.485
TS03-041	ppbv	0.606	3.162	0.131	1.416	0.035	0.075	0.878	0.284	0.298	0.111	0.343	0.591	0.217	0.031	0.109	0.402	0.162	0.118	0.051	1.006	0.078	0.135	0.132	0.527	0.078	0.484
TS03-042	ppbv	0.579	2.801	0.118	1.430	0.033	0.068	0.804	0.270	0.221	0.135	0.319	0.560	0.208	0.023	0.107	0.398	0.146	0.108	0.047	1.099	0.066	0.205	0.139	0.730	0.070	0.461
TS03-043	ppbv	3.403	3.300	0.856	4.988	0.132	0.208	2.190	0.682	0.125	0.158	0.957	1.752	0.395	0.074	0.194	0.393	0.430	0.293	0.132	1.074	0.106	0.182	0.199	0.559	0.052	0.409
TS03-044	ppbv	0.610	2.747	0.200	1.194	0.079	0.117	1.849	0.609	0.055	0.130	0.791	1.572	0.258	0.054	0.157	0.385	0.310	0.219	0.096	0.894	0.090	0.097	0.086	0.289	0.049	0.563
TS03-045	ppbv	2.028	3.414	0.911	3.180	0.133	0.213	1.778	0.516	0.227	0.172	1.081	1.915	0.560	0.081	0.204	0.394	0.485	0.322	0.146	1.264	0.118	0.157	0.145	0.454	0.051	0.492
TS03-046	ppbv	1.352	3.699	0.495	2.108	0.096	0.197	1.463	0.531	0.114	0.318	0.822	1.425	0.413	0.080	0.196	0.421	0.417	0.284	0.130	1.562	0.134	0.184	0.197	0.551	0.052	0.446
TS03-047	ppbv	1.258	3.862	0.669	2.481	0.110	0.166	1.496	0.545	0.099	0.338	0.848	1.477	0.468	0.083	0.213	0.480	0.434	0.298	0.131	1.975	0.142	0.185	0.212	0.530	0.056	0.444
TS03-048	ppbv	0.940	3.664	0.347	1.815	0.074	0.111	1.254	0.460	0.122	0.293	0.742	1.258	0.374	0.069	0.158	0.306	0.346	0.230	0.109	1.051	0.101	0.134	0.130	0.395	0.048	0.510
TS03-049	ppbv	1.032	2.647	0.372	1.686	0.070	0.128	0.840	0.547	0.043	0.432	0.642	0.959	0.290	0.057	0.112	0.241	0.255	0.171	0.083	1.245	0.093	0.270	0.319	1.055	0.065	0.410
TS03-050	ppbv	1.069	2.515	0.342	1.961	0.060	0.101	0.796	0.425	0.053	0.292	0.585	0.885	0.254	0.062	0.103	0.219	0.239	0.161	0.067	0.947	0.086	0.219	0.265	0.800	0.045	0.568
TS03-051	ppbv	1.292	1.969	0.454	1.812	0.099	0.144	1.688	1.264	0.065	1.256	1.076	1.733	0.380	0.082	0.167	0.324	0.376	0.249	0.121	1.656	0.113	0.393	0.430	1.372	0.105	0.551
TS03-052	ppbv	1.061	2.709	0.476	1.975	0.061	0.183	1.409	0.559	0.107	0.672	0.903	1.476	0.348	0.246	0.151	0.326	0.364	0.247	0.114	1.604	0.123	0.167	0.180	0.521	0.055	0.404
TS03-053	ppbv	0.958	2.707	0.571	1.411	0.133	0.170	1.421	0.645	0.150	0.225	0.968	1.593	0.430	0.032	0.040	0.400	0.416	0.286	0.074	1.525	0.139	0.163	0.148	0.476	0.053	0.399
TS03-054	ppbv	0.870	2.553	0.387	1.398	0.090	0.120	1.089	0.487	0.116	0.206	0.771	1.142	0.327	0.062	0.131	0.269	0.298	0.200	0.086	1.339	0.115	0.136	0.118	0.384	0.057	0.488
TS03-055	ppbv	0.988	2.621	0.245	1.060	0.047	0.097	0.547	0.254	0.027	0.067	0.251	0.431	0.447	0.018	0.066	0.276	0.176	0.181	0.040	0.379	0.035	0.045	0.042	0.130	0.017	0.430
TS03-056	ppbv	0.483	2.563	0.198	1.182	0.040	0.064	0.523	0.236	0.019	0.067	0.239	0.405	0.340	0.020	0.063	0.236	0.162	0.161	0.040	0.299	0.034	0.043	LDL	0.119	0.018	0.447
TS03-057	ppbv	0.494	2.579	0.106	1.108	0.026	0.039	0.676	0.328	0.025	0.066	0.218	0.368	0.319	0.016	0.044	0.152	0.113	0.096	0.031	0.266	0.031	0.039	0.034	0.094	0.018	0.436
TS03-058	ppbv	0.903	2.711	0.316	1.230	0.058	0.123	0.894	0.292	0.085	0.126	0.414	0.717	0.309	0.041	0.088	0.237	0.211	0.156	0.065	0.566	0.065	0.097	0.076	0.242	0.026	0.470
TS03-059	ppbv	0.983	2.814	0.384	2.213	0.057	0.099	0.984	0.325	0.076	0.115	0.411	0.721	0.332	0.043	0.090	0.249	0.207	0.155	0.067	0.500	0.061	0.098	0.090	0.252	0.026	0.454
TS03-060	ppbv	1.050	2.731	0.388	1.127	0.064	0.110	1.055	0.314	0.071	0.225	0.481	0.849	0.369	0.048	0.113	0.353	0.263	0.193	0.082	0.524	0.067	LDL	0.095	0.097	0.025	0.427
TS03-061	ppbv	0.644	2.817	0.148	1.398	0.036	0.073	0.983	0.325	0.095	0.098	0.367	0.624	0.310	0.030	0.075	0.268	0.188	0.156	0.049	0.546	0.052	0.133	0.089	0.347	0.023	0.485
TS03-062	ppbv	0.641	2.843	0.114	1.350	0.031	0.040	0.921	0.331	0.069	0.103	0.381	0.644	0.327	0.032	0.078	0.277	0.193	0.157	0.049	0.608	0.055	0.127	0.133	0.339	0.024	0.418
TS03-063	ppbv	0.643	2.498	0.201	1.446	0.043	0.066	1.318	0.327	0.129	0.110	0.400	0.677	0.394	0.036	0.086	0.256	0.216	0.178	0.057	0.831	0.052	0.213	0.157	0.607	0.027	0.390
TS03-064	ppbv	0.351	2.891	0.018	1.108	0.009	0.037	1.264	0.149	0.186	0.051	0.095	0.159	0.105	0.003	0.008	0.039	0.036	0.026	0.006	0.116	0.009	0.008	0.004	0.009	0.004	0.466
TS03-065	ppbv	0.367	2.477	0.009	1.104	0.006	0.035	1.237	0.150	0.203	0.051	0.098	0.165	0.113	0.003	0.009	0.043	0.038	0.030	0.006	0.105	0.008	0.009	0.004	0.008	0.004	0.488
TS03-066	ppbv	0.364	2.863	0.023	1.082	0.012	0.022	1.190	0.139	0.131	0.051	0.090	0.152	0.124	0.004	0.007	0.029	0.029	0.020	0.012	0.107	0.007	0.010	0.116	0.076	0.005	0.487
TS03-067	ppbv	0.832	2.493	0.164	1.392	0.081	0.114	2.173	0.673	0.113	5.250	0.945	2.034	0.259	0.060	0.137	0.255	0.349	0.226	0.108	1.375	0.068	0.156	0.150	0.499	0.040	0.381
TS03-068	ppbv	0.769	2.577	0.158	1.256	0.075	0.096	2.128	0.693	0.107	4.643	1.131	2.298	0.265	0.066	0.161	0.282	0.398	0.257	0.118	0.774	0.075	0.194	0.176	0.615	0.034	0.313
TS03-069	ppbv	1.184	2.553	0.221	1.245	0.045	0.084	0.840	0.330	0.114	2.921	0.415	0.803	0.231	0.045	0.085	0.165	0.205	0.134	0.063	0.914	0.071	0.120	0.109	0.388	0.041	0.576

Table A31: Sampling Information, York University, July 2003.

Lab #	site	canister	date	time-start	time-end	time [min]	weather	temp[°C]	humidity	wind direct.	sp.[km/h]	Atmos. Pre.
TS03-136	Petrie roof	Y009	07/29/03	6:36	7:30	56	sunny	17	70%	W	11	101.46 and rising
TS03-137	Petrie roof	Y062	07/29/03	6:51	6:58	7	sunny	17	70%	W	11	101.46 and rising
TS03-138	Petrie roof	Y059	07/29/03	7:18	7:28	10	sunny	17	70%	W	11	101.46 and rising
TS03-139	Petrie roof	Y045	07/29/03	7:30	8:30	60	sunny	19	64	W	11	101.50 and rising
TS03-140	Petrie roof	Y034	07/29/03	7:46	7:56	10	sunny	19	64	W	11	101.50 and rising
TS03-141	Petrie roof	Y070	07/29/03	8:16	8:26	10	sunny	19	64	W	11	101.50 and rising
TS03-142	Petrie roof	Y121	07/29/03	8:30	9:30	60	sunny	21	60%	NW	13	101.52 and rising
TS03-143	Petrie roof	Y048	07/29/03	8:45	8:55	10	sunny	21	60%	NW	13	101.52 and rising
TS03-144	Petrie roof	Y094	07/29/03	9:16	9:20	10	sunny	21	60%	NW	13	101.52 and rising
TS03-145	Petrie roof	Y022	07/29/03	10:30	11:30	60	sunny	24	49%	W	9	101.58 and rising
TS03-146	Petrie roof	Y002	07/29/03	10:46	10:53	7	sunny	24	49%	W	9	101.58 and rising
TS03-147	Petrie roof	Y119	07/29/03	11:15	11:22	7	sunny	24	49%	W	9	101.58 and rising
TS03-148	Petrie roof	Y075	07/29/03	12:31	13:30	59	partly cloudy	26	39%	W	11	101.55 and falling
TS03-149	Petrie roof	Y046	07/29/03	12:45	12:52	7	partly cloudy	26	39%	W	11	101.55 and falling
TS03-150	Petrie roof	Y033	07/29/03	13:15	13:22	7	partly cloudy	26	39%	W	11	101.55 and falling
TS03-151	Petrie roof	Y060	07/29/03	14:30	15:30	60	mainly cloudy	27	44%	N	13	101.50 and falling
TS03-152	Petrie roof	Y090	07/29/03	14:45	14:52	7	mainly cloudy	27	44%	N	13	101.50 and falling
TS03-153	Petrie roof	Y061	07/29/03	15:15	15:18	3	mainly cloudy	27	44%	N	13	101.50 and falling
TS03-154	Petrie roof	Y092	07/29/03	15:30	16:30	60	partly cloudy	28	38%	W	20	101.49 and falling
TS03-155	Petrie roof	Y096	07/29/03	15:45	15:49	4	partly cloudy	28	38%	W	20	101.49 and falling
TS03-156	Petrie roof	Y028	07/29/03	16:15	16:18	3	partly cloudy	28	38%	W	20	101.49 and falling
TS03-157	Petrie roof	Y015	07/29/03	16:30	17:35	65	mainly cloudy	28	38%	W	19	101.49 and steady
TS03-158	Petrie roof	Y013	07/29/03	16:45	16:49	4	mainly cloudy	28	38%	W	19	101.49 and steady
TS03-159	Petrie roof	Y103	07/29/03	17:15	17:18	3	mainly cloudy	28	38%	W	19	101.49 and steady
TS03-160	Petrie roof	Y272	07/29/03	17:35	18:30	55	cloudy	27	39%	W	22	101.50 and rising
TS03-161	Petrie roof	Y303	07/29/03	17:47	17:50	3.5	cloudy	27	39%	W	22	101.50 and rising
TS03-162	Petrie roof	Y079	07/29/03	18:15	18:18	3	cloudy	27	39%	W	22	101.50 and rising
TS03-163	Petrie roof	Y310	07/29/03	19:30	20:30	60	mainly sunny	25	43%	W	19	101.53 and rising
TS03-164	Petrie roof	Y486	07/29/03	19:45	19:48	3	mainly sunny	25	43%	W	19	101.53 and rising
TS03-165	Petrie roof	Y416	07/29/03	20:15	20:18	3.5	mainly sunny	25	43%	W	19	101.53 and rising

Table A32: Sampling Information, Suburban/Rural (GTA), August 2003.

Lab #	site	canister	date	time-start	time-end	time [min]	weather	temp[°C]	humidity	wind direct.	sp.[km/h]
TS03-178	20	Y216	19/08/2003	11:12	12:00	0:48	mainly clear	27.5	42%	5	7
TS03-179	20	Y477	19/08/2003	11:29	11:32	0:03	mainly clear	27.5	42%	5	7
TS03-180	20	Y027	19/08/2003	11:45	11:49	0:04	mainly clear	27.5	42%	5	7
TS03-181	21	Y417	19/08/2003	12:24	13:10	0:46	mostly cloudy	28.1	40.0%	20	7
TS03-182	21	Y321	19/08/2003	12:41	12:45	0:04	mostly cloudy	28.1	40.0%	20	7
TS03-183	21	Y238	19/08/2003	13:00	13:04	0:04	mostly cloudy	28.1	40.0%	20	7
TS03-184	22	Y420	19/08/2003	13:38	14:20	0:42	mostly cloudy	28.8	40%	28	19
TS03-185	22	Y396	19/08/2003	13:50	13:54	0:04	mostly cloudy	28.8	40%	28	19
TS03-186	22	Y400	19/08/2003	14:10	14:14	0:04	mostly cloudy	28.8	40%	28	19
TS03-187	23	Y346	19/08/2003	15:06	15:51	0:45	mainly clear	29.3	39.0%	0	0
TS03-188	23	Y372	19/08/2003	15:20	15:24	0:04	mainly clear	29.3	39.0%	0	0
TS03-189	23	Y419	19/08/2003	15:40	15:44	0:04	mainly clear	29.3	39.0%	0	0
TS03-190	24	Y322	19/08/2003	16:17	17:02	0:45	mainly clear	28.4	40%	21	20
TS03-191	24	Y253	19/08/2003	16:30	16:34	0:04	mainly clear	28.4	40%	21	20
TS03-192	24	Y231	19/08/2003	16:45	16:49	0:04	mainly clear	28.4	40%	21	20
TS03-193	25	Y298	19/08/2003	17:31	18:16	0:45	mainly clear	27.5	42.0%	17	17
TS03-194	25	Y406	19/08/2003	17:46	17:50	0:04	mainly clear	27.5	42.0%	17	17
TS03-195	25	Y076	19/08/2003	18:00	18:04	0:04	mainly clear	27.5	42.0%	17	17
TS03-196	20	Y 290	20/08/2003	10:44	11:30	0:46	mainly cloudy	27.1	44%	30	7
TS03-197	20	Y 529	20/08/2003	11:00	11:04	0:04	mainly cloudy	27.1	44%	30	7
TS03-198	20	Y 317	20/08/2003	11:16	11:20	0:04	mainly cloudy	27.1	44%	30	7
TS03-199	21	Y 328	20/08/2003	11:46	12:30	0:44	mainly clear	29	40%	28	15
TS03-200	21	Y 516	20/08/2003	12:00	12:04	0:04	mainly clear	29	40%	28	15
TS03-201	21	Y 387	20/08/2003	12:16	12:20	0:04	mainly clear	29	40%	28	15
TS03-202	22	Y 350	20/08/2003	12:56	13:41	0:45	mainly clear	29.9	38%	29	15
TS03-203	22	Y 120	20/08/2003	13:10	13:14	0:04	mainly clear	29.9	38%	29	15
TS03-204	22	Y 200	20/08/2003	13:26	13:30	0:04	mainly clear	29.9	38%	29	15
TS03-205	23	Y 313	20/08/2003	14:25	15:10	0:45	mainly clear	30.3	36%	21	20
TS03-206	23	Y 501	20/08/2003	14:41	14:45	0:04	mainly clear	30.3	36%	21	20
TS03-207	23	Y 411	20/08/2003	14:56	15:00	0:04	mainly clear	30.3	36%	21	20
TS03-208	24	Y 476	20/08/2003	15:32	16:17	0:45	mainly clear	31	31%	22	26
TS03-209	24	Y 006	20/08/2003	15:45	15:49	0:04	mainly clear	31	31%	22	26
TS03-210	24	Y 307	20/08/2003	16:01	16:05	0:04	mainly clear	31	31%	22	26
TS03-211	25	Y 256	20/08/2003	16:41	17:26	0:45	mainly clear	29.3	43%	19	19
TS03-212	25	Y 329	20/08/2003	16:55	16:59	0:04	mainly clear	29.3	43%	19	19
TS03-213	25	Y 005	20/08/2003	17:11	17:15	0:04	mainly clear	29.3	43%	19	19

Table A33: NMHC Mixing Ratio (ppbv), Suburban/Rural (GTA), August 2003.

Lab #	ppbV	ace	nC2	propene	nC3	1-buten	iso-buten	nC4	iC4	isoprene	nC5	2MC4	Benz	nC6	2MC5	3MC5	23DMC4	Tol	nC7	C2Benz	oXyl	mpXyl	nC8	CH3I
TS03-178	ppbv	0.225	1.191	0.089	0.265	0.024	0.060	0.130	0.067	0.669	0.073	0.159	0.076	0.029	0.036	0.020	0.011	0.231	0.014	0.011	0.005	0.016	0.007	0.51
TS03-179	ppbv	0.213	1.149	0.156	0.325	0.042	0.055	0.137	0.066	1.070	0.085	0.175	0.115	0.034	0.038	0.021	0.011	0.200	0.019	0.013	0.006	0.020	0.018	0.50
TS03-180	ppbv	0.278	1.248	0.114	0.351	0.024	0.076	0.149	0.085	0.521	0.084	0.163	0.091	0.033	0.041	0.021	0.011	0.231	0.055	0.014	0.008	0.020	0.109	0.44
TS03-181	ppbv	0.145	1.132	0.060	0.347	0.018	0.077	0.140	0.076	1.246	0.076	0.150	0.067	0.025	0.032	0.018	0.009	0.267	0.017	0.010	0.007	0.020	0.006	0.38
TS03-182	ppbv	0.205	1.025	0.073	0.340	0.027	0.070	0.158	0.088	1.805	0.105	0.177	0.097	0.037	0.046	0.025	0.010	0.353	0.060	0.017	0.017	0.055	0.088	0.35
TS03-183	ppbv	0.164	1.265	0.071	0.351	0.006	0.034	0.139	0.073	1.411	0.076	0.119	0.079	0.027	0.034	0.019	0.010	0.269	0.035	0.006	0.002	0.007	0.040	0.73
TS03-184	ppbv	0.002	1.376	0.738	0.468	0.232	0.125	0.160	0.079	0.319	0.079	0.129	0.084	0.025	0.026	0.013	0.010	0.114	0.011	LDL	LDL	LDL	0.007	0.57
TS03-185	ppbv	0.204	1.406	0.067	0.489	0.013	0.037	0.167	0.093	0.173	0.069	0.133	0.087	0.025	0.028	0.014	0.009	0.263	0.023	0.006	0.004	0.009	0.046	0.34
TS03-186	ppbv	0.201	1.328	0.099	0.449	0.024	0.061	0.166	0.085	0.964	0.077	0.163	0.086	0.030	0.031	0.017	0.009	0.226	0.018	0.009	0.006	0.015	0.021	0.32
TS03-187	ppbv	0.229	1.450	0.077	0.496	0.008	0.046	0.167	0.097	0.168	0.063	0.136	0.069	0.030	0.026	0.015	0.007	0.114	0.009	0.006	0.003	0.006	0.005	0.31
TS03-188	ppbv	0.204	1.475	0.045	0.491	0.013	0.028	0.166	0.096	0.128	0.066	0.111	0.097	0.029	0.028	0.015	0.008	0.323	0.020	0.010	0.004	0.009	0.046	0.32
TS03-189	ppbv	0.193	1.390	0.042	0.452	0.014	0.041	0.145	0.095	0.190	0.057	0.117	0.086	0.023	0.022	0.012	0.007	0.166	0.011	0.005	0.002	0.005	0.018	0.35
TS03-190	ppbv	0.241	1.206	0.087	0.473	0.021	0.050	0.228	0.101	0.197	0.129	0.259	0.099	0.043	0.061	0.034	0.015	0.109	0.016	0.015	0.012	0.020	0.008	0.42
TS03-191	ppbv	0.237	1.284	0.190	0.491	0.095	0.049	0.201	0.096	0.115	0.092	0.187	0.240	0.033	0.039	0.021	0.011	0.381	0.019	0.227	0.155	0.456	0.037	0.45
TS03-192	ppbv	0.235	1.283	0.058	0.492	0.015	0.035	0.200	0.097	0.274	0.104	0.206	0.073	0.035	0.048	0.027	0.013	0.204	0.017	0.020	0.011	0.022	0.020	0.40
TS03-193	ppbv	0.152	1.154	0.045	0.398	0.010	0.050	0.148	0.073	0.873	0.064	0.135	0.075	0.023	0.027	0.015	0.008	0.090	0.011	0.012	0.006	0.012	0.007	0.31
TS03-194	ppbv	0.201	1.286	0.076	0.465	0.009	0.036	0.166	0.086	1.054	0.074	0.153	0.094	0.024	0.031	0.017	0.008	0.170	0.015	0.011	0.002	0.007	0.018	0.31
TS03-195	ppbv	0.204	1.491	0.113	0.483	0.023	0.081	0.184	0.093	0.865	0.079	0.167	0.088	0.027	0.034	0.019	0.009	0.255	0.017	0.015	0.007	0.013	0.016	0.37
TS03-196	ppbv	0.310	1.180	0.171	0.400	0.035	0.103	0.257	0.098	0.409	0.162	0.339	0.113	0.066	0.079	0.046	0.019	0.292	0.041	0.028	0.019	0.048	0.017	0.28
TS03-197	ppbv	0.252	1.008	0.062	0.363	0.022	0.032	0.306	0.101	0.252	0.259	0.437	0.124	0.108	0.146	0.089	0.032	0.304	0.059	0.031	0.024	0.061	0.031	0.36
TS03-198	ppbv	0.308	1.466	0.243	0.549	0.078	0.057	0.275	0.103	0.326	0.154	0.243	0.142	0.066	0.072	0.044	0.016	0.337	0.043	0.021	0.013	0.031	0.023	0.45
TS03-199	ppbv	0.229	1.006	1.887	0.366	0.629	0.454	0.208	0.090	0.656	0.134	0.205	0.206	0.046	0.054	0.031	0.012	0.216	0.012	0.011	0.007	0.018	0.030	0.43
TS03-200	ppbv	0.213	1.051	0.072	0.332	0.020	0.028	0.148	0.065	0.882	0.084	0.170	0.078	0.028	0.036	0.020	0.010	0.196	0.014	0.005	0.002	0.006	0.013	0.39
TS03-201	ppbv	0.275	1.138	0.081	0.427	0.018	0.040	0.178	0.082	0.832	0.108	0.212	0.114	0.049	0.052	0.032	0.014	0.345	0.026	0.014	0.006	0.019	0.018	0.34
TS03-202	ppbv	0.338	1.362	0.074	0.461	0.017	0.070	0.211	0.094	0.710	0.104	0.237	0.144	0.037	0.048	0.027	0.012	0.162	0.015	0.010	0.003	0.007	0.005	0.38
TS03-203	ppbv	0.321	1.362	0.140	0.463	0.033	0.061	0.206	0.092	0.642	0.100	0.231	0.159	0.036	0.045	0.027	0.011	0.304	0.016	0.014	0.006	0.014	0.017	0.36
TS03-204	ppbv	0.326	1.330	0.060	0.453	0.012	0.029	0.200	0.091	1.011	0.098	0.222	0.135	0.035	0.045	0.026	0.011	0.210	0.014	0.006	0.001	0.004	0.009	0.30
TS03-205	ppbv	0.234	1.203	0.043	0.369	0.014	0.052	0.209	0.105	0.108	0.116	0.284	0.120	0.031	0.050	0.028	0.014	0.124	0.016	0.005	0.003	0.005	0.005	0.35
TS03-206	ppbv	0.282	1.281	0.076	0.385	0.017	0.038	0.248	0.131	0.086	0.152	0.363	0.128	0.039	0.065	0.037	0.016	0.281	0.022	0.022	0.014	0.033	0.015	0.35
TS03-207	ppbv	0.199	0.989	0.057	0.297	0.013	0.034	0.124	0.062	0.082	0.052	0.095	0.087	0.019	0.022	0.012	0.007	0.147	0.009	0.009	0.004	0.008	0.013	0.40
TS03-208	ppbv	0.417	1.392	0.056	0.710	0.010	0.044	0.357	0.212	0.553	0.218	0.401	0.142	0.092	0.093	0.058	0.023	0.301	0.029	0.033	0.008	0.021	0.012	0.44
TS03-209	ppbv	0.371	1.131	0.094	0.589	0.024	0.056	0.291	0.181	0.386	0.182	0.288	0.127	0.080	0.075	0.047	0.019	0.313	0.028	0.038	0.017	0.029	0.020	0.39
TS03-210	ppbv	0.577	1.452	0.133	0.884	0.029	0.067	0.460	0.258	0.708	0.298	0.452	0.205	0.141	0.121	0.076	0.029	0.504	0.064	0.168	0.116	0.451	0.075	0.42
TS03-211	ppbv	0.714	1.576	0.143	1.152	0.020	0.062	0.778	0.375	1.714	0.411	0.692	0.199	0.185	0.188	0.117	0.044	0.566	0.057	0.087	0.039	0.080	0.024	0.38
TS03-212	ppbv	0.598	1.454	0.090	1.091	0.015	0.029	0.747	0.366	1.781	0.392	0.725	0.186	0.176	0.179	0.112	0.040	0.542	0.055	0.057	0.023	0.043	0.031	0.49
TS03-213	ppbv	0.599	1.394	0.088	1.053	0.016	0.029	0.791	0.360	1.646	0.385	0.634	0.220	0.183	0.180	0.113	0.040	0.615	0.054	0.096	0.036	0.066	0.031	0.45