# Stable carbon isotope composition of ambient VOC and its use in the determination of photochemical ages of air masses

by

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## ABSTRACT

Stable Carbon Isotopic Composition measurements can provide valuable information about the processing of trace gases in the atmosphere. Not only can it be used to distinguish physical processes such as dilution and mixing from photochemical ageing, but it can also be an important tool in identification of sources, in calculating the photochemical age and qualitatively and quantitatively connecting precursors with their atmospheric products.

Even though isotopic composition analysis is a valuable technique, its use is hindered by the low concentrations of compounds in the atmosphere, complexity of the samples and complex measuring instrumentation. The intention of this research project was to develop and validate sampling and instrumental analysis techniques that can be used to perform isotopic composition measurements of volatile organic compounds (VOC) and to apply these methods to analysis of ambient samples.

Since most VOC are present in the atmosphere in sub-ppbv to ppbv levels and more than 1 ng of carbon is required for isotopic analysis, collection of large volumes of air is required. A method based on sampling onto cartridges filled with an adsorbent (Carboxene-569) for VOC collection in the field has been developed. VOC are selectively collected by passing large volumes (up to 100 L) of air through the cartridges. Thermal desorption of VOC from the cartridges is followed by two step cryogenic trapping and separation by gas chromatography. Once separated, all VOC are oxidized in a combustion interface. The isotopic composition of resulting carbon dioxide is then determined on-line by isotope ratio mass spectrometry. Various validation tests were performed in order to test accuracy and precision of both the preconcentration system and sampling-desorption procedure.

The newly developed sampling and analysis techniques were applied in field studies: Border air quality study (BAQS) (2007) and Environment Canada-York University campaign (EC-YU) (2009-2010). Ambient samples were collected over various time periods and the isotopic composition of individual compounds was analyzed. Determined mixing ratios were in pptv to low ppbv ranges and isotope composition varied from -30‰ to -20‰ for most of the compounds. Analysis of mixing ratios and isotope composition, their distribution and trends indicated that sampling locations can be qualitatively classified as rural (Ridgetown), semi-rural (Harrow and Egbert) and semi-urban (Toronto) areas, with strong local vehicle emission sources. Quantitative analysis of the photochemical ages (PCA) determined using hydrocarbon and isotope hydrocarbon clocks (Egbert and Toronto samples) resulted in similar values, suggesting that both of these methods are valid and are applicable. However, while both PCA methods indicated that local sources have larger impact on the air quality in these two locations, PCA from isotope composition analysis has demonstrated that different VOC in photochemically processed air masses differ in their PCA depending on VOC reactivity.

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## ABBREVIATIONS AND SPECIAL NOTATIONS

| | |
|---|---|
| $^{12}C$ | Carbon-12 isotope of carbon |
| $^{13}C$ | Carbon-13 isotope of carbon |
| ArHC | Aromatic Hydrocarbons |
| ArRH | Aromatic Hydrocarbons |
| AVOC | Anthropogenic Volatile Organic Compounds |
| BAQS | Border Air Quality Study |
| BVOC | Biogenic Volatile Organic Compounds |
| FID | Flame ionization detector |
| GC | Gas Chromatography or Gas Chromatograph |
| GC-IRMS | Gas Chromatography Isotope Ratio Mass Spectrometry |
| HC | Hydrocarbons |
| IRMS | Isotope Ratio Mass Spectometry or Isotope Ratio Mass Spectrometer |
| $k_{Cl}$ | Rate constant of the reaction with Cl |
| KIE | Kinetic Isotope Effect |
| $k_{OH}$ | Rate constant of the reaction with OH radicals |
| NMHC | Non-Methane Hydrocarbons |
| PCA | Photochemical Age |
| ppbv | parts per billion by volume |
| pptv | parts per trillion by volume |
| R | recovery |
| RH | Alkanes |
| RSD | Relative Standard Deviation |
| SD | Standard Deviation |
| SOA | Secondary Organic Aerosol |

| | |
|---|---|
| t[OH] | Photochemical Age |
| VOC | Volatile Organic Compounds |
| V-PDB | Vienna Peedee Belemnite |
| YU-EC | York University- Environment Canada study |
| $\delta^{13}C$ | Stable carbon isotopic composition (in ‰) |
| $\varepsilon$ | Kinetic Isotope Effect (in ‰) |
| $\tau$ | Atmospheric lifetime |

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# 1. INTRODUCTION

Volatile Organic Compounds (VOC) constitute an important class of atmospheric pollutants that are emitted in large quantities from various biogenic and anthropogenic sources [*Atkinson*, 2000; *Guenther et al.*, 2000; *Guenther et al.*, 1995; *Niedojadlo et al.*, 2008; *Piccot et al.*, 1992; *Rudolph*, 2002; *Sawyer et al.*, 2000]. While present in small concentrations (from high parts per billion to low parts per trillion by volume (ppbv, pptv), these compounds play a very important role by significantly affecting the chemistry of the troposphere. For example, VOC play key roles in production of ozone, aerosol formation and regional air quality in general [*Jordan*, 2009]. While there is not yet an official definition of VOC, in atmospheric chemistry the term VOC is generally used for organic compounds with vapor pressure greater than 10 Pa at 25 °C and boiling points below 260 °C at 1 atm that contain fewer than 15 carbon atoms and possibly heteroatoms (oxygen, nitrogen, or sulfur). Although methane meets these conditions, for practical reasons it is usually not included in VOC. Non-methane hydrocarbons (NMHC) are a sub-class of VOC compounds that contain only carbon and hydrogen atoms.

On average, global emissions of VOC are about 1300-1500 TgC per year with biogenic emissions dominating anthropogenic sources by up to 90% [*Atkinson*, 2000; *Niedojadlo et al.*, 2008]. The global flux of VOC from biological sources (BVOC) has been estimated at 1150-1300 TgC per year [*Constable et al.*, 2001; *Guenther et al.*, 2000; *Guenther et al.*, 1995] with 98% of the total being emissions from vegetation. These emissions are primarily from foliage and consist on average of 57% of isoprene, 25% of terpenoids, and up to 18% of other reactive non-terpenoid compounds [*Atkinson and Arey*, 2003b; *Constable et al.*, 2001; *Guenther et al.*, 1995; *Steiner and Goldstein*, 2007]. Natural emissions of alkanes and aromatic compounds are negligible, though overestimated by some inventories [*Guenther et al.*, 2000].

The total emission of anthropogenic VOC (AVOC) is estimated at 150 TgC per year [*Niedojadlo et al.*, 2008; *Piccot et al.*, 1992]. On a global scale, about 60-80% of anthropogenic emissions are associated with fossil fuel production, distribution, use and storage, and up to 20-30% with biomass burning  [*Reimann and Lewis*, 2007; *Rudolph*, 2002]. Since anthropogenic VOC are rather diverse, detailed classification of their emission sources is quite challenging. Frequently, emissions are grouped according to the commodities or activities with which they are associated [*Niedojadlo et al.*, 2008; *Piccot et al.*, 1992; *Sawyer et al.*, 2000; *Watson et al.*, 1991].

Aromatic NMHC (ArHC) are important constituents of urban and rural air masses [*Forstener and Flagan*, 1997; *Lurmann and Main*, 1992]. ArHC are abundant components of fossil fuels, they are found in gasoline, vehicle exhaust, evaporated and spilled fuels and solvents, and many other anthropogenic-related emissions [*Hurley et al.*, 2001; *Jang and Kamens*, 2001; *Reimann and Lewis*, 2007]. 44% of urban VOC are composed of ArHC, up to 60-75% of which are benzene, toluene, ethylbenzene, and 1,2,4-trimethylbenzene [*Jang and Kamens*, 2001; *Smith et al.*, 1998]. The atmospheric oxidation processing of these aromatics and some heavy alkanes (by reaction with OH and $NO_3$) can result in formation of oxygenated and nitrated products that may contribute to the formation of secondary organic aerosol (SOA) by nucleation or gas-particle partitioning [*Forstener and Flagan*, 1997; *Jang and Kamens*, 2001]. It has been shown that SOA can represent more than 75% of total organic aerosol in polluted regions [*Odum et al.*, 1997]. Even though primary reactions of ArHC in the atmosphere have been extensively studied, further chemical transformations and resulting products still remain unknown [*Jang and Kamens*, 2001; *Odum et al.*, 1997; *Stroud et al.*, 2004]. While there have been very extensive laboratory investigations of these processes, nearly all of these studies have been conducted at VOC concentrations which exceeded ambient atmospheric levels by several orders of magnitude [*Irei et al.*, 2006]. However, there were several attempts to qualitatively and quantitatively link the precursor and its products collected from ambient air [*L Li et al.*, 2010a; *Moukhtar et al.*, 2011].

In the atmosphere VOC undergo various chemical and physical processing that leads to their transformation, removal, transport and re-distribution [*Atkinson*, 2000; *Helmig et al.*, 2008; *Jenkin and Clemitshawb*, 2000; *Parrish et al.*, 2007; *Roger*, 1990]. Since chemistry of VOC is directly related to their structure and indirectly to their origin and distribution, it has been shown that some of their properties could be used to study various chemical and physical processes affecting the chemical composition of ambient air masses. The majority of the presently used methods use concentration measurements as a main indicator of photochemical processing of the air masses. However, since the air parcel is a dynamic system, use of concentration alone as a marker for a photochemical processing is problematic [*Parrish et al.*, 2007]. The change in the relative composition of the ambient sample is considered to be a better indicator of photochemical processing, since the ratios are less affected by the physical mixing and dilution processes [*Honrath et al.*, 2008; *Kleinman et al.*, 2003a; *Kleinman et al.*, 2003b; *McKeen and Liu*, 1993; *McKeen et al.*, 1996; *Parrish et al.*, 1992; *Parrish et al.*, 2007; *Roberts et al.*, 1984; *Rudolph and Johnen*, 1990; *Warneke et al.*, 2007]. While the use of this method is common, the interpretation of the results is still quite challenging due to the complexity of the atmospheric processing and mixing, and as a result many conclusions drawn have to be based on a substantial number of assumptions [*de Gouw et al.*, 2005; *Gelencsér et al.*, 1997; *Jobson et al.*, 1998; *Kleinman et al.*, 2003b].

It has been shown by many studies that the use of the stable carbon isotope ratios is beneficial in providing insights into photochemical transformation and physical processing of VOC in ambient air [*Ghosh and Brand*, 2003; *Goldstein and Shaw*, 2003; *Meier-Augenstein*, 1999; *Rudolph*, 2007; *Rudolph et al.*, 2003; *Rudolph et al.*, 2002; *Stein and Rudolph*, 2007]. While the theory of stable isotope fractionation was introduced at the beginning of the 20th century by Lindemann, the actual measurements were limited by the availability of instruments that were sensitive enough to detect small differences in isotopic composition of ambient substances. McKinney et al. [1950] introduced one of the first mass spectrometers that was able to differentiate carbon and oxygen isotopologues in carbon dioxide and oxygen molecules [*McKinney et al.*, 1950; *Richet et al.*, 1977]. This development was followed by extensive studies of stable carbon isotopic composition of carbon monoxide, carbon dioxide and methane in ambient samples [ *Brenninkmeijer et al.*, 1995; *Lowe et al.*, 1994; *Stevens et al.*, 1972] as well as theoretical modeling and interpretations [ *Brenninkmeijer et al.*, 1995; *Craig*, 1953; *Kaye*, 1987; *Richet et al.*, 1977].

Some trace gases, such as methane, carbon monoxide, or carbon dioxide are present in the atmosphere at ppmv or high ppbv levels. However, most VOC (i.e. benzene, toluene, xylenes, etc.) are present in the atmosphere at mixing ratios that are 3-5 orders of magnitude lower than those of these common trace gases, thus measuring their isotopic composition is very challenging. In 1997 Rudolph et al. published a method for compound specific determination of the stable carbon isotopic composition for atmospheric VOC at sub-ppbv levels [ *Rudolph et al.*, 1997]. The uncertainty of the method was close to 0.5‰, and Rudolph *et al.* suggested further improvements in method may allow a precision close to 0.1‰. Within several years different research groups published results of stable carbon isotope measurements for a variety of atmospheric VOC [*Anderson et al.*, 2004; *Czapiewski et al.*, 2003; *Iannone et al.*, 2003; *Iannone et al.*, 2005; *Irei et al.*, 2006; *Norman et al.*, 1999; *Rogers and Savard*, 1999; *Rudolph et al.*, 2003; *Rudolph et al.*, 2002; *Smallwood et al.*, 2002]. Authors not only developed and applied methods to determine the isotopic composition of ambient VOC [*Czapiewski et al.*, 2003; *Norman et al.*, 1999; *Rudolph et al.*, 2002; *Smallwood et al.*, 2002; *Thompson et al.*, 2003], but also performed studies on the effects of heavier isotopologues on chemical kinetics of the molecules [*Anderson et al.*, 2003; *Anderson et al.*, 2004; *Iannone* *et al.*, 2003; *Iannone et al.*, 2005]. Nevertheless the number of publications on isotopic composition measurements and their application is still quite limited due to the need for elaborate and expensive experimental techniques and challenging data interpretation [*Eckstaedt et al.*, 2011; *Fisseha et al.*, 2009a; *Giebel et al.*, 2010; *Iannone et al.*, 2005; *Iannone et al.*, 2009; 2010; *Irei et al.*, 2006; *Q Li et al.*, 2010b; *Moukhtar et al.*, 2011].

The intention of this project was to develop and implement a method for measuring the stable carbon isotopic composition of ambient VOC. Presently the only available technique is Gas Chromatography coupled to Isotope Ratio Mass Spectrometry (GC-IRMS), which requires substantially larger samples (ideally between 10 and 50 ng of carbon per compound) than state of the art methods used for concentration measurements. Consequently, established sampling and sample preparation techniques have been revised and adapted to suit the specific needs of GC-IRMS analysis. This dissertation is part of the overall objective of Dr. Rudolph’s research group to qualitatively and quantitatively link VOC and their oxidation products in the atmosphere. Since this research primarily targets the sources of atmospheric phenols, the primary target compounds in my research were aromatic VOC (benzene, toluene, ethylbenzene, m-,p-,o-xylenes) which are precursors of atmospheric phenols. The developed methodology also allows analysis of several n-alkanes (n-hexane, n-heptanes, n-octane, n-nonane, n-decane) which were included. The developed method was subsequently used to measure concentrations and isotopic composition of these VOC during two field campaigns: Border Air Quality Study (summer of 2007) and York University-Environment Canada study (2009-2010).

The obtained data sets were used to study seasonal and spatial variation in isotope composition of ambient VOC and to determine photochemical ages (PCA) of the air masses using hydrocarbon and isotope hydrocarbon clocks. Comparison of these differently determined photochemical ages was used to compare advantages and problems of the different approaches to determine PCA. Results were then used to interpret the extent of chemical processing of VOC in the troposphere, to identify possible local and regional emission sources and evaluate their impact on the air quality.

The chemistry of ambient VOC, stable carbon isotopic composition theory, use of hydrocarbon and isotope hydrocarbon clocks in a determination of the photochemical age of air masses and identification of the emission sources are explained in Chapter 2 (Theory). Description and characteristic parameters of sampling and analysis setups for ambient compounds are provided in Chapter 3 (Experimental), followed by details of the developed method, analysis parameters, method characterization and evaluation tests. Chapter 4 (Results) includes isotopic composition of selected VOC obtained for ambient samples and their application in the PCA determination. Proposed sampling and analysis techniques are discussed in 5.1 (Discussion: Sampling and analysis), while the overall method is evaluated in 5.2 (Discussion: Method Evaluation). Analysis of determined mixing ratios and stable carbon isotope composition, their comparison to previously published data, trends and correlations is provided in 5.3.1, 5.3.2 and 5.3.3. Applications of hydrocarbon and isotope hydrocarbon clocks, and their comparison are discussed in 5.3.4 (Discussion: Ambient Volatile Organic compounds), followed by conclusions and future method applications in Chapter 6 (Conclusion).

In addition, developed instrumentation for sample processing was used to determine stable carbon isotope composition of the VOC collected during studies of biodiesel fuel emissions by Environment Canada (2008), providing first set of data collected for this fuel type. These results are presented in Chapter 4 (4.3.3).

# 2. THEORY

## 2.1 Chemistry of VOC in the atmosphere

In the atmosphere aromatic NMHC (ArHC) and alkanes undergo chemical transformation via gas-phase reactions with hydroxyl radicals (OH•), nitrate radicals ($NO_3$), chlorine atoms (Cl) and ozone ($O_3$), with OH• contributing the most to these oxidation processes. On a global average Cl most likely will have a low impact on the tropospheric oxidation of alkanes and aromatic HC, however due to the high reactivity of many VOC towards Cl-atoms, on a local scale Cl atoms can play a significant role in the removal of several alkanes and aromatic VOC [*Atkinson*, 2000; *Finlayson-Pitts and Pitts*, 2000; *Rudolph*, 2002]. Reaction rates of $O_3$ and $NO_3$ with both aromatics and alkanes are significantly slower and can usually be ignored [*Atkinson*, 2000; *Atkinson and Arey*, 2003a; *Finlayson-Pitts and Pitts*, 2000].

Oxidation of alkanes with either Cl or OH· starts with H abstraction (R2.1, R2.2) from the C-H bonds for alkanes (RH) and alkyl substituent groups of aromatic NMHC (ArRH) or from the C-H bonds of the aromatic ring in case of benzene; or with OH· addition to the aromatic ring (R2.3) (for aromatic NMHC),

$$\mathrm{OH\bullet + RH \rightarrow R\bullet + H_2O} \qquad \text{R2.1}$$

$$\mathrm{OH\bullet + ArRH \rightarrow ArR\bullet + H_2O} \qquad \text{R2.2}$$

$$\mathrm{OH\bullet + ArRH \rightarrow ArRHOH\bullet} \qquad \text{R2.3}$$

Due to the accessibility and presence of hydrogen atoms, rate constants for reactions for R2.1 increase with increasing size of the molecule and decrease with the number of hydrogen atom attached to carbon atom [*Atkinson*, 1990; *Reimann and Lewis*, 2007]. Reaction 2.2 occurs at high temperatures and its rate constant increases with increasing temperature and has a similar dependence on the structure of alkyl groups as the rate constant for R2.1. The addition reaction of OH• (R2.2) takes place at lower temperatures, and while this process has been widely studied, kinetics of the adduct formation and the following transformations are still poorly understood [*Finlayson-Pitts and Pitts*, 2000]. At room temperature and atmospheric pressure hydroxyl radical addition to the aromatic ring (R2.2) dominates and H-abstraction accounts for only about 10% loss of aromatic VOC [*Atkinson*, 1990; *Atkinson and Arey*, 2003a; *Finlayson-Pitts and Pitts*, 2000; *Reimann and Lewis*, 2007].

## 2.2 Stable carbon isotope ratios

### 2.2.1 Definitions

Stable carbon isotopic ratio is defined as a ratio of number of $^{13}$C atoms to that of $^{12}$C ($^{13}$C/$^{12}$C). This ratio is usually given relative to a reference point- a standard with known isotope composition. For carbon it is Vienna Peedee Belemniete (V-PDB) with R=0.0112372 [*Craig*, 1953]. This is an international standard based on carbon dioxide that is prepared from $CaCO_3$ deposits from the Peedee formation of South Carolina (USA) [*Craig*, 1953; *Goldstein and Shaw*, 2003]. Although Peedee Belemnite reference material is no longer available, effectively all reference standards used today are traceable to V-PDB and carbon isotope ratios are presented relative to V-PDB. Since deviations in $^{13}$C/$^{12}$C are small and measurable in the fourth significant digit [*Goldstein and Shaw*, 2003], the isotope ratios are typically expressed in delta notation ($\delta^{13}$C) as per mille values (‰):

$$\delta^{13}C \text{ ‰ } = \frac{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{V-PDB}}{(^{13}C/^{12}C)_{V-PDB}} \times 1000\text{‰} \qquad (2.1)$$

In this work all delta values are expressed in parts per thousand (‰) and are determined relative to V-PDB.

Since VOC include more than one carbon in their molecule, any $^{12}$C can be potentially substituted by $^{13}$C atom leading to multiple labeling by $^{13}$C, however for ambient VOC with small number of C-atoms due to the low natural abundance of $^{13}$C (1.01%) this probability is insignificant and thus usually ignored. It is often assumed that $^{13}$C is randomly distributed throughout the molecule, a simplification which in many cases provides very useful approximations [*Rudolph*, 2007].

### 2.2.2 Kinetic Isotope Effect and Rayleigh Fractionation

Isotopologues, compounds that contain different isotopes of one or more atoms, have slightly different chemical properties due to the difference in vibrational zero point energy that is caused by the shift in the vibrational frequencies of C-C bonds upon substitution of $^{12}$C with $^{13}$C[*Craig*, 1953; *Richet et al.*, 1977]. Consequently, while they undergo similar chemical transformations, the reaction rates for these processes differ slightly due to the differences in activation energies [*Kaye*, 1987].

The kinetic isotope effect (KIE) is defined as a ratio of the rate constants for $^{12}$C and $^{13}$C containing compounds (2.2):

$$KIE = \frac{^{12}k}{^{13}k} \tag{2.2}$$

Since a $^{13}$C-containing bond has a zero point energy that is lower than that of the only $^{12}$C-containing isotopologue, more energy is required to break the chemical bond. As a result, a molecule that contains only $^{12}$C usually reacts faster than a molecule with a $^{13}$C atom and thus KIEs are generally larger than unity (normal KIE). Since the difference in rate constants is generally very small, KIEs are usually very close to one. Therefore KIEs are often presented as the relative difference between the rate constants in epsilon notation (ε) in parts per thousand (‰) (2.3)

$$\varepsilon_{OH} \ ‰ = \frac{^{12}k - {}^{13}k}{^{13}k} \times 1000‰ \tag{2.3}$$

As a result of the difference in the reaction rates during chemical processing, the $^{13}$C-containing isotopologue is removed at a slower rate than the only $^{12}$C- containing one, this results in an enrichment of $^{13}$C in the unreacted VOC, the magnitude of which depends on the extent of processing. While the KIE of an individual isotopologue depends on the site of the $^{13}$C atom, currently used KIE values have been determined for random distribution of the $^{13}$C atoms ($\varepsilon$) and do not differentiate between reactions at different carbon atoms present in the molecular chain of VOC [*Anderson et al., 2004]*.

### 2.2.3 Two-endpoint mixing

If no chemical reaction is occurring, the stable carbon isotope composition of an ambient compound can be described as

$$\delta_{ambient} = \frac{\sum [VOC]_i \delta_i}{[VOC]_{ambient}} \tag{2.4}$$

where $[VOC]_i$ and $\delta_i$ are VOC mixing ratio and isotope composition from different sources that contribute into an overall air mass [*Rudolph*, 2007]. However, elimination of any photochemistry or presence of just one emission source is not convincing, thus two-endpoint mixing relation is derived:

$$\delta_{ambient} = \frac{\delta_1 [VOC]_1 \dfrac{[VOC]_{ambient} - [VOC]_2}{[VOC]_1 - [VOC]_2} + \delta_2 [VOC]_2 (1 - \dfrac{[VOC]_{ambient} - [VOC]_2}{[VOC]_1 - [VOC]_2})}{[VOC]_{ambient}} \tag{2.5}$$

where $[VOC]_1$, $[VOC]_2$ and $\delta_1$, $\delta_2$ are concentrations and isotope compositions of VOC from different air parcels. For a simplification purpose, it is usually assumed that $[VOC]_1 >> [VOC]_2$ and thus equation 2.5 becomes

$$\delta_{ambient} = \delta_1 + \frac{(\delta_2 - \delta_1)[VOC]_2}{[VOC]_{ambient}} \tag{2.6}$$

This simplification is applicable for those cases where one dominant emission source is present and fresh pollution is mixed with background air, but the background levels are not negligible [*Rudolph*, 2007]. $\delta_1$ is then determined as intercept from the plot of $\delta_{ambient}$ versus inverse of VOC mixing ratio. This approach is valuable not only to identify isotope composition of the emission source ($\delta_1$), but also to visualize (if present) the direct dependence of photochemical processing ($\delta_{ambient}$) on changes in concentration.

## 2.3 Photochemical Age Determination

The "Photochemical Age", denoted in the following as PCA, is a metric for photochemical processing of VOC and usually is defined as the time integral of the OH radical concentration for an air mass. PCA can be determined based on the changes of mixing ratios of VOC, this approach is known as hydrocarbon clock method [*Jobson et al.*, 1999; *Jobson et al.*, 1998; *Kleinman et al.*, 2003b; *Parrish et al.*, 1992; *Parrish et al.*, 2007] or based on the changes of VOC isotope ratios, known as isotope hydrocarbon clock [*Rudolph et al.*, 2003; *Rudolph and Czuba*, 2000; *Stein and Rudolph*, 2007; *Thompson*, 2003].

### 2.3.1 Hydrocarbon Clock

Removal of VOC by chemical reaction with OH• can be described as second order reaction as function of VOC concentration [VOC] and OH-radical concentration [OH] and rate constant k.

$$\frac{d[VOC]}{dt} = -k_{OH}[VOC][OH] \tag{2.7}$$

Consequently, if t is the time that has passed, and

$$\int_0^t [OH]dt = t[OH]_{av} = t[OH] \tag{2.8a}$$

the change in concentration of VOC as function of time can be written as

$$[VOC]_t - [VOC]_0 = \exp^{(-k_{OH}[OH]t)} \tag{2.8b}$$

or

$$\ln\frac{[VOC]_t}{[VOC]_0} = -k_{OH}[OH]t \tag{2.8c}$$

where $[VOC]_t$ and $[VOC]_0$ are the VOC concentrations at time t and the beginning of the reaction. This is only valid for a closed system and has to be modified for the atmosphere where mixing and dilution also cause a change in VOC concentrations:

$$\ln\frac{[VOC]_t}{[VOC]_0} = -k_{OH}[OH]t + \ln D(t) \tag{2.9}$$

Here $[VOC]_t$ and $[VOC]_0$ are the VOC concentrations at the study site (receptor) and at some point directly influenced by strong emissions, respectively, [OH] is the average concentration of OH for time interval t, D(t) is a dilution factor, and t is the time interval between the two observations.

Using (2.9) PCA can be determined based on the mixing ratios of $VOC_1$, $VOC_2$, …$VOC_n$ and corresponding reaction rate constants by plotting $\ln\left(\frac{VOC\ _t}{[VOC]_0}\right)$ versus $k_{OH}$ assuming that D(t) is independent of the VOC. Since atmospheric mixing is turbulent, this assumption is justified as long as the VOC concentration in the diluting air masses is negligible (small compared to $[VOC]_t$). The slope of the linear regression line of $\ln\left(\frac{VOC\ _t}{[VOC]_0}\right)$ versus $k_{OH}$ is [OH]t (PCA) and the intercept is ln[D(t)]. This approach was initially introduced by Rudolph and Johnen [1990] and has been developed further by Kleinman [2003b]. It is based on the assumptions that in the atmosphere VOC undergo reaction only with the hydroxyl radical, are emitted from the same single source and have a distinct travel time. The choice of a specific set of VOC is based on several criteria, such as low background levels, high concentrations, wide range of the reactivity with $k_{OH} \leq 2.6 \times 10^{-11}$, and a chemical lifetime dominated by the reaction with OH radicals [*Gelencsér et al.*, 1997]. Application of (2.9) is not necessarily limited to using the concentration at the point of emission, $[VOC]_0$ can in principle be any reference point common to all VOC used for the linear regression as long as it is representative for sources with identical emission patterns for the selected set of VOC. In this case [OH]t represents the difference in OH processing between reference point and observation and D(t) the difference in dilution.

In another method PCA can be determined based on a specific pair of VOC. Applying (2.9) to a pair allows elimination of lnD(t). A specific application using toluene and benzene has been suggested by *Gelencsér et al.* [1997]:

$$t\ OH = \frac{\ln(\frac{[Tol]_r}{[Benz]_r}) - \ln(\frac{[Tol]_s}{[Benz]_s})}{k_B - k_T} \tag{2.10}$$

Here r and s refer to concentrations at the receptor and source location, respectively, $k_B$ and $k_T$ are the rate constants for reactions of benzene and toluene with the OH-radical.

While being widely used, hydrocarbon clock methods are limited by the assumption that the VOC in the studied air mass have the same photochemical history. However, it has been demonstrated that the ratio of concentrations can be significantly affected by mixing processes [*McKeen and Liu*, 1993; *McKeen et al.*, 1996]. Consequently the true photochemical age of compounds with a long atmospheric residence time is often higher than that of compounds with short atmospheric life time and only under specific conditions is the photochemical age of compounds with different average atmospheric life times identical. This creates potential bias in PCAs determined from hydrocarbon ratios and indeed PCA for the same air mass determined from different sets of compounds or using different approaches often differ.

### 2.3.2 Isotope Hydrocarbon Clock

Use of isotope ratios in the PCA determination was initially introduced by Rudolph and Czuba under the isotope hydrocarbon clock concept [2000]. A major obstacle in the hydrocarbon clock approach was finding compounds with rate constants that are different by not more than a few percent [ *Rudolph*, 2007; *Rudolph and Czuba*, 2000] and have emission ratios that are constant. Rudolph and Czuba were the first who identified the potential in implementation of isotopologues for PCA determination since the difference of their rate constants is in the parts per thousand range.

Equation (2.10) can be re-written using isotope ratios as

$$t\ OH\ = \frac{\ln(\frac{[^{13}C]_r}{[^{12}C]_r}) - \ln(\frac{[^{13}C]_s}{[^{12}C]_s})}{^{12}k_{OH} - {}^{13}k_{OH}} \tag{2.11}$$

with r and s referring to isotopic composition of VOC at the receptor and source location.

Using delta notation ($\delta$) and equation 2.11, isotopic composition of ambient VOC can be expressed as

$$\delta_R^{13}C = \delta_S^{13}C + k_{OH}\varepsilon_{OH}[OH]t \tag{2.12}$$

where $\delta_s^{13}C$ and $\delta_R^{13}C$ are the stable carbon isotope composition of VOC at the source and receptor locations, $k_{OH}$ is the reaction rate constant (VOC + OH), $\varepsilon_{OH}$ is the KIE, and [OH]t average photochemical age (PCA).

Since stable carbon isotope composition changes due to the chemical transformations, a valid linear approximation can be found which allows us to determine the average age for VOC from air with different PCA with an error that is below any realistic measurement error. As a result, obtained PCA is not biased by mixing or dilution processes and independent of the differences in chemical processing of air parcels that contribute to composition of the air mass investigated. The only assumption used in this approach, is that all contributing sources of the studied VOC have the same initial isotope composition.

## 2.4 State of the art instruments: sampling and processing of ambient VOC

Nowadays, there are many methods for observation and monitoring of ambient VOC concentrations. On-line measurements are performed in a real time and are carried out using automatic GC or HPLC systems for separation of individual compounds followed by detection with various sensors (mass spectrometers, flame ionization, electron capture or any spectroscopic detectors); off-line measurements employ similar instrumentation, but have an additional sample collection step [*Apel et al.*, 1998; *Bacsik et al.*, 2004; *Badjagbo et al.*, 2007; *Heland and Schäfer*, 1997; *Jurvelin et al.*, 2001; *Lamanna and Goldstein*, 1999; *Liu et al.*, 2008; *Warneke et al.*, 2003; *Williams and Koppmann*, 2007].

### 2.4.1 Sampling of VOC

There are two fundamentally different experimental approaches that are used for collection of VOC from ambient air: whole air sampling into bags or canisters [*Camel and Caude*, 1995; *Schmidbauer and Oehme*, 1988; *Tolnai et al.*, 2000] or selective sampling onto adsorbents [*Dettmer and Engewald*, 2002; *Tolnai et al.*, 1999; *Vogel*, 2005].

Collection of whole-air samples into special containers is one of the simplest sampling procedures currently available. Due to the inertness of the internal material (usually electropolished stainless steel) there are almost no blank values associated with physical degradation, no sample loss due to absorption by the walls and as a result compound-independent collection of samples and high recovery efficiency [*Camel and Caude*, 1995; *Jayanty*, 1989]. In addition, tightly closed containers allow sample storage over long time periods and replicate analysis of the sample if needed. However, there are several disadvantages of this sampling method. While for simple applications regular portable pumps can be used, a complex sampling apparatus might be occasionally required. Due to the importance of the inner surface, these containers have to be properly cleaned-up to avoid cross-contamination, regularly maintained, accurately transported and stored [*Camel and Caude*, 1995; *Jayanty*, 1989; *Ras et al.*, 2009; *Tolnai et al.*, 2000]. Often air is collected as "grab samples" within 1-2 minutes by simply opening the valve of an evacuated container. In this case the mass of air collected is limited by the size of the container and ambient pressure [*Ras et al.*, 2009; *Schmidbauer and Oehme*, 1988].

Sampling of VOC on adsorbents allows collection of larger volumes over operator-controlled time intervals. During active sampling air is pumped through a cartridge- usually a quartz or stainless steel tube filled with a solid adsorbent while during passive sampling the sampling rate is limited by diffusion into the adsorbent containing tube [*Camel and Caude*, 1995; *Ras et al.*, 2009]. Depending on the VOC and type of adsorbent some VOC are trapped on the surface of the solid adsorbent which typically is a porous polymer. To avoid sampling of water vapor mostly hydrophobic and inert polymers are used [*Fastyn et al.*, 2003; *Harper*, 2000; *Helmig and Vierling*, 1995].

Sampling of VOC on adsorbents is determined by the frontal chromatography principles, where the sample is continuously introduced into a column (in this case the column is the cartridge packed with adsorbent) and the analyte is distributed between the mobile and stationary phases:

$$[VOC]_m \rightleftarrows [VOC]_s \tag{2.13}$$

with the partition coefficient K, capacity ratio k and fraction of a solute in the mobile phase f

$$K = \frac{[VOC]_s}{[VOC]_m} \tag{2.14}$$

$$k = K\frac{V_s}{V_m} \tag{2.15}$$

$$f = \frac{1}{1+k} \tag{2.16}$$

The linear migration rate of a solute (υ) is

$$\nu = u \times f = u \times \frac{1}{1+k} = u \times \frac{1}{1+K\frac{V_s}{V_m}} \tag{2.17}$$

where u is the linear rate of movement of the mobile phase molecules.

The retention time (t) of the analyte in the cartridge with the length L is

$$t = \frac{L}{\nu} = \frac{L}{u \times \frac{1}{1+k\frac{V_s}{V_m}}} \tag{2.18}$$

[*Barry*, 1995; *Cazes and Scott*, 2002]

There are currently a significant number of adsorbents available on the market and the choice of the specific adsorbent is usually based on the adsorption strength and absence of possible artifacts during sampling and storage [*Dettmer and Engewald*, 2002; *Harper*, 2000]. The strength of the adsorbent is usually characterized by the Break Through Volume (BTV) that depends on the VOC concentration and the sampling flow rate, and identifies the point at which an adsorbate appears in the effluent [*Brown and Purnell*, 1979]. Usually the BTV values are experimentally determined [*Dettmer and*

*Engewald*, 2002] and are provided by the manufacturer for each adsorbent, however they can be approximated by rearranging 2.18 as

$$t \times u = L(1 + K\frac{V_s}{V_m}) \tag{2.19}$$

than BTV ($V_b$) is

$$V_b = u \times A \times t = L \times A(1 + K\frac{V_s}{V_m}) = V_m(1 + K\frac{V_s}{V_m}) = V_m + K \times V_s \tag{2.20}$$

where A- is the area [*Barry*, 1995; *Cazes and Scott*, 2002].

$V_b$ is temperature dependent, and the BTV are usually provided for a certain range of temperatures (Table 2.1) [*Katsanos et al.*, 1998].

Compounds are recovered from the cartridge by solvent extraction or thermal desorption techniques. Solvent extraction is usually used for thermally-unstable compounds, does not require use of complicated equipment and results in large volume samples that could be analyzed repeatedly. However, this technique has a potential of sample contamination by the solvent, resulting samples are diluted, and commonly used volume reduction steps, for example solvent evaporation, can lead to the loss of volatile compounds [*Ras et al.*, 2009; *Reimann and Lewis*, 2007]. Thermal desorption is a solvent-free method; compounds are extracted from adsorbent using high temperatures and sometimes high gas flow rates. The thermally desorbed mixture usually is injected directly and completely into a GC, often in combination with sample focusing or preconcentration steps. This minimizes loss during sample processing (i.e. extraction, evaporation and storage stages) and eliminates the risk of solvent-contamination [*Harper*, 2000; *Sunesson et al.*, 1995]. However, recovery by thermal desorption is not always complete and recovery yields of VOC from an adsorbent have to be determined experimentally, for example from the ratio of the signals for recovered VOC over that of the loaded mass of a VOC [*Q Li et al.*, 2004] (Table 2.2).

Table 2.1: The breakthrough volumes ($V_b$, L $g^{-1}$) of some aromatics and alkanes on Carbopack B, Carboxene 569 and Tenax TA at 20-40 °C.

| Compound | Carbopack B | Carboxene 569 | Tenax TA |
|---|---|---|---|
| n-pentane | 13-43 (c) , 4-6.6 (e) | 100-200 | 1.25 (a), 1.1-5.0 (d) |
| n-hexane | 34-430 (c) | 1200-2600 (d) | 7.16 (a), 19.1 (b), 5.6-31.6 (d) |
| benzene | 5.5-12.0 (e) | 33-53 (d) | 1.28 (a), 36.9 (b), 18-40 (d) |
| n-heptane | 52.5-137.5 (e) | 6000-11000 (d) | 20-100 (d) |
| toluene | 32.9-60.8 (e) | 1300-2700 (d) | 84.2 (a) |
| n-octane | 80-302.6 (e) | >10000 (d) | 90-590 (d) |
| ethylbenzene | 65-124.8 (e) | 2500-3000 (d) | 200-1400 (d) |
| m-xylene | 71.2-235.2 (e) | 6200-11000 (d) | 230-1550 (d) |
| p-xylene | 77.6-224.6 (e) | 10000-11000 (d) | 230-1550 (d) |
| o-xylene | 75.3-252.6 (e) | 4000-7500 (d) | 250-1650 (d) |
| n-nonane | 89.5-406.2 (e) | >10000 (d) | 251-2000 (d) |
| n-decane | 96.8-449.7 (e) | >10000 (d) | 500-3900 (d) |

(a) [*Kroupa et al.*, 2004], (b) [*Prado et al.*, 1996], (c) [*Brown*, 1996], (d) [*SIS*, 1996-2010], (e)[*Foley et al.*, 2001]

One of the major advantages of cartridges is the fact that the sampling itself already acts as a preconcentration step, allowing collection of substantial masses even for trace compounds [*Hallama et al.*, 1998; *Sunesson et al.*, 1995; *Vogel*, 2005].

Table 2.2: The recoveries (%) of some aromatics and alkanes from Carbopack B, Carboxene 569 and Tenax TA.

| Compound | Carbopack B | Carboxene 569 | Tenax TA |
|---|---|---|---|
| n-pentane | 96(±2)*-103(±5)(a) | 84(h) | 81.0(±1.2)(g) |
| n-hexane | 98 (±3)-102(±5)(a) | 94(±5.9)(b) | 95.1(±0.8)(g) |
| benzene | 100 (±4)-105(±5) (a),<br>88.2(±2.5)(c) | | 89.6(± 6)(d),<br>99 (±3)(f) |
| n-heptane | 98 (±5)-104(±4)(a) | | 93.2(±1.7)(g) |
| toluene | 100 (±5)-104(±4) (a) | 98(e) | 93.8 (±4.9)(c), 102(e),<br>99 (±4)(f) |
| n-octane | | | 89.9±1.6(g) |
| ethylbenzene | 93 (±2)-92 (±4) (a) | | |
| p-xylene | 92 (±2) (a) | | 102(±3)(f) |
| o-xylene | 99 (±2)-94.3(±3(a) | 83(e) | 100 (±2)(f), 75(e) |
| n-decane | | | 80 (±4)(d) |

* where applicable: Standard Deviations determined from repeat measurements

(a) [*Q L Li et al.*, 2004], (b) [*Dettmer et al.*, 2000], (c) [*Rothweiler et al.*, 1991], (d) [*Volden et al.*, 2005], (e) [*Matney et al.*, 2000], (f)[*Cao and Hewitt*, 1993], (g) [*Baya and Siskos*, 1996], (h) [*Rabaud et al.*, 2002]

Unfortunately, use of cartridges can be complicated by several factors. Adsorbents are to some extent compound specific. Nevertheless, finding an adsorbent that allows sampling of a wide range of VOC, but at the same time does not collect potential interferences such as water or carbon dioxide is challenging. In addition, the adsorbent has to allow efficient desorption of the sampled VOC without thermal decomposition. Finally there often is a substantial background signal associated with packing materials [*Cao and Hewitt*, 1994; *Lee et al.*, 2006; *Palluau et al.*, 2007; *Sunesson et al.*, 1995].

One of the requirements for accurate GC-IRMS measurements is sufficient mass of the injected carbon. Under optimum conditions GC-IRMS detection requires 3 ng to 5 ng of carbon for each VOC depending on the instrumentation and method used [*Goldstein and Shaw*, 2003; R*udolph et al.*, 1997; *Thompson*, 2003]. Consequently compounds present at low pptv levels need to be extracted from 30 or more liters of air. Since canisters sampling of samples of this size is extremely challenging, sampling onto adsorbent is the preferred technique.

### 2.4.2 Sample Processing

Prior to the injection into a chromatographic column, samples from either canisters or cartridges are typically concentrated using one or more so called pre-concentration traps. These traps are either open tubes or tubes packed with a solid adsorbent or glass beads. Often these traps are cooled during the pre-concentration stages. The canister or cartridge is connected to the trap and VOC are transferred to the trap in a gas flow.  In the case of canister samples the gas used for sample transfer typically is the collected air. The flow is induced by a pressure gradient. This gradient can be created by the  internal pressure of the sampling canister, reduced pressure after the trap or, in the case of cartridges, by using a carrier gas [*Kohno and Kuwata*, 1991; *Reimann and Lewis*, 2007]. Once sample transfer is completed the trap is heated and VOC are injected into GC column or undergo a second sample focusing step [*Jayanty*, 1989; *Juillet et al.*, 2005; *Reimann and Lewis*, 2007; *Rudolph et al.*, 1990; *Schmidbauer and Oehme*, 1988]. The use of several focusing steps is often necessary since the flow rate for state of the art high resolution GC columns are only small (mL/min) and not compatible with the flow rates needed for efficient desorption from the first trapping step.

Trapping efficiency depends on the length of the trap, the trapping temperature, the flow rate of a gas and the coating and/or packing (if applicable) of the trap [*X-L Cao and Hewitt*, 1992]. The most commonly used cooling is by liquid nitrogen that can provide temperature ranging from -20 °C to -196 °C [*Czuba*, 1999; *Rudolph et al.*, 1997; *Thompson*, 2003]. While trapping efficiency is sensitive to the flow rate, it has been suggested that for most of the traps (both filled and unfilled) it is high for <100 mL/min flow rates [*Cao and Hewitt*, 1992]. Glass beads are widely used packing material, as they can withstand temperatures from -196 °C to 200 °C, do not result in significant background signal and are easy in maintenance [*Czuba*, 1999; *Rudolph*, 2007; *Rudolph et al.*, 1997; *Thompson*, 2003]. In general, the choice of the trapping temperature, material and the flow rate is based on the individual experimental requirements.

# 3. EXPERIMENTAL

## 3.1 Overview

In this research project on-line GC-IRMS was adapted for compound specific stable carbon isotopic composition analysis of ambient VOC. GC-IRMS combines GC separation with on-line oxidation followed by IRMS detection. On-line GC-IRMS was firstly introduced in 1978 by Matthews and Hayes and has been used in many studies [*Goldstein and Shaw*, 2003; *Meier-Augenstein*, 1999; *Rudolph*, 2007; *Schmidt et al.*, 2004]. However, its application for ambient VOC analysis is still infrequent (explained in Section 1).

In this chapter sampling and analysis techniques to measure concentrations and isotopic composition of ambient VOC are described. This includes a newly developed methods as well as adoption and modification of established methods. The newly developed method consists of four steps: sampling, sample processing (preconcentration and separation), on-line VOC combustion and IRMS measurement.

VOC were collected onto adsorbent packed cartridges from ambient air. In the lab the VOC were desorbed from the cartridges and concentrated cryogenically using a specially developed instruments (Tekmar 5010 and TSPS). The sample recovery was followed by GC separation, combustion of separated VOC in a furnace and IRMS detection. Even though every component is widely used in other well-developed analytical techniques, significant modifications had to be applied to combine the different components into a system suitable for VOC isotopic composition analysis.

Off-line IRMS was used for isotopic composition analysis of samples of pure VOC taken from commercially available bulk material. $CO_2$ samples were prepared for each compound individually. Following combustion in quartz vials $CO_2$ was extracted into glass vials and the $CO_2$ isotope ratio determined by IRMS through a dual inlet analysis. Bulk VOC were used to prepare mixtures of known composition and isotope ratio in helium for testing the accuracy of the GC-IRMS measurements and evaluation of method integrity and performance.

## 3.2 Ambient Air Sampling

VOC were collected by two different methods. Whole air samples were collected into 2 L stainless steels canisters with electropolished internal surfaces. Filling of these canisters was performed by pressurizing with ambient air using portable battery powered pumps. Prior to sampling, canisters were leak tested and evacuated to a pressure below $5 \cdot 10^{-7}$ torr [*Czuba*, 1999; *Rudolph et al.*, 1997; *Thompson*, 2003].

Selective VOC sampling from volumes of 20-100 L of ambient air was done on adsorbent filled cartridges as described in principle in Section 2.4.1. The set-up for cartridge sampling consisted, in addition to the sampling cartridge, of the following components: a stainless steel inlet line, a mass flow controller coupled with a flow totalizer, an optional water trap and a pump (Figure 3.1) [*Brown*, 1996; *Camel and Caude*, 1995; *Dettmer and Engewald*, 2002; *Harper*, 2000; *Schmidbauer and Oehme*, 1988].

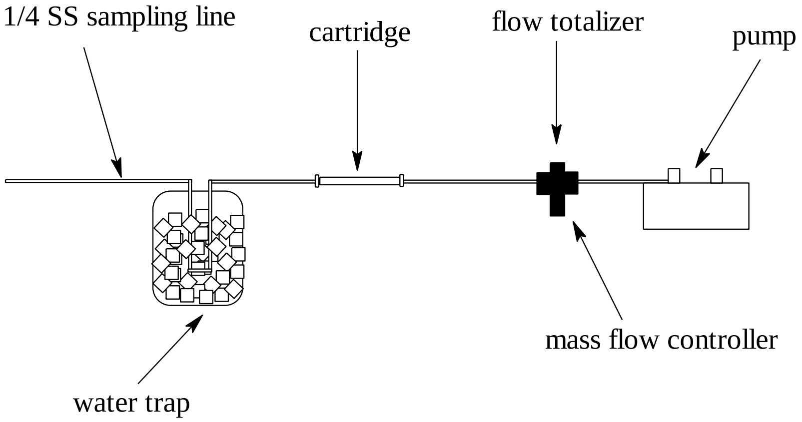


Figure 3.1: Setup for VOC collection from ambient air on cartridges

Ambient air was drawn through the adsorbent filled cartridge at flow rates between 10-50 mL/min for varying time intervals using an electrical pump. The sample flow rate was controlled by a Mass Flow Controller and the total volume was recorded by a flow totalizer.

Water trap, cartridge, mass flow controller and pump were placed inside a metal housing (1 m x 0.5 m x 1.5 m, L x W x H) to prevent physical damage from the environment (snow, rain, wind, intensive solar heating etc). A plastic funnel was attached to the downward pointing end of the sample inlet line to prevent precipitation from entering the sampling system.

For sampling at very humid summer days a water trap was added to the sampling line (Figure 3.1). For testing purposes the trap was cooled by an ice bath and for field sampling the trap was cooled by a Portable Ice Machine (Polar by Greenway, USA). A detailed schematic of the water trap is shown in Figure 3.2. The removable plug at the bottom of the water trap allowed easy, regular removal of collected water from the trap once a week.

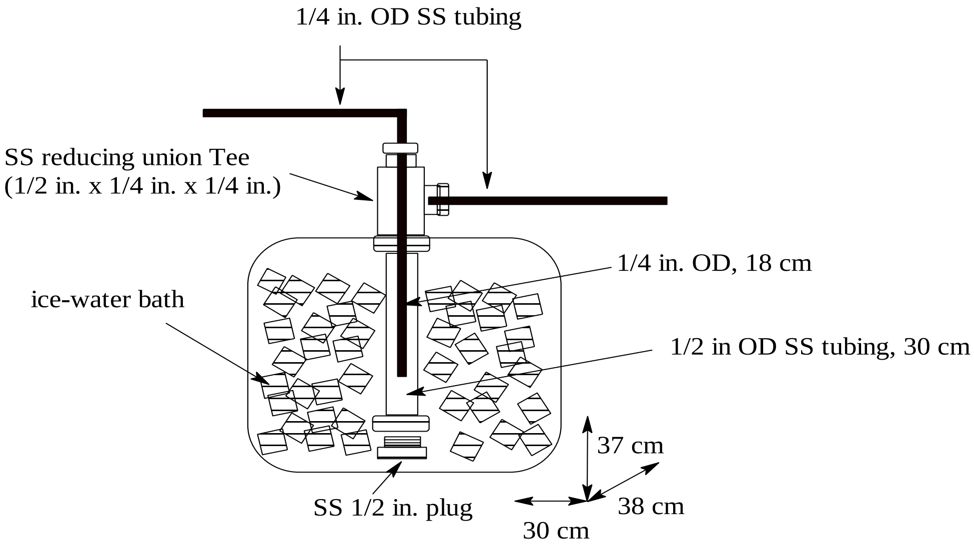


Figure 3.2: The water trap assembly

To change sampling automatically between two different cartridges (for example day and night sampling), a sampling system with timer-controlled solenoid valves was built (Figure 3.3). This system was very similar to the one-cartridge sampling setup described above (Figure 3.1), except its inlet was split into two lines that were connected to two cartridges and two mass flow controllers. The solenoid valves were controlled by an electrical timer which allowed to set the times at which sampling was switched between cartridges. This setting was used to sample over several days, alternating between night-time (7 PM-7 AM) and day-time (7AM-7PM).

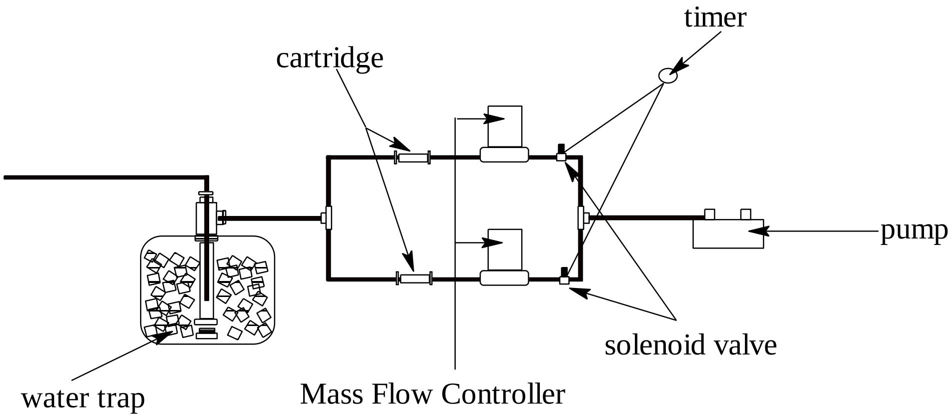


Figure 3.3: Timer controlled system for VOC sampling for automated alternating day-night sampling

## 3.3 Sample Processing and Analysis

Volatile organic compounds were analyzed in the laboratory using a sequence of several instruments coupled to each other. Analysis included several steps: cartridge desorption, preconcentration of desorbed compounds with a specially developed preconcentration system, separation by gas chromatography, and detection with Flame Ionization Detector (FID) for quantification of concentrations or with Isotope Ratio Mass Spectrometer (IRMS) for isotopic composition analysis. This chapter contains detailed description of the instrumentation, analysis methods, and the tests conducted to evaluate performance.

### 3.3.1 Cartridge Desorption

VOC were extracted from cartridges by thermal desorption. The cartridge was connected to a helium supply line and preconcentration system (Tekmar 5010 or TSPS) by 1/16" heated stainless steel tubing and placed in a temperature controlled furnace. During desorption the cartridge was purged with pure BIP grade helium (Linde, Canada). The furnace was equipped with two side covers for better isolation and its temperature was automatically controlled by a temperature controller (Omega, USA) (Figure 3.4)

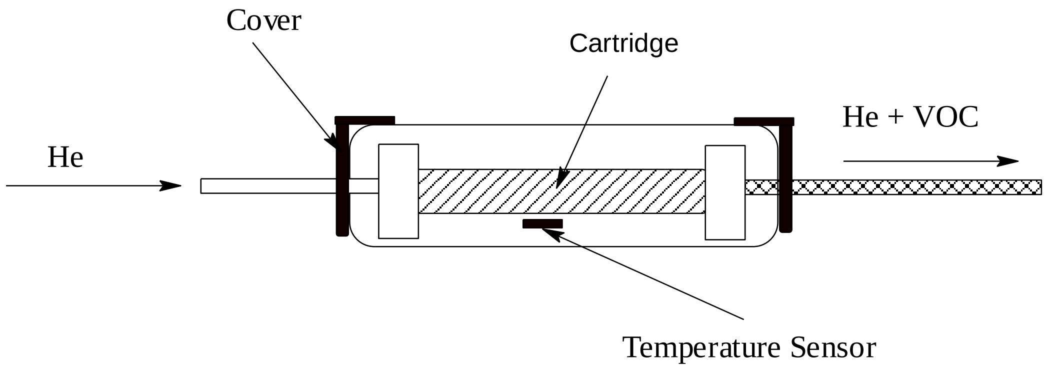


Figure 3.4: The set-up of a desorption furnace

Various experimental parameters (furnace dimensions, temperature, carrier gas flow rate) were tested to optimize VOC desorption from the cartridge. They are listed in Table 3.1

Table 3.1: Range of parameters examined for the optimization of thermal desorption procedure[a]

| Parameter | Specification Variations | Test ID |
|---|---|---|
| Flow rate of carrier gas | from 30 mL/min to 100 mL/min | D-1 |
| Desorption Temperature | from 523 to 623 K | D-2 |
| Desorption Time | from 10 min to 50 min | D-3 |
| Furnace Length | 15 cm and 30 cm | D-4 |

(a) Lists detailing the parameters used for testing can be found in section 4.1.1, Table 4.2, 4.3, 4.4

### 3.3.2 Preconcentration Systems

Following desorption from the cartridge into the carrier gas stream, VOC were cryogenically trapped using a two- stage preconcentration system (introduced in Section 2.4.2). Initially an existing concentration system built by Byron Kieser and optimized by Alex Thompson was used (Thompson, 2003). Later during method testing and development two somewhat different systems were used. The first one was based on a commercially available cryofocusing apparatus (Tekmar 5010). It was used during early stages of method testing and development as well as for analysis of ambient samples collected during the BAQS campaign. Based on experience with the Tekmar 5010 a Two Stage Preconcentration System (TSPS) was designed and built. This optimized custom made system was used in the EC-York study and in most of the method evaluation and validation tests.

#### *3.3.2.1 Tekmar 5010 Preconcentrator*

A schematic diagram of the Tekmar 5010 is shown in Figure 3.5. The unit was refurbished by replacing all original tubing with heated stainless steel tubing, connectors and valves.

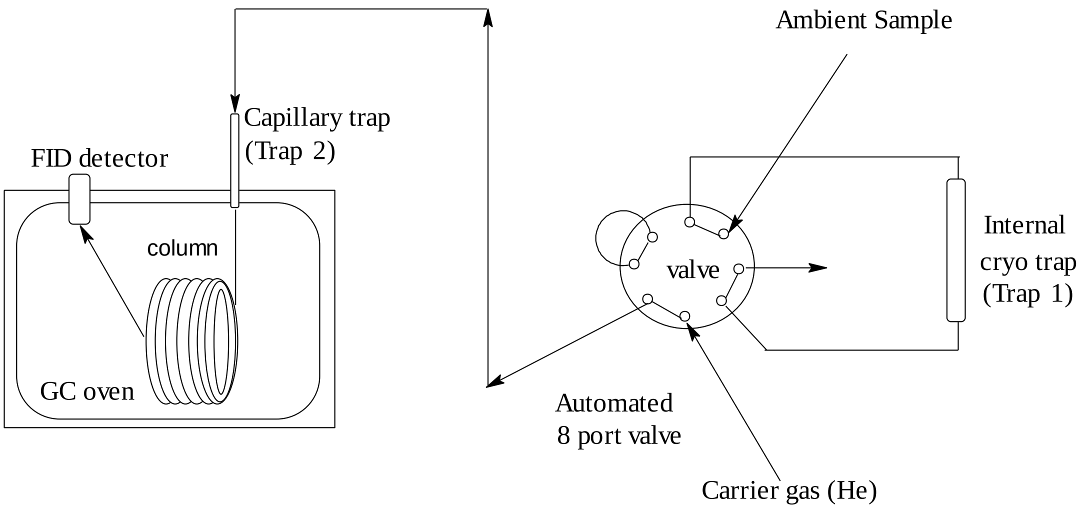


Figure 3.5: Schematic Diagram of Tekmar 5010 Preconcentrator. It should be noted that due to the direct connections between two ports of the 8-port valve this set-up is equivalent to using a 6- port valve.

The unit included two traps; the first trap (Trap 1) was made of 1/16″ (OD) stainless steel tubing packed with 60/80 mesh glass beads (Chromatographic Specialties Inc., Canada). The second capillary trap (Trap 2) used a section of the capillary column (DB1) which was placed inside a 15 cm 1/16" piece of stainless steel tubing. The GC column was passed through the inside of this tubing and directly connected via a valco zero volume connector (VICI, USA) to the 1/32" stainless steel tube attached to an 8 port valve. This two-position 8 port valve (VICI, USA) was used to automatically switch between carrier gas flow through Trap 1 or carrier gas bypassing Trap 1.

All stainless steel transfer lines and valves were kept at 473 K during the procedure. Both traps were cooled automatically using two solenoid valves to 97 K during the loading stage and then rapidly heated to 398 K (trap 1) and 493 K (trap 2) by electrical heaters (Omega, USA) (Figure 3.6). The temperature was determined by a temperature sensor (Quick disconnect thermocouple assembly with 12" and 18" 1/16" 304 stainless steel probes (Omega, USA)).

To improve the cooling efficiency, modifications were made in the setup of the cryotraps. In the Tekmar design both traps were soldered to tubes that were cooled with liquid nitrogen at some point of the procedure (Figure 3.7 a). In the modified design the traps were placed inside the cooling tubes and directly exposed to the cooling media (Figure 3.7 b).

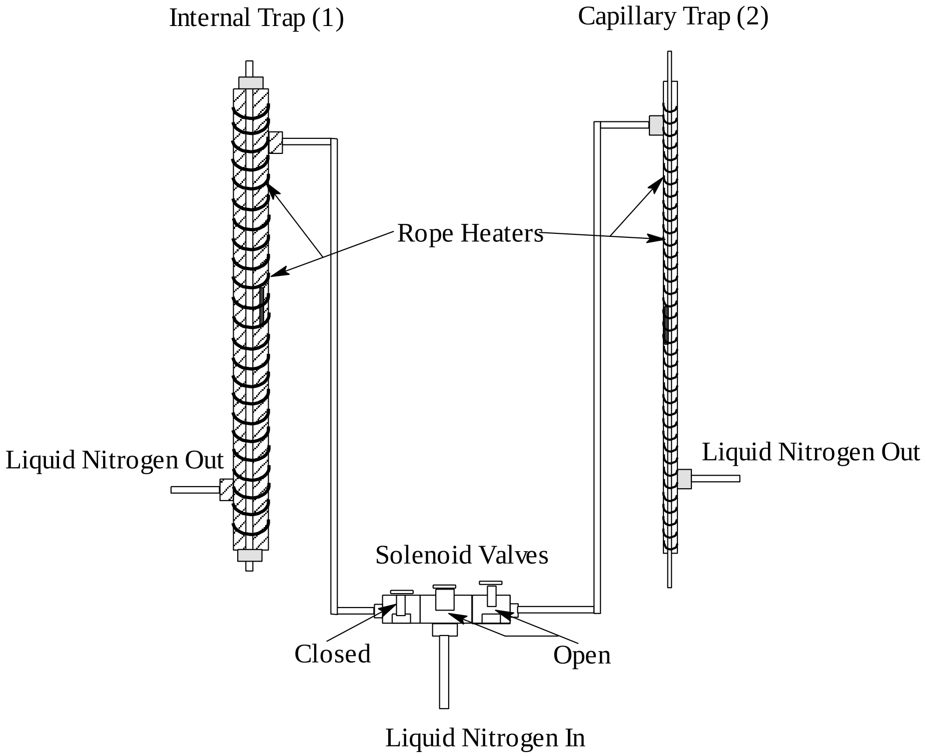


Figure 3.6: Schematics of the trap cooling and heating system of the Tekmar 5010 after modification (Figure 3.7 B)

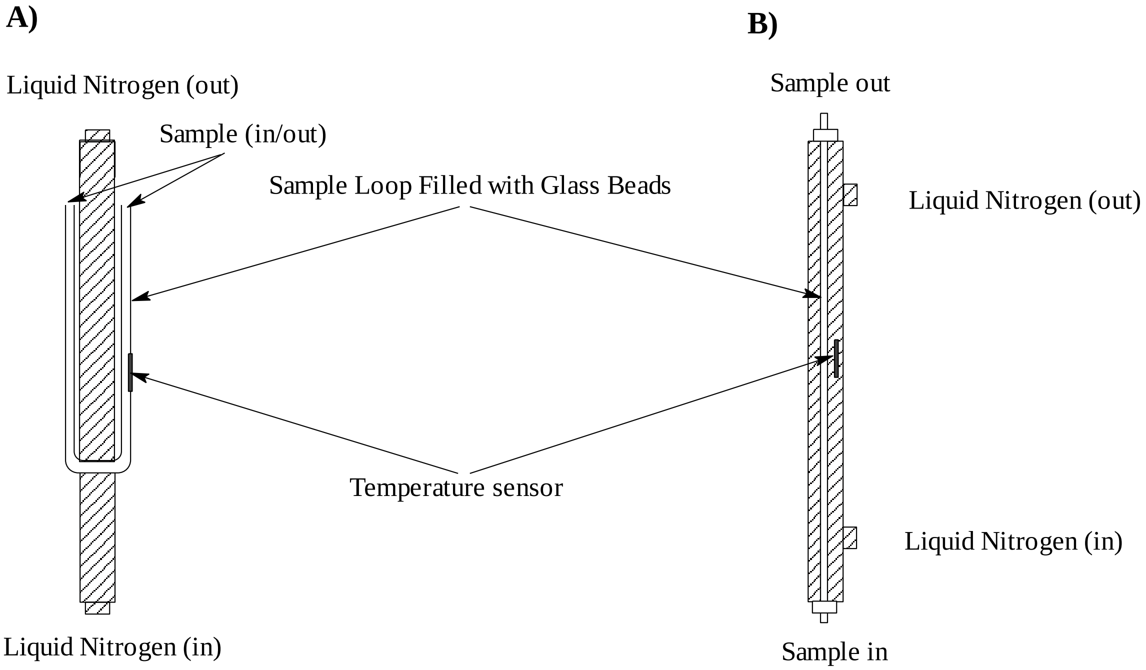


Figure 3.7: Schematics of the hardware adjustment in Trap 1 (A-before, B-after)

#### *3.3.2.2 Two stage preconcentration system (TSPS)*

Similarly to the Tekmar, the TSPS had two preconcentration stages. One was a 1/8″ OD stainless steel trap filled with glass beads (Trap 1), the other consisted of 15 cm of 1/32″ GC capillary column placed in a 1/16″ OD stainless steel tube (Trap 2) (Figure 3.8).

The major technical change of this new instrument was a re-design of the sample loops. The first trap was made in a U-shape form and was placed outside on the side of the instrument. This set up allowed the sample loop to be cooled down by simply immersing it in a dewar with liquid nitrogen when needed. Another improvement was flash heating for the second trap by passing a 10 A current by applying a voltage of 2-3 Volts through the stainless steel capillary (Figure 3.8).

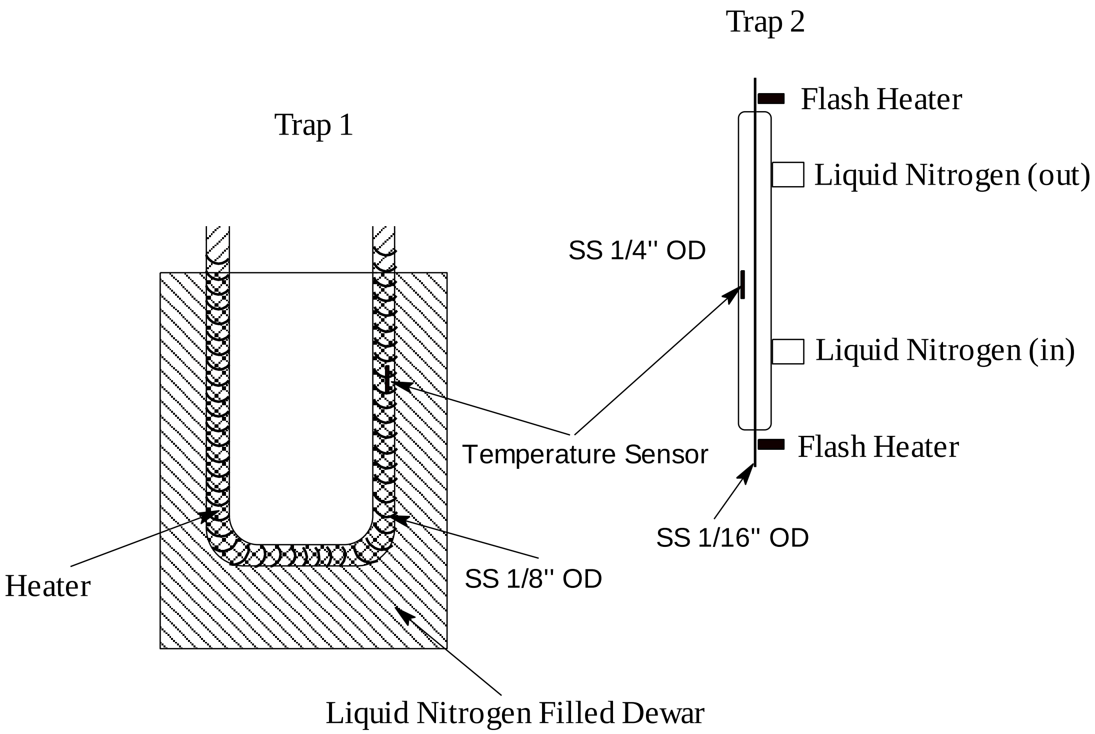


Figure 3.8: TSPS cryogenic traps

#### *3.3.2.3 Sample processing*

Both Tekmar 5010 and TSPS contained two-position automated valves that allowed control and directing of the gas flow in the system. The Tekmar 5010 had an 8 port valve that was modified to act as a 6 port valve and the TSPS included a 6 port valve (Figure 3.9). In position A the gas flow from the cartridge desorption unit was introduced through port 1 into the sample loop (Trap 1) connected to ports 3 and 6, while the carrier gas flowed into the GC column through ports 4 and 5. Upon switching into Position B the carrier gas was directed through Trap 1 (ports 4, 3, and 6) resulting in sample injection into the GC column through port 6 (Figure 3.9).

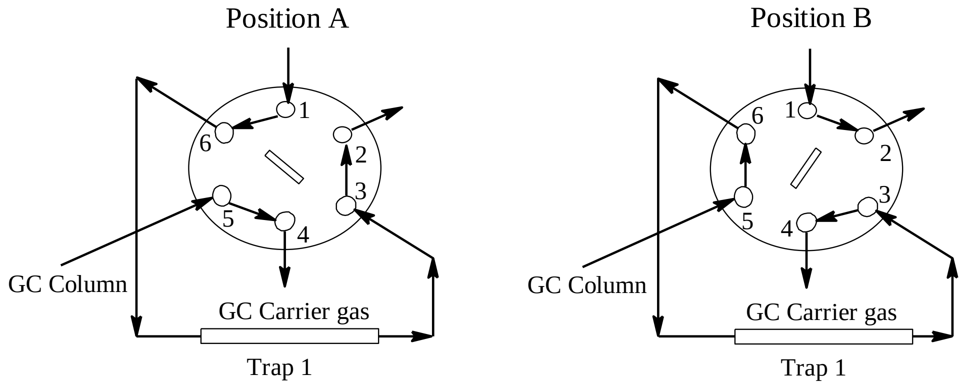


Figure 3.9: Configuration of the two way six port valve.

By default the 6 port valve was set into Position B prior to starting the analysis. The sample cartridge was placed in the furnace (Figure 3.4) and connected at both ends to the transfer lines. The cartridge was then purged with pure helium for 5 min, at the same time Trap 1 was cooled to 97 K by liquid nitrogen. For the desorption step, the valve was set into Position A and the cartridge was rapidly heated to a set temperature. This resulted in desorption of VOC from the cartridge and trapping them in Trap 1. At the end of this stage, Trap 2 was cooled to 97 K. Once the desorption step was completed, the furnace heating and desorption carrier gas flow were turned off, and the valve was manually rotated into Position B, directing GC carrier gas through the rapidly heated Trap 1 to Trap 2 resulting in transfer of the VOC from Trap 1 to Trap 2. Finally, Trap 2 was rapidly heated and VOC were injected into the GC column (Figure 3.10).

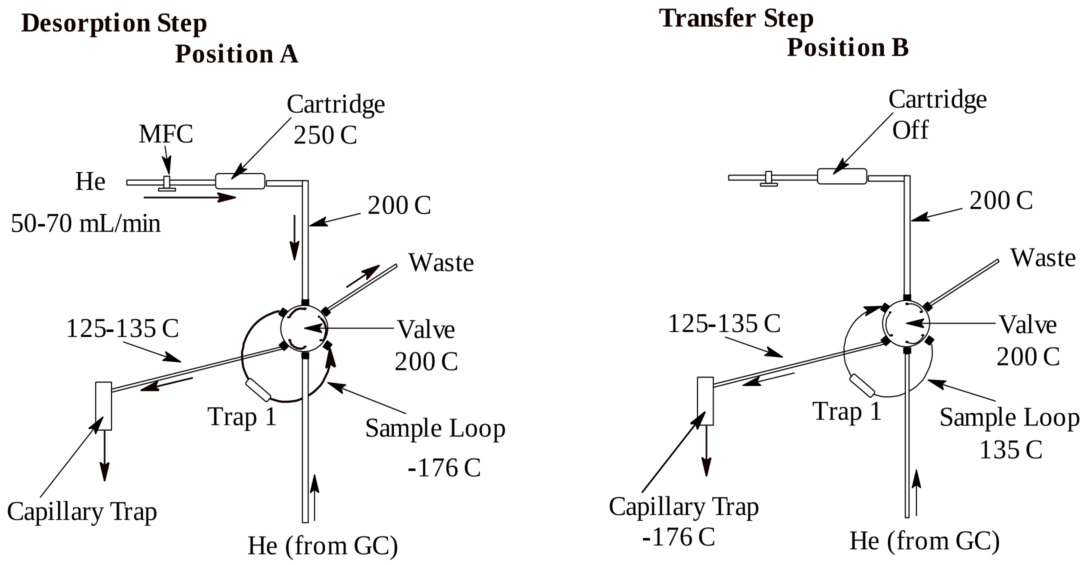


Figure 3.10: Schematic Representation of Desorption (Position A) and Transfer (Position B) steps

To allow tests using artificial mixtures a 6 port valve was placed in the transfer line, replacing the sampling cartridge (Figure 3.11). A 10 mL sample loop was connected to this 6 port valve to allow accurate and reproducible injection of test mixtures from a stainless steel canister.

Various operational parameters (cryo-focusing and heating temperatures, flow rates, transfer and injection times) of both preconcentration systems were tested to optimize performance of sample processing and are listed in Table 3.2.

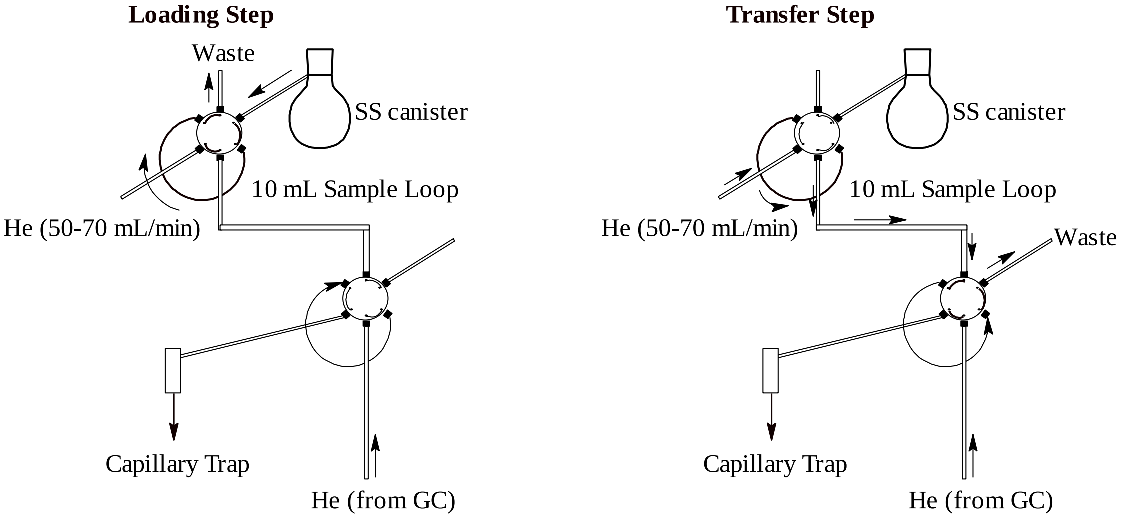


Figure 3.11: Schematics of the set up for introducing gaseous samples from SS canisters into the preconcentrating system

Table 3.2: Experimental parameters[a] tested during optimization of the preconcentration systems

| System | Parameter | Specification Variations | Index |
|---|---|---|---|
| Tekmar 5010 | Trapping Temperatures (Trap 1, 2) | 123 K, 116 K, 93 K | T-Trap |
| | Transfer Temperature (Trap 1)<br>Transfer Time | from 393 K to 513 K<br>from 5 to 35 min | T-T-Tmp<br>T-T-Tme |
| | Injection Temperate<br>Injection Time | 393 K, 483 K, 513 K<br>1 to 15 min | T-I-Tmp<br>T-I-Tme |
| TSPS | Transfer Time | from 5 to 20 min | TSPS-T-Tme |
| | Injection Time | from 20 sec to 10 min | TSPS-I-Tme |

(a) More details about the experimental parameters can be found in section 4.2.1, Table 4.10

### 3.3.3 Chromatographic Separation

VOC separation was done using a gas chromatograph (HP5890 Series II) equipped with a capillary column. For separation various temperature programs were created (Table 3.3). At the end of each analysis of an ambient sample the oven temperature was manually set to 473 K and maintained there for 10-20 min. Helium was used as a carrier gas for all samples, its flow rate of 1.8-2.2 mL/min was kept constant by an electronic pressure controller (EPC).

Table 3.3: Summary of GC column parameters and separation conditions

| GC Column | Specifications | Test ID | Oven Temperature Program | VOC analyzed |
|---|---|---|---|---|
| HP1 | 60 m, 0.32 mm ID, 0.5 µm film thickness | HP1-A | A. 308 K, ramp 4 K/min to 473 K | Alkanes: $C_5$, $C_6$, $C_7$, $C_8$, $C_9$, $C_{10}$.<br>Aromatics: benzene, toluene, m-, o-, p-xylenes, ethylbenzene |
| | | HP1-B | B. 308 K, ramp 2 K/min to 323 K, ramp 3 K/min to 363 K, ramp 5 K/min to 423 K, hold 15 min. | |
| | | HP1-C | C. 313 K for 10 min, ramp 2 K/min to 333 K, ramp 3 K/min to 373 K, ramp 2 K/min to 423 K, hold 5 min. | |
| | | HP1-D | D. 313 K for 5 min, ramp 2 K/min to 333 K, ramp 3 K/min to 373 K, ramp 1.5 K/min to 423 K, hold 3 min. | |

Table 3.3 (cont'd): Summary of GC column parameters and separation conditions

| GC Column | Specifications | Test ID | Oven Temperature Program | VOC analyzed |
|---|---|---|---|---|
| DB1 | 60 m, 0.25 mm ID, 0.5 µm film thickness | DB1-60-A | A. 308 K for 5 min, ramp 2 K/min to 423, hold 2 min. | Alkanes: $C_5$, $C_6$, $C_7$, $C_8$, $C_9$, $C_{10}$. |
|  |  | DB1-60-B | B. 298 K for 15 min, ramp 3 K/min to 373 K, hold 2 min, ramp 15 K/min to 423 K, hold 1 min. | Aromatics: benzene, toluene, m-, o-, p-xylenes, ethylbenzene |
| DB1 | 100 m, 0.25 mm ID, 0.5 µm film thickness | DB1-100-A | A. 243 K for 1 min, ramp 4 K/min to 493 K | Alkanes: $C_5$, $C_6$, $C_7$, $C_9$, $C_{10}$. |
|  |  | DB1-100-B | B. 298 K for 10 min, ramp 2 K/min to 323 K, ramp 5 K/min to 363 K, ramp 15 K/min to 423 K, hold 8 min. | Aromatics: benzene, toluene, m-, p-xylenes |
|  |  | DB1-100-C | C. 298 K for 10 min, ramp 2 K/min to 323 K, ramp 3 K/min to 363 K, ramp 10 K/min to 403 K, hold 10 min. |  |
|  |  | DB1-100-D | D. 303 K for 10 min, ramp 2 K/min to 323 K, ramp 3 K/min to 363 K, ramp 10 K/min to 403 K, hold 10 min. |  |

### 3.3.4 Detection

VOC were quantitatively and qualitatively analyzed using flame ionization detection (FID) and Isotope Ratio Mass Spectrometry (IRMS). The FID was used during method development and all validation tests were initially performed with the FID. Compounds were identified by comparison of retention times with those of standards. Signals were recorded and later analyzed using Hewlett Packard ChemStation Software.

IRMS was used to determine the isotopic composition of individual VOC from various ambient samples and of some carbon dioxide samples prepared in the lab. On-line analysis was performed with an Isoprime IRMS (Isomass Scientific Inc., Canada) coupled to a GC via a combustions interface. Off-line measurements were made using a dual inlet system connected to the Isoprime IRMS. These instruments were made available by Lin Huang's research group at Environment Canada.

## 3.4 Isotope Ratio Mass Spectrometry

Isotope composition analysis of VOC was performed by a direct injection of $CO_2$ samples (known as the Dual Inlet Method, or off-line method) or employing a GC-IRMS system (known as Continuous Flow Method, or on-line method).

In IRMS for analysis of stable carbon isotope ratios three ion currents for $CO_2^+$ (m/z 44, 45, and 46) are simultaneously recorded (Table 3.4). Each ion current is a combination of all isotopic contributions at the specific m/z.

Table 3.4: Isotopologues of $CO_2^+$ detected by the IRMS

| m/z $CO_2^+$ | Isotopologues |
|---|---|
| 44 | $^{12}C^{16}O_2$ |
| 45 | $^{12}C^{17}O^{16}O$, $^{12}C^{16}O^{17}O$, $^{13}C^{16}O_2$ |
| 46 | $^{12}C^{17}O^{17}O$, $^{13}C^{16}O^{17}O$, $^{13}C^{17}O^{16}$, $^{12}C^{16}O^{18}O$, $^{12}C^{18}O^{16}O$ |

The isotope ratios $^{45}R$ and $^{46}R$ are determined from the ratios of the integrated peak areas for the individual masses [*Rudolph*, 2007]: $^{45}R = \frac{^{45}CO_2}{^{44}CO_2}$ and $^{46}R = \frac{^{46}CO_2}{^{44}CO_2}$.

Since isotopes of oxygen contribute to m/z 45 ($^{12}C^{17}O^{16}O$ and $^{12}C^{16}O^{17}O$) (Table 3.4), m/z 46 is used for correction of m/z 45 signal [*Craig*, 1957; *Santrock et al.*, 1985].

### 3.4.1 Measurements of Isotope Ratios by Dual Inlet Method

In early stages of method development, the isotopic composition of VOC was measured by the Dual Inlet Method. In this method, pure samples of specific VOC are combusted at high temperatures in vacuum sealed tubes containing CuO. Resulting $CO_2$ is cryogenically separated, extracted and later introduced directly to IRMS. The dual inlet system itself includes two gas reservoirs (known as bellows) - one for the reference $CO_2$ and one for compound-derived $CO_2$ [*McKinney et al.*, 1950] (Figure 3.12).

In dual inlet IRMS the isotope ratio is determined by alternating analysis of sample and reference bellows introducing each into the IRMS for 20 s. Each $CO_2$ sample was analyzed six times and their average was used to determine off-line $\delta^{13}C$ for every individual compound [*Czuba*, 1999; *Thompson*, 2003].

While this method exhibits a high precision (0.01-0.03‰), it is a quite time consuming and elaborate technique that requires large samples (from sub-nanomoles to micromoles of compound). Consequently nowadays it is used mostly for analysis of ambient $CO_2$ as well as for calibration and method validation purposes [*Barrie et al.*, 1984; *Goldstein and Shaw*, 2003].

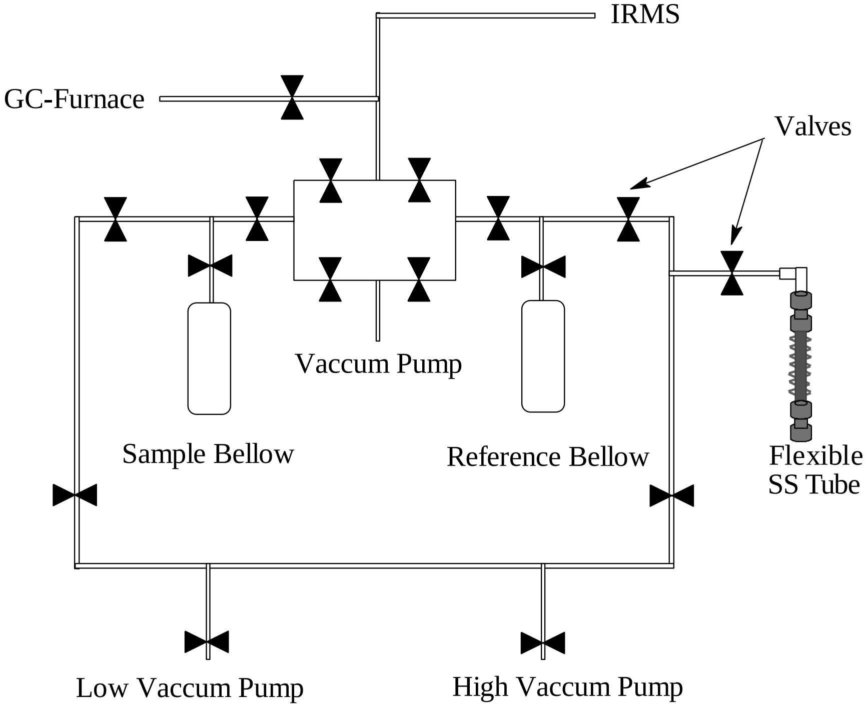


Figure 3.12: Simplified diagram of dual inlet IRMS (Courtesy of Huang, L.)

### 3.4.2 Measurements of Isotope Ratios by GC-IRMS

Use of gas chromatography combined with isotope mass spectrometer (GC-IRMS) to measure isotope ratios of VOC was initially introduced by Mattews and Hayes [1978]. They suggested incorporation of sample purification, separation and transformation steps into on-line measuring techniques. The main disadvantage of the original Mattews and Hayes technique, the use of a single collector mass spectrometer [1978], was resolved by exchanging it with a multicollector mass spectrometer [*Barrie et al.*, 1984]. This technique was extensively assessed, further developed and applied in various chemical and environmental studies [*Brand*, 1996a; b; *Fisseha et al.*, 2009b; *Giebel et al.*, 2010; *Griebler et al.*, 2003; *Iannone et al.*, 2007; *Q Li et al.*, 2010b; *Meier-Augenstein*, 1999; *Ricci et al.*, 1994; *Rudolph et al.*, 2002; *Rudolph et al.*, 1997].

VOC analysis by GC-IRMS included several steps: compound separation by gas chromatography, combustion into $CO_2$ and $H_2O$, water removal, and $CO_2$ analysis by IRMS. Each step included components that were designed based on well-known measurement techniques.

The GC-column was connected to the IRMS with a continuous flow interface (Figure 3.13).

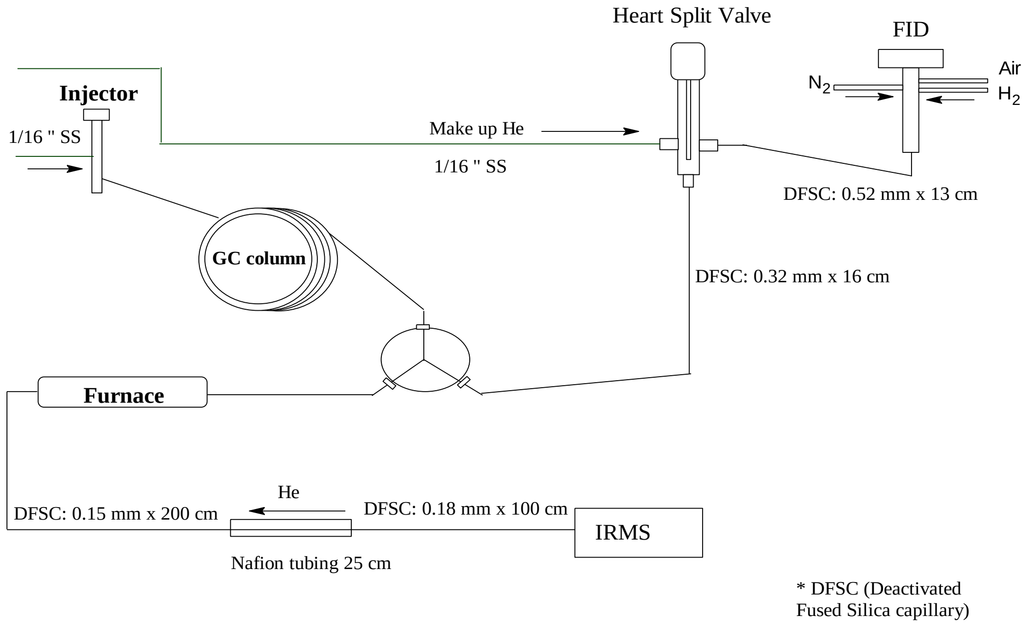


Figure 3.13: Schematic diagram of GC-C-IRMS setup

Once separated in the GC, VOC were directed either to the FID or the combustion interface (furnace) by opening or closing a pneumatic valve (heart-split valve). The interface was assembled from a ¼″ ceramic tube (0.5 mm I.D. x 44 cm) with copper, nickel and platinum wires braded inside (Irei, 2008).

High temperature inside (950 °C), and CuO and NiO formed on the wire surfaces allowed to create an oxidizing environment where VOC were quantitatively converted into $CO_2$ and $H_2O$ (Figure 3.14). Addition of He containing traces of oxygen as make up gas at the inlet of the furnace prevented peak tailing and ensured suitable levels of oxygen inside the furnace during the whole procedure. Every night the oxide layers on the Cu and Ni wires were regenerated by reducing the interface temperature to 550 °C and flushing the furnace and adjacent tubing with the mixture of helium and oxygen. A flow restrictor-split was used to split some of the outcoming flow, so that only a small quantity (10-20%) of formed $CO_2$ was introduced into IRMS and the rest was vented to maintain a constant flow of He to the IRMS that is consistent with optimum conditions for the operation of the IRMS (Figure 3.14).

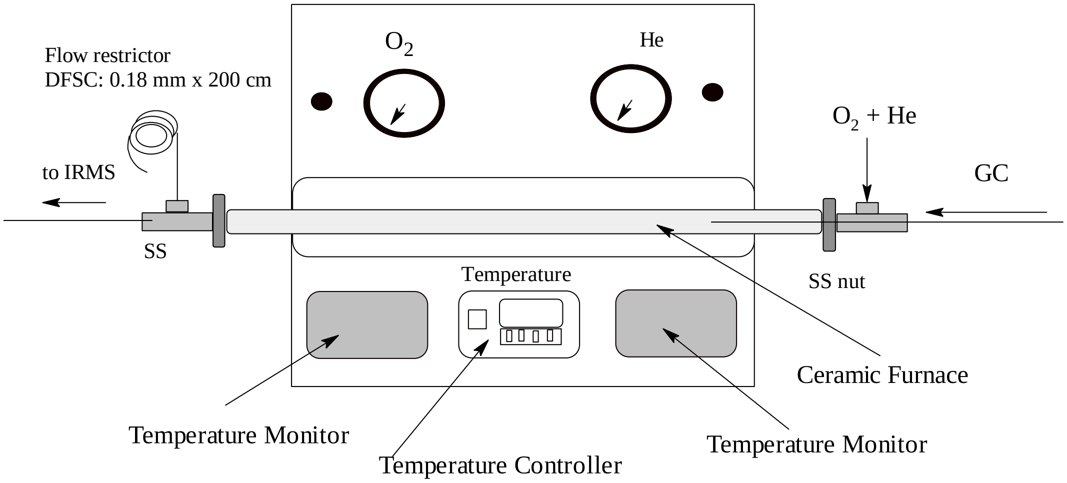


Figure 3.14: Schematic Diagram of the Combustion Furnace.

The He flow from the combustion furnace was passed through a 25 cm, 0.6 mm (ID), 0.8 mm (OD) Nafion Dryer where water was removed. Finally the mixture of carrier gas and $CO_2$ was introduced into IRMS.

## 3.5 Preparation of calibration and test mixtures

Gaseous test mixtures in helium were prepared for twelve hydrocarbons: pentane, hexane, heptane, octane, nonane, decane, benzene, toluene, ethylbenzene, m-xylene, o-xylene, and p-xylene. All chemicals used were >99.5 % purity and were obtained from Aldrich (Canada). These mixtures were prepared from the same batches that were analyzed by off-line combustion and subsequent dual-inlet IRMS for their $\delta^{13}C$ value.

### 3.5.1 Oxidation of individual VOC to $CO_2$

VOC were converted into carbon dioxide and water using CuO at 950 °C for 24 hours according to the following reaction:

$$iHC + jCuO \rightarrow kCu_2O + lO_2 + mH_2O + nCO_2$$

where i, j, k, l, m, n are the corresponding coefficients.

Quartz vials were made from 9.53 mm (OD) tubing (Pegasus Industrial Specialties Inc., Canada). The quartz tubing was cut into 26-28 cm pieces and each piece was sealed at one end. Tubes were then cleaned with water, distilled water and acetone. Copper (II) oxide particles were prepared by grinding commercially available small rods (Sigma-Aldrich, Canada) of copper (II) oxide. Very small particles were removed by sieving with a 420 micron sieve (40-mesh). The CuO was rinsed with acetone and baked at 180 °C under vacuum.

About 4 g of CuO was placed into each quartz tube which then was plugged with a leak-proof rubber stopper. The vial was then attached to the extraction line with the needle of a gas-tight 5 mL syringe (Hamilton, USA) piercing the rubber stopper. The system was evacuated ($P<4.0x\ 10^{-4}$ torr), and the quartz tube was cooled with liquid nitrogen to 93 K. 2-5 μL of the individual hydrocarbon was injected through the stopper using a 10 μL gas tight syringe (Hamilton, USA) (Figure 3.15). After 2 minutes the vial was thermally sealed. Oxidation was done by baking the vial at 950 °C for 24 hours in a muffle furnace.

Carbon dioxide was then extracted from the sample using the extraction line shown in Figure 3.15. The quartz vial was placed in a flexible stainless steel tube connected to the extraction system. The quartz vial was broken by bending the stainless steel tube. Water and other gaseous impurities were removed by stepwise trapping the mixture using a bath of ethanol and dry ice while stepwise condensing $CO_2$ in traps 1 and 2 which were immersed in liquid nitrogen. Finally the extracted $CO_2$ was collected in 15 cm 3.2 mm (ID) Pyrex vials (Pegasus Industrial Specialties Inc., Canada), which were subsequently thermally sealed. The samples were later analyzed by dual inlet IRMS.

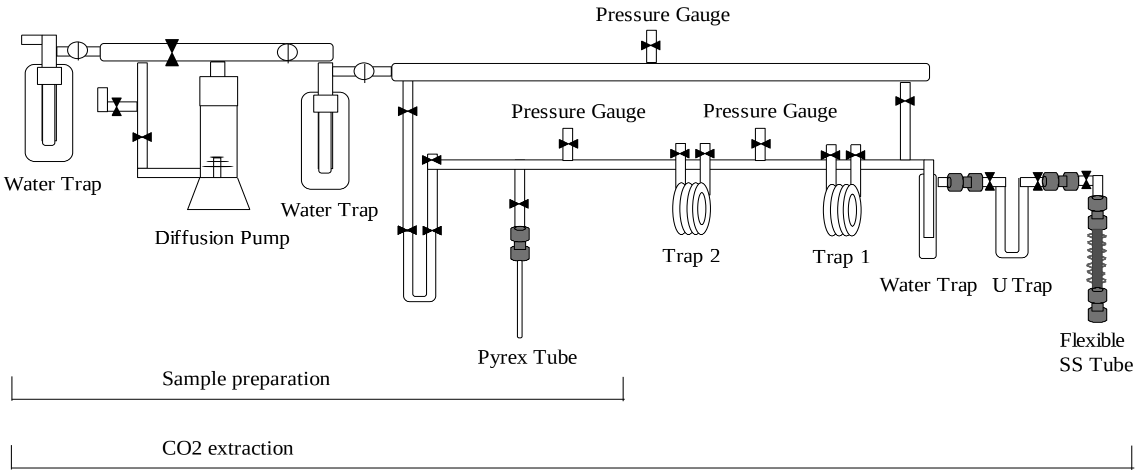


Figure 3.15: Schematic Diagram of the Extraction Line Components Used for preparation and extraction $CO_2$ samples (Courtesy of Huang, L.).

### 3.5.2 Calibration standards and test mixtures

Mixtures of hydrocarbons in helium with mixing ratios in the ppm range were prepared in stainless steel canisters. The first set of mixtures was made in two steps. Firstly, a high concentration gas mixture was prepared in a stainless steel canister with 2 valves. One valve was connected to the helium gas line and the other to a pressure gauge. 10 µL of each compound were injected into a helium flow and the canister was then pressurized with helium to 30-36 PSI. In the second step using a similar procedure, a set of ppm level standards was prepared in 2 valve stainless steel canisters by injecting 5, 20, 40, 80, 120, or 160 mL of the previously prepared mixture using a six port valve (Vici, Canada) into the helium flow that was used to pressurize the canisters.

Another set of mixtures was prepared by injections of 0.2, 0.4, 0.6, 0.8 and 1 μL of a liquid NMHC mixture into a helium flow that was directed into a stainless steel canister. The solution was prepared from 12 hydrocarbons by mixing equal volumes of each of the twelve NMHC. The 2 L canisters were pressurized with helium to 20-30 psi.

## 3.6 Cartridges

### 3.6.1 Preparation and cleaning

Cartridges were made by packing 13-15 cm 1/4″ OD silcosteel or stainless steel tubes with solid sorbents. Tubes were cleaned with methanol and baked overnight in an oven at 523 K.

The cartridges were filled with 0.8-1.2 g of solid adsorbents: Tenax TA, Carbopack B, or Carboxene 569 (Supelco Inc., Bellefonte, USA). Both ends were plugged with 0.3 g of silanized glass wool (Supelco Inc., USA) or quartz wool (Restek, USA). All cartridges were equipped with ½ " SS Swagelok nuts at both ends. During storage and transport all cartridges were closed with ½ " SS caps (Figure 3.16).

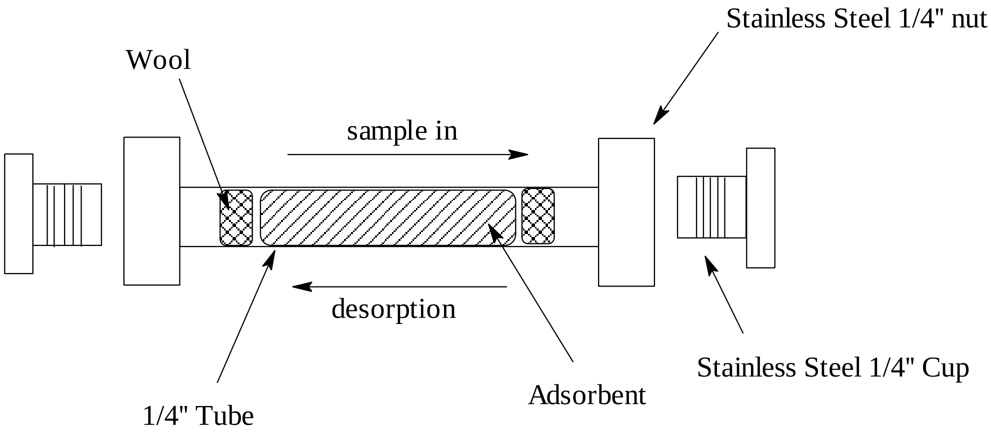


Figure 3.16 Schematic Diagram of the Cartridge

Tubes filled with adsorbent were cleaned by heating to 523-573 K in a furnace while continuously purging them with a flow of 160-200 mL/min pure helium (Air Liquid, Canada; Linde, Canada). A stainless steel manifold with several Swagelok connectors allowed simultaneous cleaning of up to five tubes at a time (Figure 3.17). Clean cartridges were capped and stored at room temperature in closed glass containers.

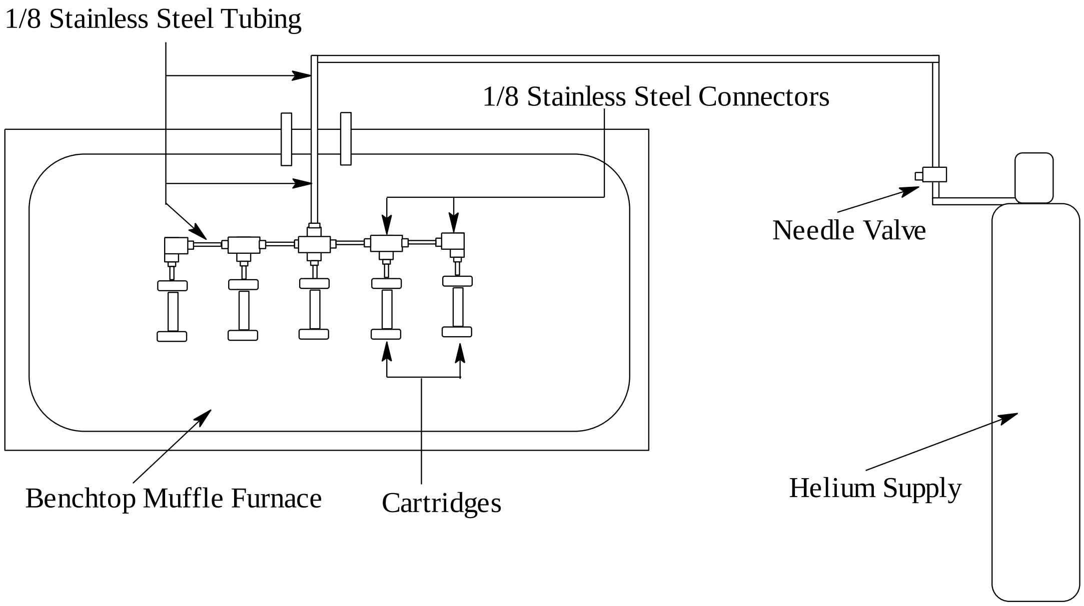


Figure 3.17: Schematics of the setup for cartridge cleaning

### 3.6.2 Loading with standards

For testing purposes cartridges were loaded with 10 mL of gaseous test mixtures containing between 1 and 60 ng of hydrocarbons. The experimental set up is outlined in Figure 3.18.

The six port valve (Vici, USA) was connected to a helium supply line as well as the canister containing the test mixture at elevated pressure. Firstly, the 10 mL sample loop was flushed with the gas mixture for about 1 min at a 15-20 mL/min flow rate (Figure 3.18, Position A). Afterwards the 6 port valve was rotated (Figure 3.18, Position B) redirecting the helium flow of 60-80 mL/min through the sampling loop so that the hydrocarbons were transferred to the adsorbent filled cartridge. The helium flow was maintained for a few hours so that the total volume of gas that passed through the cartridge was around 15-25 L. The cartridges were then capped and stored in a closed glass jars at room temperature (18-20 °C) or in a freezer (-40 °C).

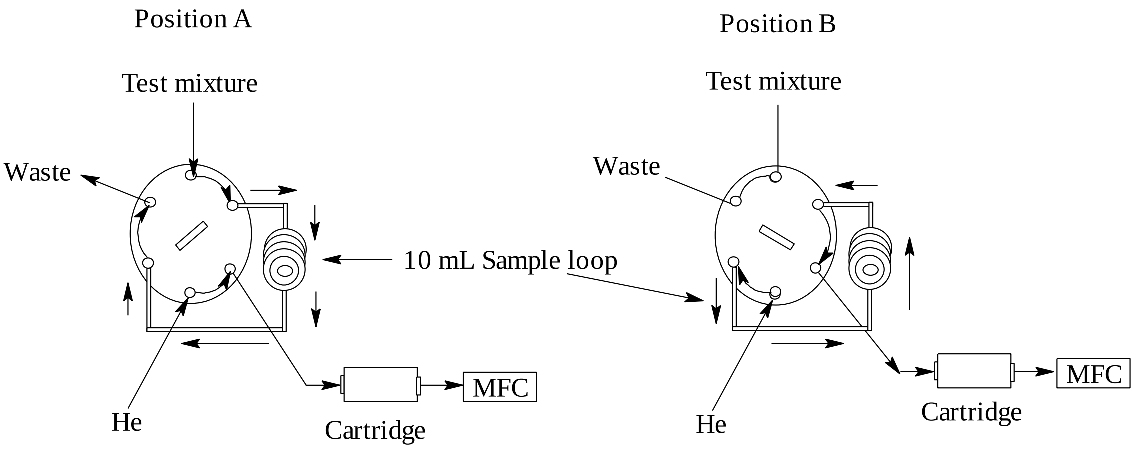


Figure 3.18: Schematic representation of cartridge-loading procedure (Position A- Filling of the sample loop; Position B- Loading of the cartridge).

## 3.7 Ambient Measurements

Ambient measurements were conducted during two field campaigns in 2007 (BAQS-Met), and in 2009-2010 (EC-York). Furthermore, samples of exhaust from diesel and biodiesel fueled vehicles were analyzed.

### 3.7.1 Border Air Quality and Meteorology study (2007)

The BAQS-Met field study included two measurement sites (Ridgetown and Harrow) in Southwestern Ontario (Figure 3.19). Ridgetown (42°26´N, 81°53´W, elevation 212 m) is a small city with a total population of about 3400 people. It is located remote from industrial centers (London and Windsor, ON), about six km south of the McDonald-Cartier Freeway, and seven km north of the northwest shore of Lake Erie. The sampling site at the Guelph University Ridgetown campus was surrounded mainly by agricultural fields and local roads. There were no identified major point sources of important trace gases such as industrial complexes, or neighboring cities with high population.

Harrow (42°02´N, 82°55´W, elevation 191 m), a town of around 3000 inhabitants was chosen for its closeness (approximately 40 km) to Windsor and Detroit (total population close to a million). The sampling site was located in an open field surrounded by farm land and local roads.

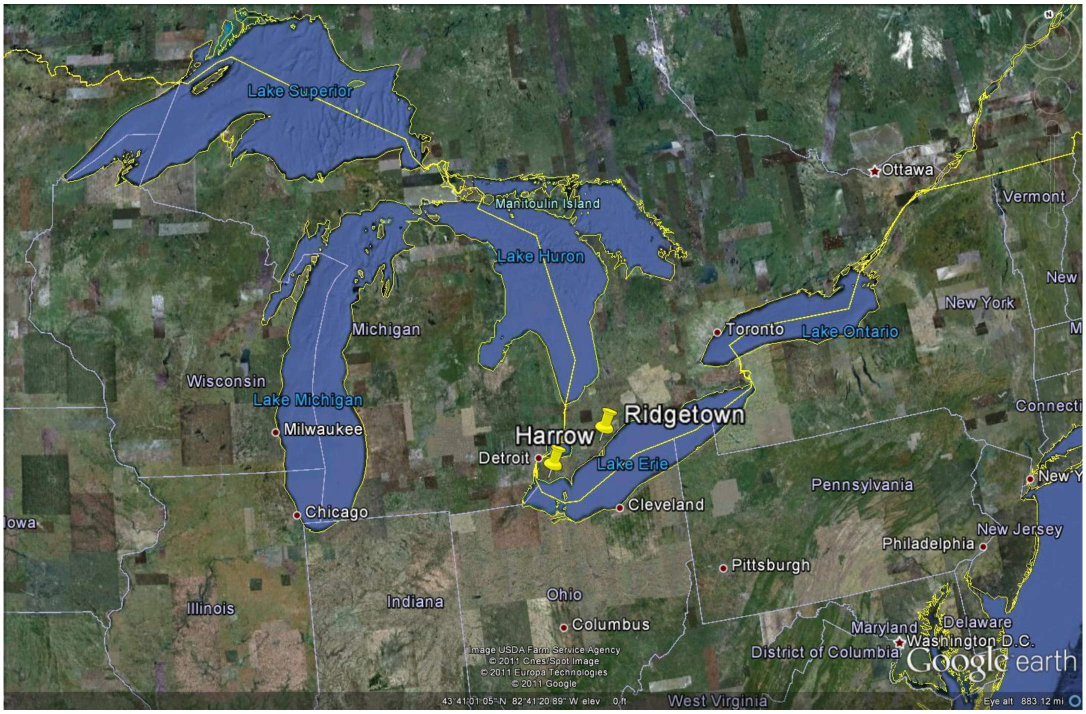


Figure 3.19: Map of the locations of Harrow and Ridgetown sampling sites (Google maps)

VOC samples were collected using whole air sampling and selective sampling onto adsorbent cartridges as described above (Section 3.2). Four to five samples were collected into canisters every day at the two sites. Usually samples were taken in the morning, noon, afternoon and evening. It took only around 1 min to pressurize one of the 3 L SUMMA® evacuated electropolished stainless steel canister, thus each sample should be considered to represent a single point in time and space. Cartridges were used for 24-

hours collection of VOC from 30-40 L of ambient air at a flow rate of 22-28 mL/min. In total 121 canister samples (34 at Harrow and 87 at Ridgetown), and 37 cartridges (17 at Harrow and 20 at Ridgetown) were collected and analyzed (Table 3.6).

### 3.7.2 Environment Canada-York University campaign (2009-2010)

The EC-YU field study was conducted at two sites: Egbert and Toronto (Figure 3.20). The Egbert sampling site (44°12´N, 79°48´W, elevation 251 m) was located on the premises of Centre for Atmospheric Research Experiments (CARE) of Environment Canada. The center is mainly surrounded by agricultural fields and some forested regions with no major anthropogenic sources nearby (~ 100 km). Cartridge samples were collected daily from October 19, 2009 to January 25, 2010. There was no sample collection from December 17, 2009 to January 18, 2010.

Urban samples were collected at the north of the Greater Toronto Area (GTA) (43°46´N, 79°28´W, elevation 185 m) on the Downsview campus of Environment Canada. The Greater Toronto region is one of the largest metropolitan areas of Canada with a population exceeding 6 million. The sampling line inlet was placed on the roof of a two floor building, 20 feet above street level. Sampling at Toronto was conducted from October 13, 2009 to December 18, 2009, and than resumed from January 18, 2010 to January 25, 2010.

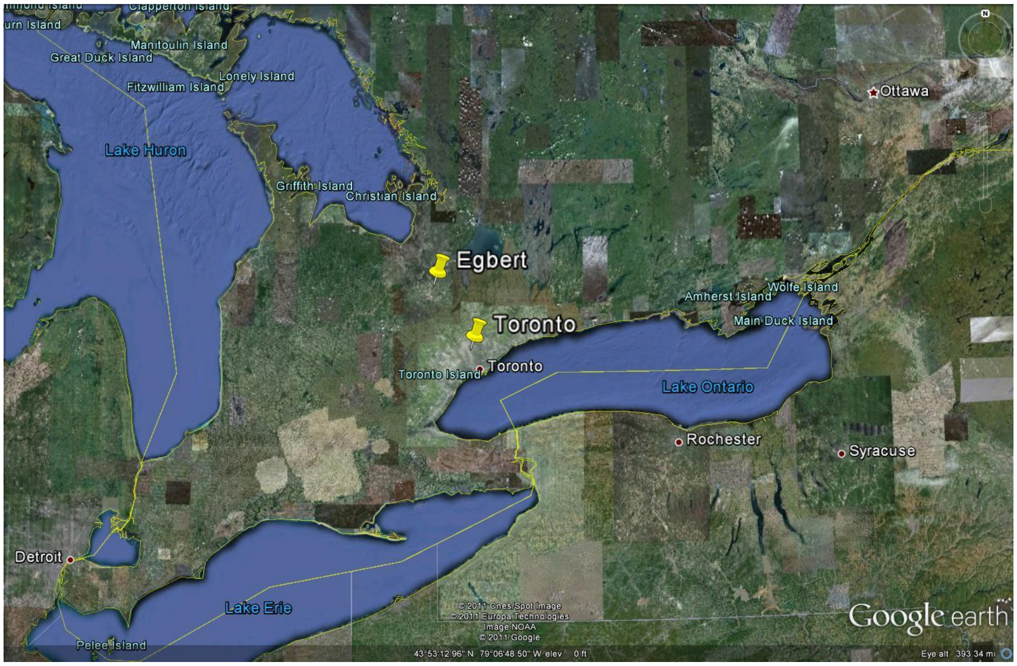


Figure 3.20: Map of the locations of Egbert and Toronto sampling sites (Google maps)

At both locations samples were collected from Monday to Thursday over 24 hrs time periods (7 AM- 7 AM), Friday sampling lasted 6-8 hrs (7 AM to 4 PM) and Friday-Saturday-Sunday samples were collected over 64 hrs (4 PM on Friday to 7 AM on Monday). The average flow rate was set at 24-25 mL/min. In total 58 samples were collected at Egbert and 55 in Toronto (Table 3.6).

Occasional sampling at the Toronto site continued throughout 2010. There were 10 samples (24 hrs sampling each) collected between March 6 to March 23 and 2 samples on August 30 and September 1. Simultaneous collection of two samples in parallel was made between September 7 and September 13. Furthermore, several 12 hrs samples (7 AM to 7 PM and 7 PM to 7 AM) were collected from September 13 to September 24 (Table 3.6).

### 3.7.3 Biofuel Study

Seven samples were supplied by the research group of Dr.Huang at Environment Canada as part of a Carbon Isotope Characterization of Diesel Engine Emissions study conducted by Environment Canada in 2008. The objective of this study was to establish chemical composition and the isotopic signature of exhaust from vehicles using regular biodiesel.

Fuel was combusted in a 1.9L 4 cylinder, turbocharged Volkswagen (VW) engine (Model: ALH l, 1998-2003, from 2001 VW Beetle). Studied fuel mixtures consisted of commercial Ultra Low Sulphur Diesel (ULSD) and 100% soy biodiesel (B100). For each test cycle one sample of diluted engine exhaust was collected into an evacuated 1.8 L canister. Table 3.5 contains information with different test parameters for these canisters.

Table 3.5: Fuel characteristics and engine test cycles (B: biodiesel, RD: regular ultra low sulphur diesel).

| Sample | RPM | Torque |
|---|---|---|
| Ambient Air | - | - |
| B100-Idle | 900 | 0 |
| B100-M2 | 1700 | 47 |
| RD-Idle | 900 | 0 |
| RD-M2 | 1700 | 47 |
| RD-M3 | 2250 | 47 |
| RD-M5 | 1200 | 47 |

For the VOC analysis part, the content of each 1.8 L canister was transferred into 3 L stainless steel canister and pressurized with pure helium to 35 psi. Each canister was then analyzed for VOC concentrations using GC-FID and compound specific isotopic composition analysis using the TSPS-GC-IRMS system.

Table 3.6: Overview of field study campaigns

| Campaign | Location | Dates | Air Samples | Sampling Frequency | Number of Samples |
|---|---|---|---|---|---|
| BAQS-Met | Ridgetown, ON , Canada (42°36´N, 81°53´W) | June-July 2007 | Rural Air | daily<br>24 hrs cartridge samples<br>and 3-4 canister samples/day | 20 cartridges<br>87 canisters |
| | Harrow, ON , Canada (42°02´N, 82°55´W) | | Urban Air | | 17 cartridges<br>34 canisters |
| | | | | Total Cartridges:<br>Total Canisters: | 37<br>121 |
| EC-YU | Egbert, ON, Canada<br>(44°12´N, 79°48´W | October, 2009-January 2010 | Rural Air | daily,<br>24 hrs samples | 58 |
| | Toronto, ON<br>Canada<br>(43°46´N, 79°28´W) | | Urban Air | | 55 |
| | | | | Total Cartridges: | 113 |
| EC-Toronto | Toronto, ON<br>Canada<br>(43°46´N, 79°28´W) | throughout 2010 | Urban Air, | 24 hrs samples,<br>parallel sampling<br>diurnal samples | Total Cartridges: 24 |
| Biofuel Study | EC Laboratory | Fall 2008 | Diesel and Biodiesel exhaust | various gaseous exhaust samples | Total Canisters:<br>7 |

# 4. RESULTS

## 4.1 Method Development and Optimization

Since the system developed for isotopic composition and concentration analysis of ambient VOC included several steps and components, various sampling and experimental parameters were evaluated and optimized for its better performance. The results of these tests and the corresponding conditions are presented in this section.

### 4.1.1 Cartridges

*4.1.1.1 Adsorbents and their trapping efficiency*

The trapping efficiencies of Carbopack B, Carboxene 569 and Tenax TA were tested by sampling ambient air through two cartridges connected in series. Breakthrough values were calculated as the percentage of VOC mass found on the back cartridge relative to the mass on the front cartridge (Table 4.1)

Table 4.1: Experimental data[a] of breakthrough values (%) of compounds on Carbopack B, Tenax TA and Carboxene 569.

| **Adsorbent** | | V sampled | **% of breakthrough** | | | | |
|---|---|---|---|---|---|---|---|
| Adsorbent | mass used | | n-pentane | n-hexane | benzene | toluene | octane |
| | g | L | % | | | | |
| Carbopack B + Tenax TA | 0.12 + 0.3 | 50 | 49 | 26 | 44 | 10 | 3 |
| Tenax TA | 0.36 | 15.12 | N/A[b] | 8 | 12 | 8 | N/A |
| Carbopack B | 0.55 | 3.36 | 21 | 4 | 10 | 2 | 40 |
| Carboxene 569 | 0.53 | 37 | N/A | 0.4 | 4 | 0.8 | 8 |
| Carboxene 569 | 1 | 82 | 1 | 0.2 | 3 | 0.3 | 0.3 |

(a) Results obtained using GC-FID system, (b) N/A no results available

*4.1.1.2 Cartridge Blank*

The analysis of clean cartridges was performed to determine any possible background signal (blanks) associated with used materials. Firstly, silanized glass wool used in cartridges to keep an adsorbent in place was tested at different temperatures. A series of tests was conducted where the temperature for wool-only containing cartridges was varied from 293-296 K to 573-583 K (Table 4.2).

Table 4.2: FID signal intensity[a] (peak area, AU[b] ×$10^3$) at different desorption temperatures (K) for a cartridge containing only silanized glass wool

| Test # | 1 | 2 | 3 | 4 | 5 | 6[d] |
|---|---|---|---|---|---|---|
| **Temperature[c] (K)/Compound** | **293-296** | **378-386** | **483-490** | **573-583** | **573-583** | **493-503** |
| n-butane | LDL[e] | LDL | LDL | 20 | 10 | 3 |
| n-pentane | LDL | LDL | 0.2 | 4 | 10 | 3 |
| 1-hexene | LDL | LDL | LDL | 2 | 1 | 4 |
| n-hexane | LDL | LDL | LDL | 1 | 4 | 0.2 |
| t-2 hexene | LDL | LDL | LDL | 1 | 0.9 | 8 |
| benzene | LDL | 0.2 | 1 | 40 | 40 | 7 |
| cyclohexane | LDL | LDL | LDL | 3 | 7 | 0.6 |
| cyclohexene | LDL | LDL | 0.2 | 1 | 10 | 0.4 |
| n-heptane | LDL | LDL | 2 | 6 | N/A[f] | 10 |
| toluene | LDL | 0.3 | 0.4 | 10 | 30 | 3 |
| 1-octene | LDL | LDL | LDL | 10 | 8 | 2 |
| n-octane | LDL | 0.2 | 1 | 4 | 8 | 2 |
| m-xylene | LDL | 0.4 | 0.6 | 8 | 2 | 0.7 |
| p-xylene | LDL | 0.2 | 0.2 | 3 | 9 | 1 |
| o-xylene | LDL | 0.2 | 0.2 | 5 | N/A | N/A |

(a) 1 ng of compound produces a signal with area in the range of 2.5-4 ×$10^3$ AU. (b) AU- arbitrary units. (c) Desorption time varied from 10-15 min, flow rate from 60-80 mL/min. (d) Test 6 (493-503K) was conducted on a cartridge that was previously tested at higher temperatures (Test 5, 573-583K). (e) LDL- lower than detection limit (section 4.2.3). (f) N/A- data is not available.

The results show that at high temperatures silanized glass wool not only yields significant background signals (Tests 3, 4, 5) but that the blank depends on previous heating of the silanized glass wool (Test 6).

As an alternative, quartz wool was similarly tested (Table 4.3):

Table 4.3: FID signal intensity (peak area, AU ×$10^3$) at different desorption temperatures (K) for a cartridge containing only quartz wool[a]

| Test # | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| **Temperature (K)** | **293-296** | **393-403** | **473-483** | **583-593** |
| n-butane | LDL[a] | LDL | LDL | LDL |
| n-pentane | LDL | LDL | LDL | LDL |
| 1-hexene | LDL | LDL | LDL | LDL |
| n-hexane | LDL | LDL | LDL | LDL |
| t-2 hexene | LDL | LDL | LDL | LDL |
| benzene | LDL | LDL | 0.2 | 2 |
| cyclohexane | LDL | LDL | LDL | LDL |
| cyclohexene | LDL | LDL | LDL | LDL |
| n-heptane | LDL | LDL | LDL | LDL |
| toluene | LDL | LDL | LDL | LDL |
| 1-octene | LDL | LDL | LDL | LDL |
| n-octane | LDL | LDL | LDL | LDL |
| m-xylene | LDL | LDL | LDL | LDL |
| p-xylene | LDL | LDL | LDL | LDL |
| o-xylene | LDL | LDL | LDL | LDL |

(a) Desorption time varied from 10-15 min, flow rate 60-80 mL/min. (b) lower than detection limit (section 4.2.3).

These results demonstrated that quartz wool does not contribute significantly to blanks.

Subsequently Carboxene 569 was tested for blank values at different desorption temperatures, results for these tests are summarized in Table 4.4

Table 4.4: FID signal intensity (peak area, AU ×$10^3$) at different desorption temperatures (K) for cartridges containing 1 g of Carboxene 569 and quartz wool

| Test # | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| **Temperature (K)** | **468-473** | **468-483** | **473-483** | **503-513** | **503-513** | **573-593** |
| Time | 10 | 10 | 10 | 15 | 15 | 10 |
| Flow rate | 60 | 60 | 60 | 60 | 100 | 150 |
| n-pentane | LDL[a] | LDL | 0.2 | 0.5 | 0.2 | 0.5 |
| 1-hexene | LDL | LDL | LDL | 0.2 | LDL | LDL |
| n-hexane | LDL | LDL | LDL | LDL | LDL | LDL |
| t-2 hexene | LDL | LDL | LDL | LDL | LDL | LDL |
| benzene | 0.3 | 0.7 | 2 | 0.8 | 0.3 | 2 |
| n-heptane | LDL | LDL | LDL | 0.2 | LDL | LDL |
| toluene | LDL | LDL | 0.2 | 0.2 | LDL | LDL |
| 1-octene | LDL | LDL | LDL | 0.2 | LDL | LDL |
| n-octane | LDL | LDL | LDL | LDL | LDL | LDL |
| p,m-xylene | LDL | LDL | LDL | LDL | LDL | LDL |
| o-xylene | LDL | LDL | LDL | LDL | LDL | LDL |

(a) lower than detection limit (section 4.2.3).

It was established that Carboxene 569 produced no background signals for most of the target compounds at temperatures ranging from 473 K to 573K. Sometimes minor blanks were observed for benzene and pentane (less than 1 ng), but they were insignificantly small compared to ambient samples that usually contained more than 3-5 ng per injection (Section 4.1.4, Figure 4.3, Table 4.14, Section 4.3).

Based on the results of the blank tests (Table 4.1, 4.3 and 4.4), Carboxene 569 and quartz wool were selected as materials to be used in the cartridges. Figure 4.1 shows an example of a chromatogram obtained for blank cartridge with GC-IRMS.

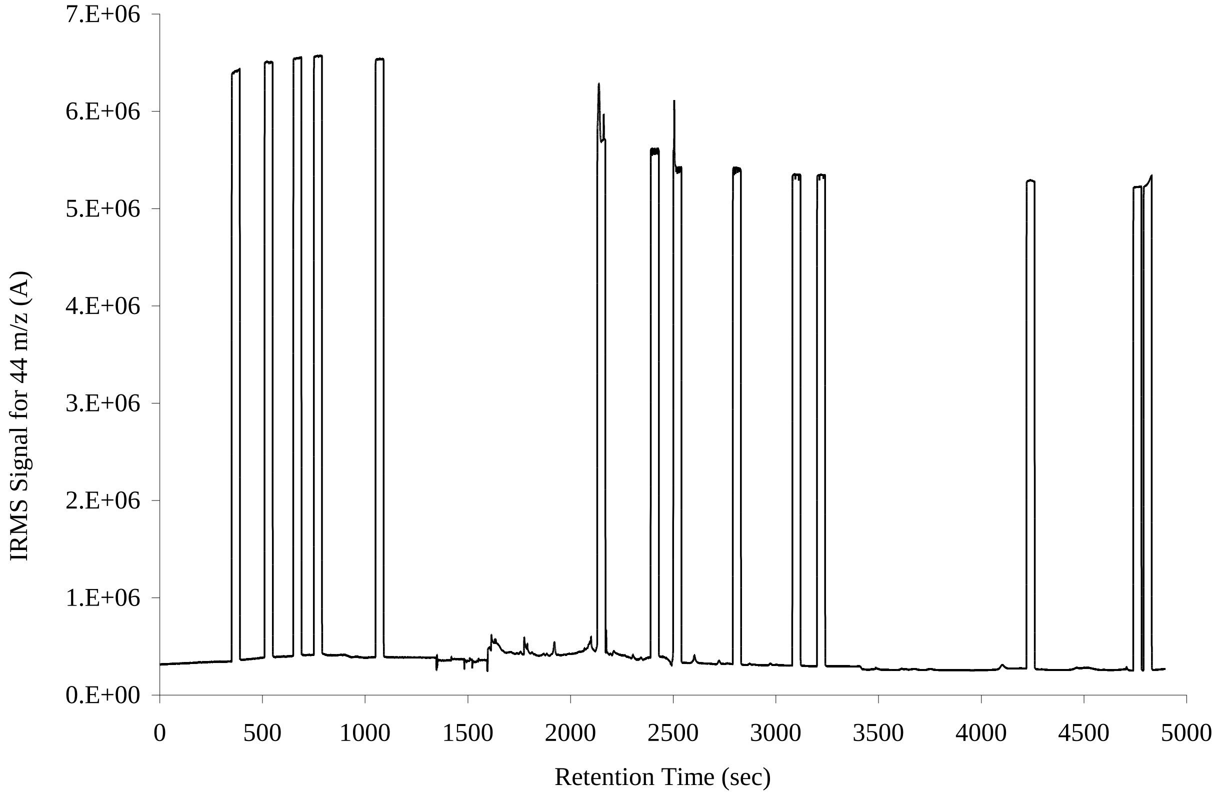


Figure 4.1: 44 m/z Chromatogram obtained from analysis of a blank cartridge*. Rectangular peaks are from reference $CO_2$ injections (*desorption parameters: carrier gas flow rate: 56 mL/min, desorption time: 40 min, desorption temperature: 553 K).

### *4.1.1.3 Desorption parameters*

Experimental conditions for desorption of VOC from cartridges were tested using two approaches. One approach was to re-analyze already desorbed cartridges that previously contained ambient samples under the same conditions as the first desorption. The experimental parameters tested and an assessment of the desorption completion are listed in Table 4.5. For the second approach, cartridges were loaded with standard mixtures as described in section 3.6.2 and then desorbed under various conditions. The recoveries are provided in Table 4.5. Parameters such as temperature, time and carrier gas flow rate were varied to determine the optimum desorption conditions.

Table 4.5: Dependence of the recovery (R, %)[a] on various experimental parameters[b] (using FID signal peak areas)

| Test # | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Time (min) | 10 | 15 | 15 | 20 | 20 | 30 | 25 |
| Temperature (K) | 483 | 503 | 503 | 553 | 573 | 563 | 523 |
| Flow rate (mL/min) | 50 | 100 | 150 | 65 | 150 | 65 | 53 |
| Compound | | | | | | | |
| n-pentane | 79 | 91 | 98 | 99 | 99 | 72 | 93 |
| n-hexane | 76 | 83 | 94 | 98 | 98 | 99 | 100 |
| benzene | 79 | 71 | 100 | 75 | 76 | 79 | 99 |
| n-heptane | 77 | 70 | 84 | 87 | 96 | 95 | 100 |
| toluene | 76 | 69 | 81 | 58 | 98 | 88 | 93 |
| n-octane | 79 | 73 | 83 | 76 | 94 | 94 | 99 |
| m-xylene | 74 | 67 | 68 | 75 | 70 | 94 | 100 |
| p-xylene | 74 | 64 | 67 | 57 | 73 | 94 | 98 |
| o-xylene | 75 | 68 | 69 | 93 | 64 | 93 | 98 |

(a) $R = \frac{A_2(VOC)}{A_1(VOC) + A_2(VOC)} \times 100\%$, were $A_1$ and $A_2$ are the VOC masses recovered during the first and second desorption. (b) Results were obtained with Tekmar 5010. (c) Desorption temperature.

From the desorption recovery, yields can be calculated based on the assumption that the efficiency of the first and second desorption step is identical. However, for ambient samples the actual mass of VOC collected is unknown, and therefore the validity of this assumption cannot be tested using ambient samples. Hence recovery from cartridges loaded with test mixtures containing known masses of VOC was examined (Table 4.6).

Table 4.6: Dependence of the recoveries[a] (R, %) from a cartridge on various desorption parameters[b,c] (using FID signal peak areas)

| Test # | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Time (min) | 20 | 20 | 20 | 26 | 15 |
| Temperature (K) | 523 | 533 | 558 | 543 | 573 |
| Flow rate (mL/min) | 48 | 54 | 72 | 99 | 81 |
| pentane | 79 | 90 | 100 | 98 | 101 |
| hexane | 41 | 44 | 82 | 82 | 97 |
| benzene | 49 | 51 | 86 | 93 | 97 |
| heptane | 16 | 14 | 46 | 46 | 72 |
| toluene | 16 | 16 | 52 | 50 | 69 |
| octane | 13 | 10 | 30 | 38 | 54 |
| ethylbenzene | 6 | 8 | 30 | 24 | 52 |
| p,m-xylene | 3 | 4 | 21 | 18 | 46 |
| o-xylene | 9 | 7 | 30 | 32 | 51 |
| n-nonane | 76 | 53 | 93 | 81 | 101 |

(a) $R = \frac{A(VOC)_{recovered}}{A(VOC)_{loaded}} \times 100\%$, where R is recovery and A the masses of VOC recovered and loaded. (b) Results were obtained with TSPS. (c) Based on one measurement.

To identify possible reasons for the low recoveries the temperature distribution inside the furnace was measured using a thermocouple sensor attached to an empty cartridge. It was found that there is a significant gradient in temperatures along the 15 cm long furnace (Table 4.7).

Table 4.7: Temperature gradient inside the furnace (using additional thermocouple)

| Distance[a] | Temperature (K) | |
|---|---|---|
| cm | Furnace Reading | Test TC[b] |
| 5.6 | 526 | 526 |
| 4.5 | 526 | 519 |
| 2.7 | 520 | 519 |
| 1.5 | 521 | 499 |
| end | 523 | 425 |

(a)Distance is the distance between the furnace edge and the thermocouple in the empty cartridge. (b)TestTC- test thermocouple

Results of desorption tests with a 30 cm furnace are given in Table 4.8.

Table 4.8: Recoveries of VOC (%) obtained using a longer furnace with minimized temperature gradient (analyzed with FID or IRMS)[b]

| Test# | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Time (min) | 15 | 15 | 15 | 20 | 25 | 30 | 30 | 40 |
| Temperature (K) | 523 | 553 | 573 | 673 | 573 | 573 | 583 | 553 |
| Flow rate (mL/min) | 55 | 53 | 54 | 78 | 58 | 58 | 53 | 60 |
| pentane | 93 | 101 | 134 | 102 | 114 | 109 | 102 | 100 |
| hexane | 70 | 107 | 164 | 102 | 106 | 104 | 102 | 102 |
| benzene | 73 | 105 | 148 | 104 | 106 | 105 | 108 | 113 |
| heptane | 39 | 93 | 102 | 99 | 96 | 97 | 96 | 100 |
| toluene | 43 | 96 | 110 | 103 | 100 | 100 | 102 | 103 |
| octane | 20 | 58 | 60 | 69 | 78 | 75 | 85 | 79 |
| ethylbenzene | 29 | 74 | 77 | 86 | 87 | 86 | 87 | 90 |
| p,m-xylene | 24 | 65 | 67 | 82 | 90 | 87 | 97 | 95 |
| o-xylene | 25 | 68 | 64 | 81 | 85 | 84 | 92 | 94 |
| n-nonane | N/A[a] | 33 | 84 | N/A | 96 | 71 | 99 | 78 |
| n-decane | N/A | 22 | 121 | N/A | 102 | 79 | 118 | 109 |

(a) N/A- data is not available, (b) Based on one measurement

#### *4.1.1.4 Storage*

Storage conditions were tested by loading cartridges with test mixtures and analyzing them after storage at room temperature and/or in the freezer. The results are presented in Table 4.9.

Table 4.9: VOC recovery[a] (%) from cartridges for different storage (values obtained with FID and IRMS) (desorption parameters: carrier gas flow rate: 40-60 mL/min, desorption time: 30-40 min, desorption temperature: 553 K)[b].

| Storage Time | 1-3 hours | 1-2 weeks | 6-7 months |
|---|---|---|---|
| Storage Temperature (K) | - | 296 | 253 |
| Detector | FID or IRMS | FID | IRMS |
| Compound | | | |
| hexane | 102 | 111 | 114 |
| benzene | 113 | 113 | 118 |
| heptane | 100 | 98 | 86 |
| toluene | 103 | 105 | 88 |
| octane | 79 | 90 | 75 |
| ethylbenzene | 90 | 99 | 86 |
| p,m-xylene | 95 | 98 | 85 |
| o-xylene | 94 | 98 | 80 |
| n-nonane | 78 | 65 | 66 |
| n-decane | 109 | 104 | 117 |

(a) $R = \frac{A(VOC)_{recovered}}{A(VOC)_{loaded}} \times 100\%$, where R is recovery and A the masses of VOC recovered and loaded. (b) Based on 1-3 measurements, for repeated measurements relative standard deviation was below 15%.

### 4.1.2 Preconcentration systems

Various operating conditions of the preconcentration systems were tested using artificial test mixtures. Identical masses of mixtures were introduced into the system, processed and analyzed with GC-FID and GC-IRMS. Sets of operating conditions tested and reproducibility of the measurements are provided in Table 4.10. RSD values were determined based on at least four measurements. In some cases peak shapes were significantly distorted; results from distorted peaks were not included in the data analysis.

Table 4.10: Dependence of Tekmar 5010 precision (RSD, %) on various analysis parameters[a] (using FID signal peak areas)

| **Trap-1 Temp (K)** | 93 | 113 | 113 | 93 | 93 | 113 | 113 | 93 | 93 | 123 | 93 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Trap-2 Temp (K)** | 223 | 113 | 93 | 93 | 93 | 123 | 113 | 123 | 123 | 93 | 93 |
| **Trap-1 Transfer (K)** | 503 | 363 | 413 | 413 | 428 | 426 | 426 | 453 | 473 | 483 | 513 |
| **Transfer Time (min)** | 15 | 7 | 10 | 15 | 10 | 10 | 30 | 10 | 10 | 12 | 15 |
| **Injection Temp (K)** | 493 | 393 | 393 | 393 | 393 | 483 | 483 | 453 | 483 | 493 | 513 |
| **Injection Time (min)** | 15 | 5 | 5 | 5 | 10 | 15 | 15 | 20 | 20 | 15 | 20 |
| pentane | N/A[b] | N/A | N/A | N/A | N/A | 22 | 2 | 9 | 15 | 10 | 4 |
| n-hexane | 117 | N/A | N/A | N/A | N/A | 11 | N/A | N/A | N/A | N/A | 5 |
| benzene | N/A | 85 | 12 | 29 | 109 | 24 | 14 | 6 | 64 | 83 | 2 |
| n-heptane | 7 | 49 | 46 | 9 | 67 | 13 | 4 | 16 | 44 | 65 | 6 |
| toluene | 1 | 20 | 39 | 30 | 37 | 7 | 7 | 13 | 2 | 3 | 7 |
| p-xylene | 5 | 35 | 29 | 47 | 14 | 23 | 8 | 8 | 18 | 14 | 9 |
| n-nonane | 10 | 40 | 26 | 46 | 12 | 22 | 7 | 7 | 15 | 12 | 9 |
| n-decane | 3 | 27 | 39 | 67 | 18 | 23 | 8 | 8 | 18 | 14 | 8 |

(a) Average and RSD values were calculated based on at least 4 measurements. (b) N/A compounds were not detected with FID

Trapping at temperature of 93 K and subsequent desorption at 513 K for 15 and 20 min respectively, resulted in the lowest standard deviations for most hydrocarbons. However, it should be noted that relative standard deviations of less than 5% for all tested VOC could only be achieved with the improved cooling system for the traps (3.2.2.1). A comparison is given in Table 4.11.

Similarly to Tekmar 5010, TSPS analysis parameters were evaluated for precision of the measurements (Table 4.12).

Table 4.11: Reproducibility (RSD[a], %) of the signals (FID) before and after the modification of Trap 1 and Trap 2 set-ups (trapping temperature: 93 K, desorption temperature: 513 K, desorption time: 15-30 min)

| Compound | Reproducibility (%) | |
|---|---|---|
| Test Conditions | Initial set-up | Modified traps |
| Number of measurements | 6 | 18 |
| pentane | 29.0 | 1.3 |
| n-hexane | 8.4 | 1.5 |
| benzene | 11.9 | 2.9 |
| n-heptane | 11.0 | 5.2 |
| toluene | 20.5 | 5.2 |
| p-xylene | 37.4 | 4.8 |
| n-nonane | 30.9 | 3.9 |
| n-decane | 37.8 | 5.0 |

(a) Average and RSD values were calculated based on at least 3-4 measurements

Table 4.12: Dependence of TSPS precision (RSD[a], %) on experimental parameters (using FID signal peak areas)

| **Trap-1 Transfer Temp (K)** | 393 | 393 | 393 | 393 | 393 | 513 | 443 | 423 |
|---|---|---|---|---|---|---|---|---|
| **Transfer Time (min)** | 15 | 15 | 15 | 15 | 18 | 7 | 7 | 7 |
| **Injection Temp (K)** | 493 | 493 | 493 | 493 | 493 | 493 | 493 | 493 |
| **Injection Time (min)** | 1 | 3 | 5 | 13 | 5 | 5 | 5 | 7 |
| **Transfer Lines Temp (K)** | 373 | 373 | 373 | 373 | 373 | 373 | 373 | 423 |
| pentane | >50 | 0.4 | 1.4 | 0.8 | 0.5 | 4.0 | 1.8 | 0.3 |
| n-hexane | >51 | 2.5 | 2.0 | 0.4 | 0.9 | 8.6 | 1.9 | 0.8 |
| benzene | >52 | 4.8 | 2.7 | 1.1 | 1.8 | 43.6 | 2.3 | 0.5 |
| n-heptane | >53 | 6.1 | 2.6 | 0.7 | 3.1 | 2.5 | 3.2 | 1.0 |
| toluene | >54 | 9.0 | 8.6 | 29.0 | 28.2 | 21.4 | 36.1 | 0.7 |
| p-xylene | >55 | 9.5 | 1.7 | 0.5 | 4.5 | 4.9 | 5.5 | 1.0 |
| n-nonane | >56 | 22.7 | 7.5 | 11.9 | 9.3 | 31.1 | 66.6 | 0.2 |
| n-decane | >57 | 54.9 | 24.7 | 25.7 | 14.1 | 48.3 | N/A | 0.1 |

(a) Average and RSD values were calculated based on at least 6 best measurements

### 4.1.3 Chromatographic separation

VOC were separated using non-polar dimethyl polysiloxane (HP-1 and DB-1) columns. The retention times for the target compounds are provided in Table 4.13 for the different conditions described in section 3.2.3.

Table 4.13: Retention times (min) of the target compounds obtained by GC-FID[a]

| ID[2] | pentane | hexane | benzene | heptane | toluene | octane | ethylbenzene | p,m-xylene | o-xylene | nonane | decane |
|---|---|---|---|---|---|---|---|---|---|---|---|
| HP1-A | 2.58 | 4.28 | 7.25 | 12.33 | 16.70 | - | - | p-21.59 | - | 22.30 | 25.55 |
| HP1-B | - | 5.26 | 6.60 | 8.97 | 12.51 | - | - | p-21.43 | - | 25.76 | 33.43 |
| HP1-C | - | 4.75 | 6.01 | 8.31 | 11.88 | - | - | p-21.12 | - | 25.39 | 32.56 |
| HP1-D | - | 4.12 | 6.80 | 9.26 | 12.78 | 48.90 | 56.23 | 21.56 | - | 25.66 | 33.69 |
| DB1-60-A | 4.06 | 5.25 | 6.67 | 9.02 | 12.56 | - | - | p-21.48 | - | 25.78 | 33.41 |
| DB1-60-B | 3.57 | 5.03 | 6.55 | 9.16 | 13.37 | - | - | p-23.63 | - | 27.50 | 34.13 |
| DB1-100-A | 16.79 | 22.63 | 25.58 | 28.28 | 31.33 | 33.48 | 36.10 | m-34.49, p-36.54 | 37.61 | 38.25 | 42.50 |
| DB1-100-B | 10.80 | 17.09 | 21.33 | 26.17 | 30.89 | - | - | p- 38.50 | - | 40.51 | 45.27 |
| DB1-100-C | 12.35 | 19.00 | 23.41 | 28.10 | 32.91 | - | - | 39.56 | - | 41.48 | 45.29 |
| DB1-100-D | - | 18.81 | 23.13 | 27.90 | 32.75 | - | - | m-39.93, p-40.08 | - | 42.16 | 47.29 |

(a) Peak width ranged from 0.12 to 0.17 min (with GC-FID). (b) ID correspond to ID used in Table 3.3 and corresponding experimental parameters described in Section 3.2.3

An example of a chromatogram obtained by GC-IRMS is shown in Figure 4.2.

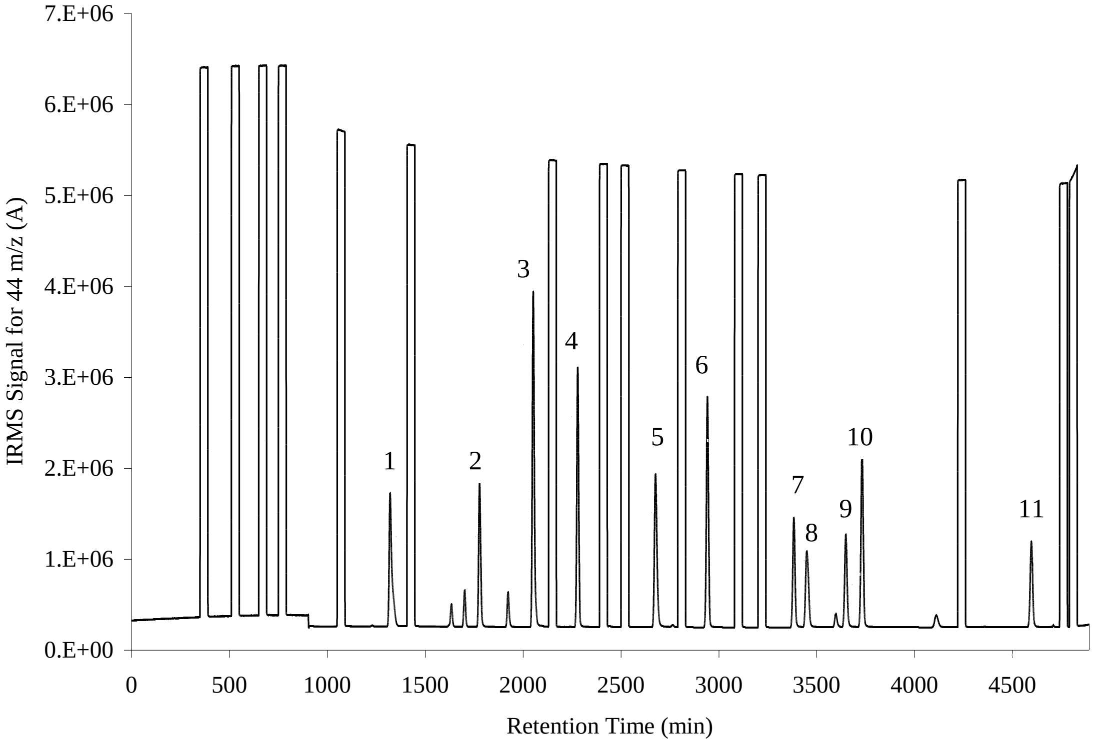


Figure 4.2: Chromatogram obtained by GC-IRMS for a test mixture with 11 target compounds and on-line reference gas injections. Rectangular peaks are reference $CO_2$ signals and peaks numbered from 1-11 correspond to n-pentane (30 ng[*]), n-hexane (27 ng), benzene (25 ng), n-heptane (50 ng), toluene (60 ng), n-octane (56 ng), ethylbenzene (47 ng), p,m-xylene (75 ng), o-xylene (32 ng), n-nonane (39 ng), n-decane (12 ng) respectively ([*]Masses were calculated using calibration curves described in 4.1.4).

### 4.1.4 Calibration

For all targeted compounds calibration curves were constructed by plotting FID and/or IRMS signal area versus injected mass. An example is shown in Figure 4.3. The intercepts for linear regression were set to zero; tests using regression that allowed non-zero intercepts consistently resulted in y-axis intercepts that were statistically not different from zero. Table 4.14 summarizes the least squares regression analysis of calibration curves for GC-FID and GC-IRMS measurements.

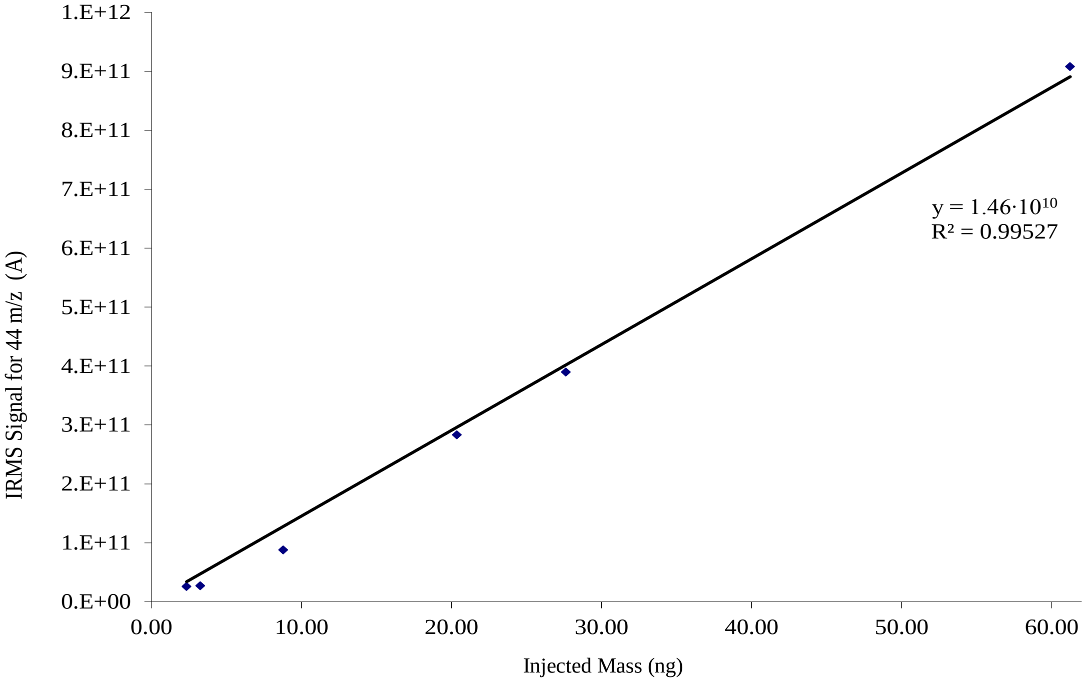


Figure 4.3: Calibration curve for toluene (based on GC-IRMS measurements).

Table 4.14: Regression analysis for the calibration curves constructed for target compounds in the concentration range 0.4-200 ng VOC.

| Compound | FID | | IRMS | |
|---|---|---|---|---|
| | slope (counts/ng) | $R^2$ | $10^{10}$ x Slope (A/ng) | $R^2$ |
| pentane | 4714 | 1 | | |
| hexane | 3765 | 1 | 1.18 | 0.9993 |
| benzene | 4814 | 9.9997E-01 | 3.44 | 0.9992 |
| heptane | 2817 | 1 | 1.42 | 0.9981 |
| toluene | 2970 | 1 | 1.46 | 0.9953 |
| octane | 1868 | 1 | 1.57 | 0.9985 |
| ethylbenzene | 3423 | 1 | 1.60 | 0.9948 |
| p,m,-xylene | 3423 | 1 | 1.76 | 0.9868 |
| o-xylene | 3423 | 1 | 2.30 | 0.9895 |
| n-nonane | 3495 | 1 | 2.24 | 0.9896 |
| n-decane | 5971 | 1 | 4.51 | 0.9763 |

## 4.2 Method Evaluation

Using optimized operation conditions method and system performance were evaluated using mixtures of known composition and isotope ratios. The test results on the precision and accuracy of the measurements are presented in sections 4.2.1, 4.2.2 and 4.2.3 below.

### 4.2.1 Precision

Precision of the constructed analytical systems (Tekmar 5010 and TSPS) was determined from the reproducibility of peak areas from repeat measurements. Test mixtures containing various masses of VOC were analyzed multiple times using GC-FID and GC-IRMS. The relative standard deviations for these measurements are presented in Table 4.15.

Table 4.15: Relative standard deviation (%) of peak area for repeat measurements (>10) of test mixtures using Tekmar 5010 and TSPS (A: with GC-FID and B: with GC-IRMS) using optimized operating parameters.

A: GC-FID

| **System** | **TEKMAR** | | | | **TSPS** | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Mass of VOC, ng** | 0.8-3.2 | 8-15 | 14-70 | 20-100 | 0.3-1 | 2-12 | 18-25 | 25-50 | 40-60 | 50-100 |
| pentane | 4.6 | 0.7 | 0.6 | 0.4 | 3.4 | 1.5 | 2.3 | 1.5 | 1.6 | 2.7 |
| hexane | 4.1 | 0.6 | 0.9 | 1.1 | 2.6 | 2.7 | 1.1 | 1.3 | 0.5 | 3.9 |
| benzene | 1.0 | 4.1 | 5.6 | 2.4 | 1.6 | 2.9 | 1.0 | 2.0 | 1.4 | 6.6 |
| heptane | 3.5 | 4.2 | 5.5 | 9.0 | 2.6 | 3.2 | 1.7 | 2.5 | 1.4 | 4.8 |
| toluene | 3.7 | 4.7 | 8.1 | 5.7 | 4.6 | 5.5 | 4.7 | 4.0 | 1.3 | 0.3 |
| octane | N/A | N/A | N/A | N/A | 4.1 | N/A | 3.7 | 1.4 | 2.8 | 3.1 |
| ethylbenzene | N/A | N/A | N/A | N/A | 7.5 | 6.7 | 8.2 | 4.6 | 6.2 | 1.9 |
| m-xylene | N/A | N/A | N/A | N/A | N/A | 4.3 | N/A | 10.9 | 7.2 | 1.7 |
| p-xylene | 3.7 | 3.6 | 9.7 | 4.4 | 0.2 | 5.2 | N/A | 7.0 | 5.7 | 1.5 |
| o-xylene | N/A | N/A | N/A | N/A | 6.4 | 0.9 | N/A | 8.1 | 6.6 | 1.5 |
| p,m-xylene | N/A | N/A | N/A | N/A | 6.7 | N/A | 8.5 | 9.4 | 8.3 | 1.7 |
| n-nonane | 13.1 | 0.1 | 0.9 | 2.1 | 7.3 | 9.6 | 10.4 | 5.8 | 4.9 | 1.9 |
| n-decane | 5.4 | 1.9 | 4.7 | 1.6 | 4.7 | 4.9 | 10.3 | 4.6 | 15.6 | 8.4 |

B: GC-IRMS

| **System** | **TEKMAR** | | | **TSPS** | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Mass of VOC, ng** | 8-15 | 14-70 | 20-100 | 1-3 | 2-7 | 4-10 | 10-30 | 15-40 | 25-74 |
| pentane | 11.3 | 3.1 | 2.8 | N/A* | N/A | N/A | N/A | N/A | N/A |
| hexane | 11.3 | 7.0 | 6.7 | 0.3 | 1.2 | 10.2 | 1.7 | 4.9 | 2.8 |
| benzene | 9.7 | 5.5 | 7.8 | 0.9 | 5.9 | 9.9 | 1.7 | 4.1 | 2.2 |
| heptane | 10.9 | 7.4 | 10.5 | 0.0 | 3.6 | 11.2 | 3.5 | 4.3 | 3.5 |
| toluene | 10.2 | 7.6 | 15.2 | 3.2 | N/A | 4.9 | 3.2 | 5.2 | 3.4 |
| octane | N/A | N/A | N/A | 6.0 | 4.7 | 10.3 | 7.5 | 4.5 | 3.3 |
| ethylbenzene | N/A | N/A | N/A | 5.0 | N/A | 11.6 | 3.7 | 5.9 | 3.3 |
| p-xylene | 13.2 | 11.9 | 14.7 | N/A | N/A | N/A | N/A | N/A | N/A |
| p,m-xylene | N/A | N/A | N/A | 10.3 | N/A | 6.1 | 1.9 | N/A | 15.8 |
| n-nonane | 18.5 | 16.9 | 13.8 | 3.4 | N/A | 13.8 | 8.7 | 5.3 | 5.6 |
| n-decane | 2.9 | 14.6 | 5.8 | 4.1 | 11.6 | 7.8 | 6.7 | 9.8 | N/A |

*N/A- standard deviation was not determined if less than 3 measurements were available.

### 4.2.2 Accuracy of isotope ratio measurement

The accuracy of isotope ratio measurements was tested by comparing delta values determined from off-line and on-line analyses. $\delta^{13}C$ values determined by off-line method for eleven VOC are shown in Table 4.16.

Table 4.16: $\delta^{13}C$ values for reference material determined by off-line method

| Compound | #samples | # repeats/sample | $\delta^{13}C$ (‰) | $\sigma[\delta^{13}C]$(‰) |
|---|---|---|---|---|
| pentane | 4 | 3 | -30.134 | 0.315 |
| hexane | 4 | 3 | -30.884 | 0.423 |
| benzene | 2 | 4 | -28.400 | 0.016 |
| heptane | 3 | 3 | -27.926 | 0.012 |
| toluene | 2 | 4 | -27.023 | 0.067 |
| octane | 2 | 3 | -36.310 | 0.003 |
| ethylbenzene | 1 | 6 | -26.842 | N/A |
| m-xylene | 1 | 5 | -26.918 | N/A |
| p-xylene | 2 | 4 | -25.694 | 0.046 |
| o-xylene | 2 | 4 | -28.159 | 0.065 |
| nonane | 3 | 3 | -36.862 | 0.138 |
| decane | 1 | 3 | -36.439 | N/A |

Averaged $\delta^{13}$C values for on-line analysis of target compounds are provided in Table 4.17.

Table 4.17: $\delta^{13}$C values for target compounds determined by on-line method in mixtures of reference materials in helium.

| Compound | $\delta^{13}$C (‰) | | | | | |
|---|---|---|---|---|---|---|
| Mass of VOC (ng) | 1-2 | 1-4 | 2-3 | 10-30 | 20-40 | 30-70 |
| hexane | -33.01 | -29.92 | -29.46 | -29.09 | -29.05 | -29.05 |
| benzene | -33.57 | -30.12 | -28.57 | -28.64 | -28.54 | -28.47 |
| heptane | -31.69 | -27.33 | -26.15 | -25.81 | -25.75 | -25.58 |
| toluene | -33.77 | -27.62 | -28.83 | -27.16 | -27.35 | -27.51 |
| octane | -38.03 | -36.78 | -36.92 | -33.35 | -33.21 | -33.05 |
| ethylbenzene | -37.05 | -31.96 | -30.17 | -27.02 | -27.30 | -27.38 |
| p,m-xylene | -35.59 | -33.47 | -32.52 | -26.14 | -26.26 | -26.10 |
| o-xylene | -35.40 | -32.11 | -29.79 | -28.31 | -28.45 | -28.46 |
| nonane | -37.44 | -38.32 | -37.55 | -33.53 | -33.36 | -33.49 |
| decane | -36.56 | -42.31 | -33.63 | -33.59 | -33.33 | N/A[a] |

(a) N/A- data is not available

A comparison between on-line and off-line data is presented in Table 4.18

Table 4.18: Differences between on-line and off-line $\delta^{13}$C values

| Compound | $\delta^{13}C_{on-line} - \delta^{13}C_{off-line}$ (‰) | | | | |
|---|---|---|---|---|---|
| Mass of VOC (ng) | 1-3 | 2-7 | 10-30 | 15-40 | 25-74 |
| hexane | -2.12 | 0.96 | 1.05 | 1.83 | 1.76 |
| benzene | -5.17 | -1.72 | -0.24 | -0.14 | -0.07 |
| heptane | -3.76 | 0.60 | 1.70 | 2.18 | 2.35 |
| toluene | -6.75 | -0.59 | -0.15 | -0.33 | -0.48 |
| octane | -1.72 | -0.47 | 2.96 | 3.10 | 3.13 |
| ethylbenzene | -10.21 | -5.12 | -0.18 | -0.46 | -0.54 |
| p, m-xylene | -9.28 | -7.16 | 0.16 | 0.05 | 0.13 |
| o-xylene | -7.24 | -3.95 | -0.07 | -0.29 | -0.17 |
| nonane | -0.58 | -1.46 | 3.33 | 3.50 | 3.38 |
| decane | 4.13 | -5.87 | 3.11 | 2.85 | 2.92 |

The dynamic range for the isotope measurements was established by plotting of $\delta^{13}C$ values as a function of peak area, an example of a plot is provided in Figure 4.4.

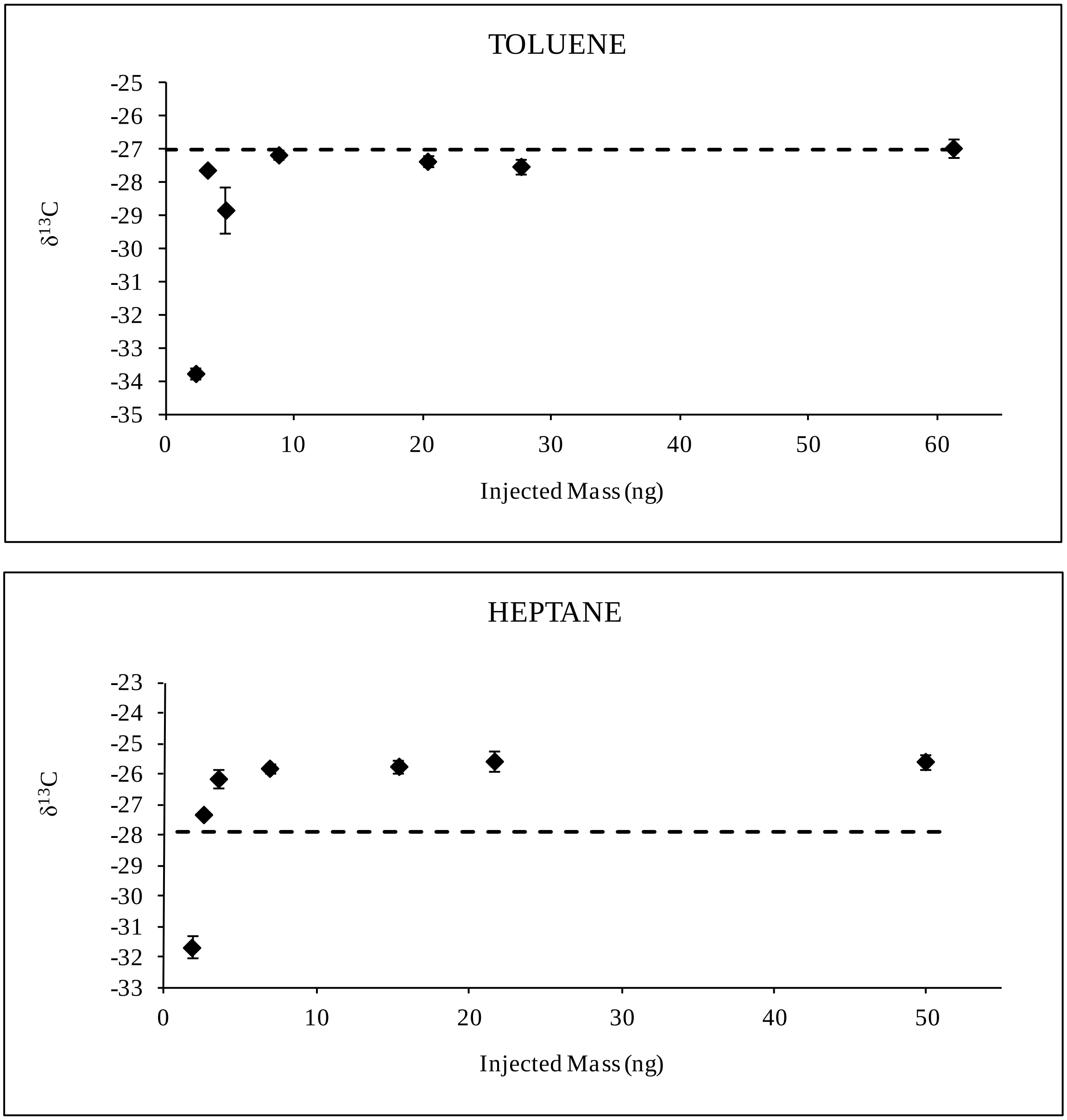


Figure 4.4: Plot of $\delta^{13}C$ values measured on-line for toluene and heptane present in test mixtures for different sample masses (dash line is the reference $\delta^{13}C$ value).

### 4.2.3 Detection Limits

Both detection systems used (FID and IRMS with a combustion interface) potentially can detect VOC masses in the range of a few pg. The use of cartridges for sampling resulted in small blank values, which determined the actual detection limits. Table 4.19 gives the detection limits in mass per cartridge three times the standard deviation of the blank values.

Table 4.19: Blank values and IRMS detection limits for target compounds (ng). Values are determined using the standard deviation of 6-8 repeat measurements of the blanks.

| Compound | Blank $10^9$ x Area[a] (As) | Blank $10^9$ x σarea[b] (As) | DL (ng) |
|---|---|---|---|
| hexane | 2.27 | 3.90 | 0.99 |
| benzene | 24.61 | 17.27 | 1.5 |
| heptane | 15.20 | 0.26 | 0.06 |
| toluene | 6.00 | 6.29 | 1.3 |
| octane | 0.88 | 0.61 | 0.12 |
| ethylbenzene | 2.26 | 3.03 | 0.6 |
| p,m-xylene | 3.58 | 3.15 | 0.5 |
| o-xylene | 13.76 | 19.09 | 2.5 |
| nonane | 12.71 | 21.11 | 2.8 |
| decane | 7.67 | 8.13 | 0.5 |

(a) Peak area determined from IRMS signals. (b) σ- standard deviation calculated from repeated measurements (5)

It should be pointed out that while detection limits were blank value limited, cartridge samples analyzed by GC-IRMS were not corrected for blank values. The main reason for this is that the blank signals were too small to allow determination of a meaningful isotope ratio. In most cases the blank values are very small compared to samples masses, which generally were in the range of 5-10 ng per compound. However results for compounds present in lower masses (3-5 ng) might be slightly affected.

## 4.3 Ambient Air Samples

Developed sampling and analysis methods were applied to determine concentrations and isotopic composition of selected target compounds in samples collected during Border Air Quality and Meteorology study (2007), Environment Canada-York University campaign and the biofuel burning experiments (2007). An overview of the results is presented in this chapter. The complete data sets and supporting meteorological information are given in Appendixes A-O. Results from distorted peaks, as well as unrealistic mixing ratios (above 3 ppbv) or delta values (lower than -32 ‰) were not included in the final data analysis.

### 4.3.1 Border Air Quality and Meteorology study (2007)

Average concentrations and isotope composition of VOC in samples collected during BAQS-Met are summarized in Table 4.20. The complete data set is presented in Appendix A.

Table 4.20: Statistical summary of concentrations and isotope ratios of VOC collected during BAQS-Met study, 2007 (N-number of samples) (from cartridge (A) and canister (B) samples)

A:

| Location | Ridgetown | | | | | Harrow | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compounds | Concentrations (ppbv) | | | | $\delta^{13}C$ (‰) | Concentrations (ppbv) | | | | $\delta^{13}C$ (‰) |
| | N | Average | Median | Max | | N | Average | Median | Max | |
| pentane | | N/A | N/A | N/A | N/A | 3 | 1.02 | 0.32 | 2.7 | N/A |
| hexane | 2 | N/A | 0.008, 0.012 | | LDL[a] | 4 | 0.02 | 0.01 | 0.07 | -25.7, -27.6, -29.0 |
| benzene | 4 | 0.05 | 0.02 | 0.15 | LDL | 5 | 0.11 | 0.02 | 0.44 | -30.6 |
| heptane | 1 | 0.04 | N/A | N/A | LDL | 3 | 0.036 | 0.04 | 0.07 | -30.1 |
| toluene | 3 | 0.16 | 0.2 | 0.28 | -34.1, -41.2 | 8 | 0.18 | 0.02 | 1.05 | -27.1, -29.9, -28.9 |
| p-xylene | 1 | 0.04 | N/A | N/A | -32.7 | 1 | 0.14 | N/A | N/A[b] | -30.7 |
| nonane | 1 | 0.05 | N/A | N/A | -35.3 | 3 | 0.03 | 0.02 | 0.06 | LDL |
| decane | 1 | 0.01 | N/A | N/A | LDL | 1 | 0.01 | N/A | N/A | LDL |

(a) $\delta^{13}C$ (‰) values are not available for compounds with less than 3 ng/sample, (b) N/A-data is not available

Table 4.20 (cont'd): Statistical summary of concentrations and isotope ratios of VOC collected during BAQS-Met study, 2007 (N-number of samples) (from cartridge (A) and canister (B) samples)

B:

| Location | Ridgetown | | | | | Harrow | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Concentrations (ppbv) | | | | | Concentrations (ppbv) | | | |
| Compounds | N | Average | Median | Min | Max | N | Average | Median | Min | Max |
| i-butane | 88 | 0.13 | 0.08 | 0.01 | 0.96 | 34 | 0.19 | 0.13 | 0.03 | 0.72 |
| butane | 87 | 0.24 | 0.17 | 0.01 | 1.12 | 34 | 0.36 | 0.26 | 0.07 | 1.15 |
| pentane | 86 | 0.12 | 0.10 | 0.01 | 0.52 | 34 | 0.18 | 0.12 | 0.04 | 0.53 |
| n-hexane | 84 | 0.04 | 0.03 | DL[a] | 0.35 | 34 | 0.06 | 0.04 | 0.01 | 0.25 |
| heptane | 85 | 0.02 | 0.01 | DL | 0.08 | 34 | 0.02 | 0.02 | 0.01 | 0.09 |
| benzene | 83 | 0.09 | 0.08 | 0.02 | 0.24 | 34 | 0.11 | 0.10 | 0.06 | 0.22 |
| octane | 84 | 0.01 | 0.01 | DL | 0.03 | 34 | 0.01 | 0.01 | DL | 0.05 |
| toluene | 85 | 0.26 | 0.23 | 0.08 | 0.63 | 34 | 0.22 | 0.16 | 0.04 | 0.57 |
| nonane | 80 | 0.01 | 0.01 | DL | 0.07 | 34 | 0.01 | 0.01 | DL | 0.03 |
| ethylbenzene | 80 | 0.01 | 0.01 | DL | 0.07 | 34 | 0.02 | 0.02 | DL | 0.08 |
| p,m-Xylene | 61 | 0.09 | 0.06 | 0.01 | 0.74 | 31 | 0.06 | 0.04 | 0.01 | 0.21 |
| o-xylene | 77 | 0.01 | 0.01 | DL | 0.05 | 34 | 0.02 | 0.01 | DL | 0.06 |

(a) DL- detection limit

### 4.3.2 Environment Canada-York University campaign (2009-2010)

Averages and some basic statistics for concentrations and isotopic composition of ambient VOC in samples collected at Egbert and in Toronto during the EC-YU campaign are summarized in Table 4.21 and Table 4.22, the complete data sets are presented in Appendix A and Appendix C.

Table 4.21: Statistical summary of concentrations and isotope ratios of VOC collected at Egbert over September-December, 2009 (N-number of samples)

| | Concentrations (ppbv) | | | | | $\delta^{13}C$ (‰) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compound | N | Average | Median | Min | Max | N | Average | Median | Min | Max |
| hexane | 26 | 2.36 | 1.53 | 0.18 | 15.88 | 23 | -26.15 | -27.05 | -29.01 | -20.21 |
| benzene | 46 | 0.14 | 0.10 | 0.03 | 0.88 | 44 | -25.25 | -25.61 | -29.63 | -15.25 |
| heptane | 43 | 0.88 | 0.40 | LDL | 4.86 | 41 | -23.96 | -24.25 | -29.69 | -17.71 |
| toluene | 44 | 0.17 | 0.13 | 0.04 | 1.15 | 44 | -24.77 | -24.93 | -28.47 | -20.84 |
| octane | 22 | 0.01 | 0.01 | 0.003 | 0.05 | 1 | -31.37 | -31.37 | -31.37 | -31.37 |
| ethylbenzene | 41 | 0.03 | 0.02 | 0.01 | 0.19 | 39 | -23.66 | -23.86 | -27.89 | -10.15 |
| p,m-xylene | 41 | 0.05 | 0.03 | 0.01 | 0.47 | 39 | -23.78 | -23.83 | -29.50 | -17.18 |
| o-xylene | 42 | 0.02 | 0.01 | LDL | 0.14 | 40 | -23.36 | -23.51 | -28.41 | -16.09 |
| nonane | 28 | 0.01 | 0.004 | LDL | 0.03 | 15 | -26.98 | -28.29 | -31.22 | -17.25 |
| decane | 18 | 0.01 | 0.003 | 0.002 | 0.03 | 7 | -25.46 | -25.11 | -27.28 | -23.04 |

Table 4.22: Statistical summary of concentrations and isotope ratios of VOC collected in Toronto over September – February, 2009-2010 (N-number of samples)

| | Concentration (ppbv) | | | | | $\delta^{13}C$ (‰) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compound | N | Average | Median | Min | Max | N | Average | median | Min | Max |
| hexane | 43 | 0.61 | 0.49 | LDL | 1.66 | 25 | -25.00 | -25.10 | -28.99 | -18.98 |
| benzene | 65 | 0.13 | 0.11 | 0.02 | 0.74 | 44 | -24.99 | -26.00 | -29.40 | -13.63 |
| heptane | 32 | 0.13 | 0.10 | 0.01 | 0.29 | 13 | -24.80 | -24.87 | -30.73 | -21.52 |
| toluene | 75 | 0.63 | 0.55 | LDL | 2.11 | 73 | -24.76 | -25.68 | -28.52 | -7.73 |
| octane | 56 | 0.10 | 0.05 | LDL | 2.37 | 19 | -23.00 | -22.08 | -31.88 | -11.26 |
| ethylbenzene | 71 | 0.06 | 0.05 | LDL | 0.26 | 58 | -24.03 | -23.45 | -34.77 | -17.39 |
| p,m-xylene | 70 | 0.17 | 0.14 | LDL | 0.74 | 56 | -24.05 | -23.83 | -34.55 | -16.36 |
| o-xylene | 68 | 0.05 | 0.04 | LDL | 0.17 | 44 | -23.26 | -23.28 | -29.96 | -16.50 |
| nonane | 35 | 0.01 | 0.01 | LDL | 0.09 | 14 | -23.44 | -23.31 | -29.16 | -17.05 |
| decane | 27 | 0.01 | 0.01 | LDL | 0.04 | 16 | -26.18 | -26.38 | -33.84 | -18.74 |

### 4.3.3 Biofuel Study

Biofuel samples contained various VOC, however only benzene and toluene were presented in high enough quantities for carbon isotope ratio analysis. Results are presented in Table 4.23.

Table 4.23: Averages of five measurements of isotope ratio of benzene and toluene in exhaust of biodiesel and regular ultra low sulphur diesel fuel samples.

| Sample ID | Number of repeats | benzene | | | toluene | | |
|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C$ (‰) | $\sigma(\delta^{13}C)^a$ (‰) | Mass (ng)* | $\delta^{13}C$ (‰) | $\sigma(\delta^{13}C)^a$ (‰) | Mass (ng)$^b$ |
| Ambient Air | 5 | LDL | | 0.3 | -28.54 | 0.13 | 20.7 |
| B100-Idle | 5 | -44.49 | 0.28 | 5.3 | -32.31 | 0.17 | 9.3 |
| B100-M2 | 5 | LDL | | | -30.29 | 0.28 | 5.0 |
| RD-Idle | 5 | -24.99 | 0.78 | 2.5 | -26.10 | 0.10 | 6.7 |
| RD-M2 | 5 | LDL | | 1.6 | -27.47 | 0.21 | 5.7 |
| RD-M3 | 5 | LDL | | | -28.01 | 0.11 | 15.4 |
| RD-M5 | 4 | LDL | | | -28.98 | 0.21 | 14.8 |

(a) σ- standard deviation calculated from repeated measurements (4 or 5). (b) Mass of VOC per injection

### 4.3.4 Characteristics and trends of ambient VOC concentrations from four different sampling locations

Box and whisker plots of VOC concentrations determined for Harrow, Ridgetown, Egbert and Toronto sampling sites are shown in Figure 4.5.

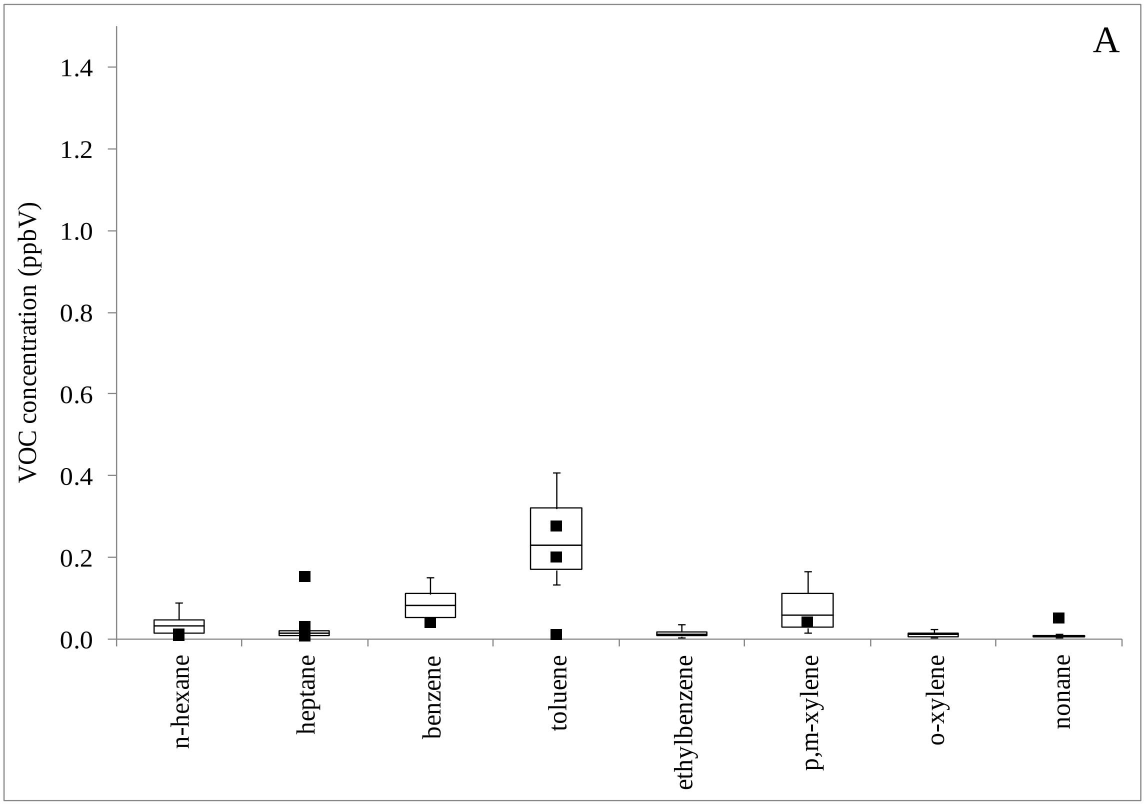


Figure 4.5: Box-and-whisker plot representing statistical analysis of concentration values of some volatile organic compounds determined from canister samples and concentrations determined from cartridge samples (Harrow (A), Ridgetown (B), Egbert (C), Toronto (D)). Upper quartile (75%) and lower quartile (25%) are indicated by upper and lower ends of the boxes and medians by vertical bars within the boxes, 10% and 90% by the end points of the vertical lines. Black triangles and squares in A and B are VOC concentrations from cartridge samples. For Egbert data for hexane (median=1.53, 25th percentile=0.87 and 75th percentile 1.96) and heptane (median=0.40, 25th percentile=0.20 and 75th percentile 1.05) are omitted to scale down Y-axes and focus on VOC with lower mixing ratios.

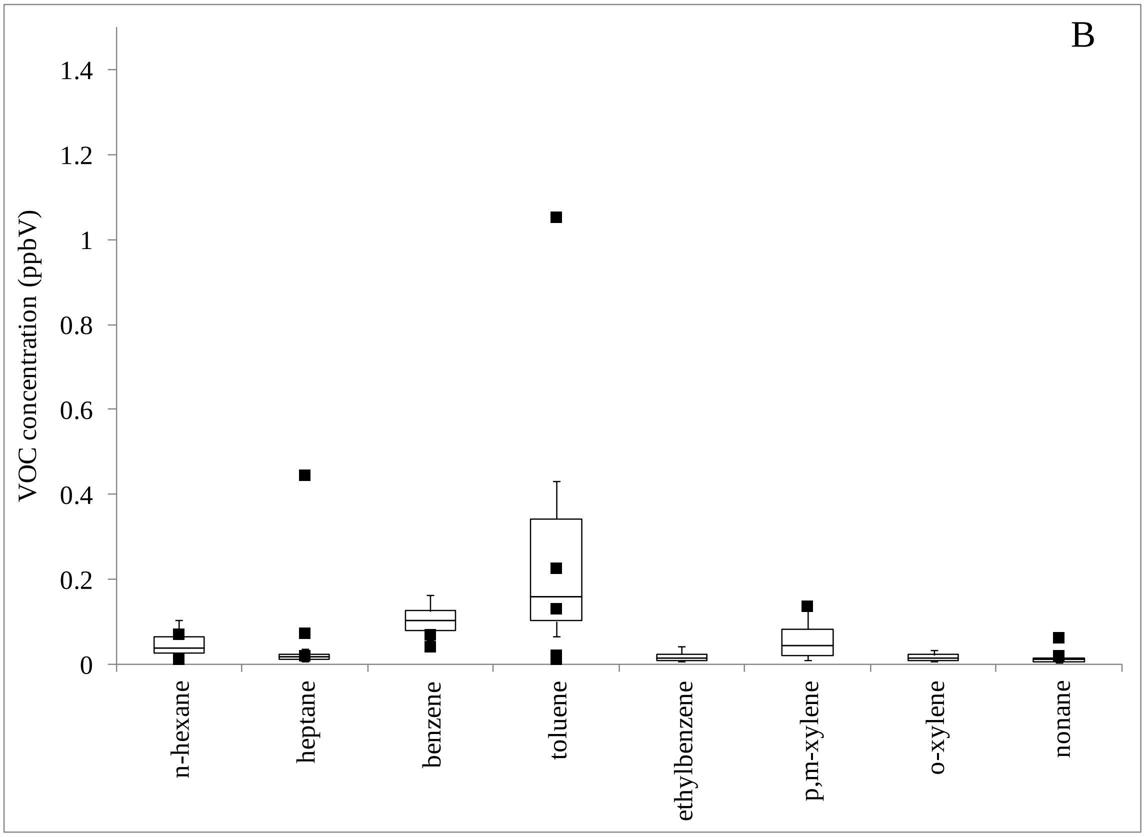


Figure 4.5 (cont'd): Box-and-whisker plot representing statistical analysis of concentration values of some volatile organic compounds determined from canister samples and concentrations determined from cartridge samples (Harrow (A), Ridgetown (B), Egbert (C), Toronto (D)). Upper quartile (75%) and lower quartile (25%) are indicated by upper and lower ends of the boxes and medians by vertical bars within the boxes, 10% and 90% by the end points of the vertical lines. Black triangles and squares in A and B are VOC concentrations from cartridge samples. For Egbert data for hexane (median=1.53, 25th percentile=0.87 and 75th percentile 1.96) and heptane (median=0.40, 25th percentile=0.20 and 75th percentile 1.05) are omitted to scale down Y-axes and focus on VOC with lower mixing ratios.

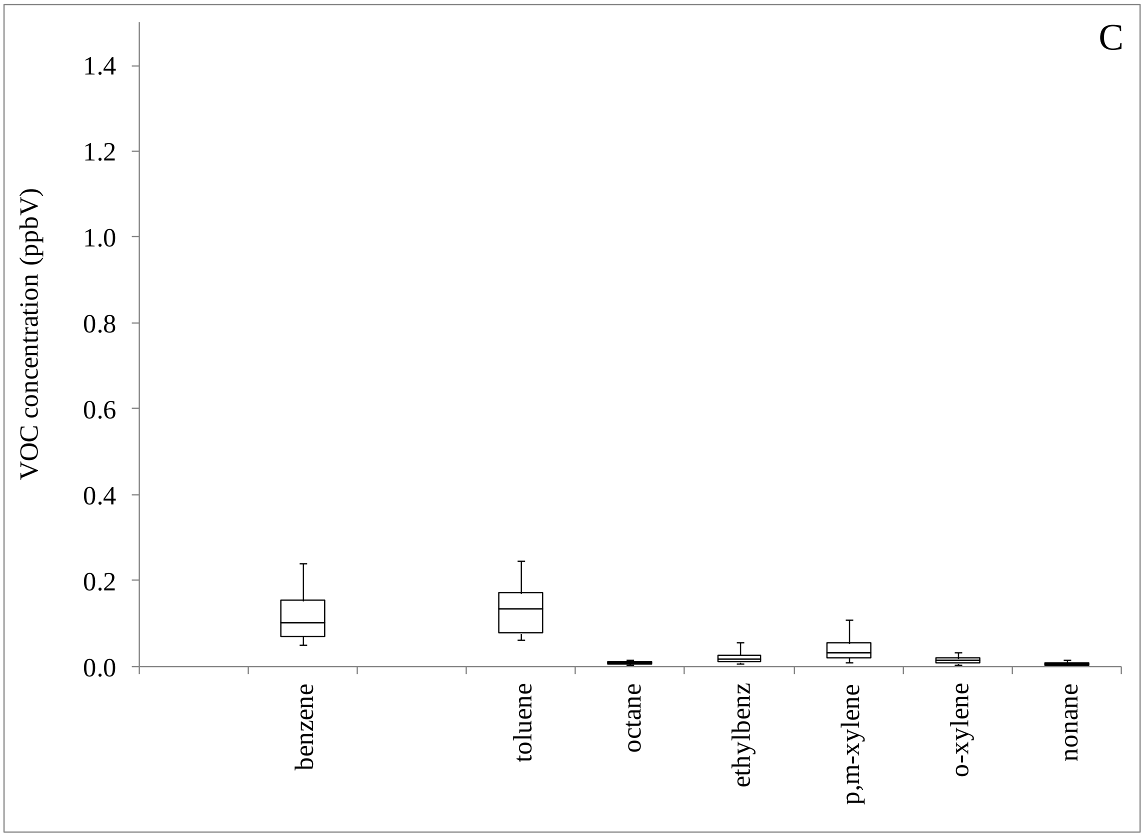


Figure 4.5 (cont'd): Box-and-whisker plot representing statistical analysis of concentration values of some volatile organic compounds determined from canister samples and concentrations determined from cartridge samples (Harrow (A), Ridgetown (B), Egbert (C), Toronto (D)). Upper quartile (75%) and lower quartile (25%) are indicated by upper and lower ends of the boxes and medians by vertical bars within the boxes, 10% and 90% by the end points of the vertical lines. Black triangles and squares in A and B are VOC concentrations from cartridge samples. For Egbert data for hexane (median=1.53, 25th percentile=0.87 and 75th percentile 1.96) and heptane (median=0.40, 25th percentile=0.20 and 75th percentile 1.05) are omitted to scale down Y-axes and focus on VOC with lower mixing ratios.

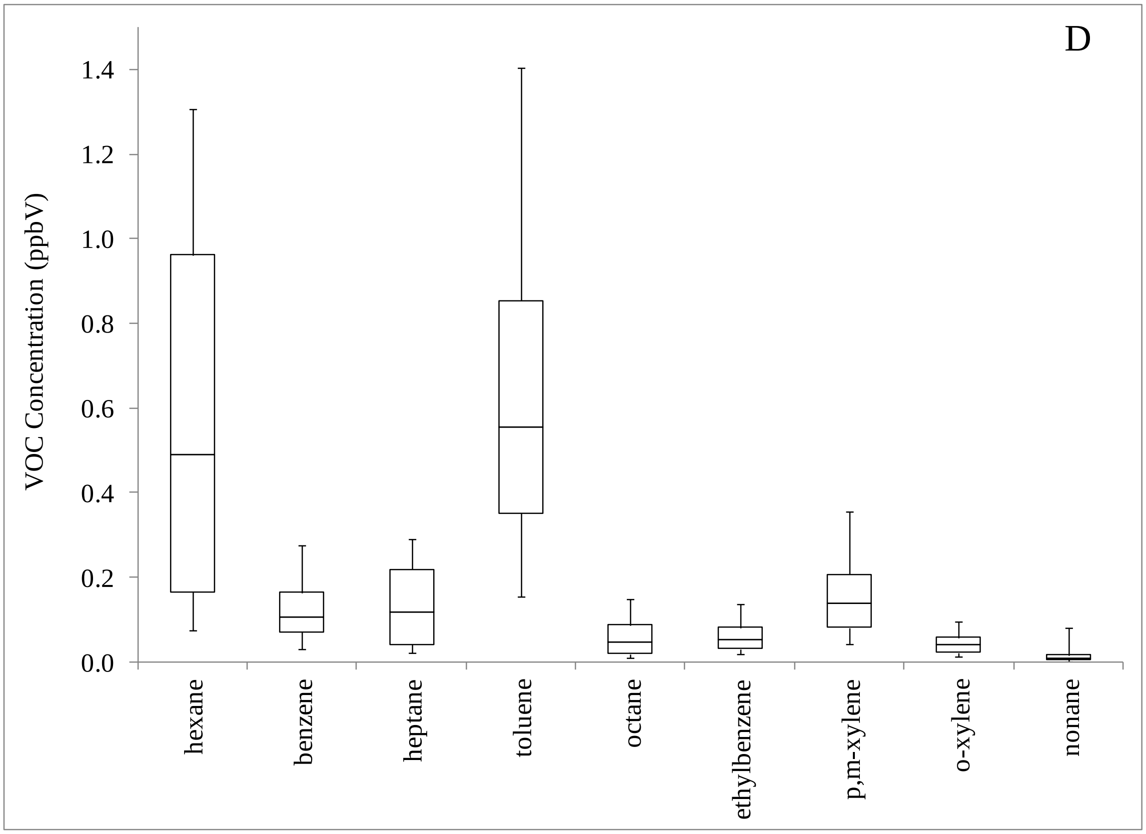


Figure 4.5 (cont'd): Box-and-whisker plot representing statistical analysis of concentration values of some volatile organic compounds determined from canister samples and concentrations determined from cartridge samples (Harrow (A), Ridgetown (B), Egbert (C), Toronto (D)). Upper quartile (75%) and lower quartile (25%) are indicated by upper and lower ends of the boxes and medians by vertical bars within the boxes, 10% and 90% by the end points of the vertical lines. Black triangles and squares in A and B are VOC concentrations from cartridge samples. For Egbert data for hexane (median=1.53, 25th percentile=0.87 and 75th percentile 1.96) and heptane (median=0.40, 25th percentile=0.20 and 75th percentile 1.05) are omitted to scale down Y-axes and focus on VOC with lower mixing ratios.

VOC concentrations in Toronto samples were higher than those determined in Egbert, Harrow and Ridgetown (Table 4.20, Table 4.21, Table 4.22, Figure 4.5), with the exception of hexane and heptane for which the highest average values were found in samples from Egbert. The lowest concentrations for most of the compounds were observed at Ridgetown, although overall concentrations of VOC from Harrow samples were similar.

Frequency distributions of VOC mixing ratios for Toronto and Egbert are compared in Figure 4.6. Except for hexane and heptane there are fewer data with high VOC mixing ratios at Egbert compared to Toronto samples.

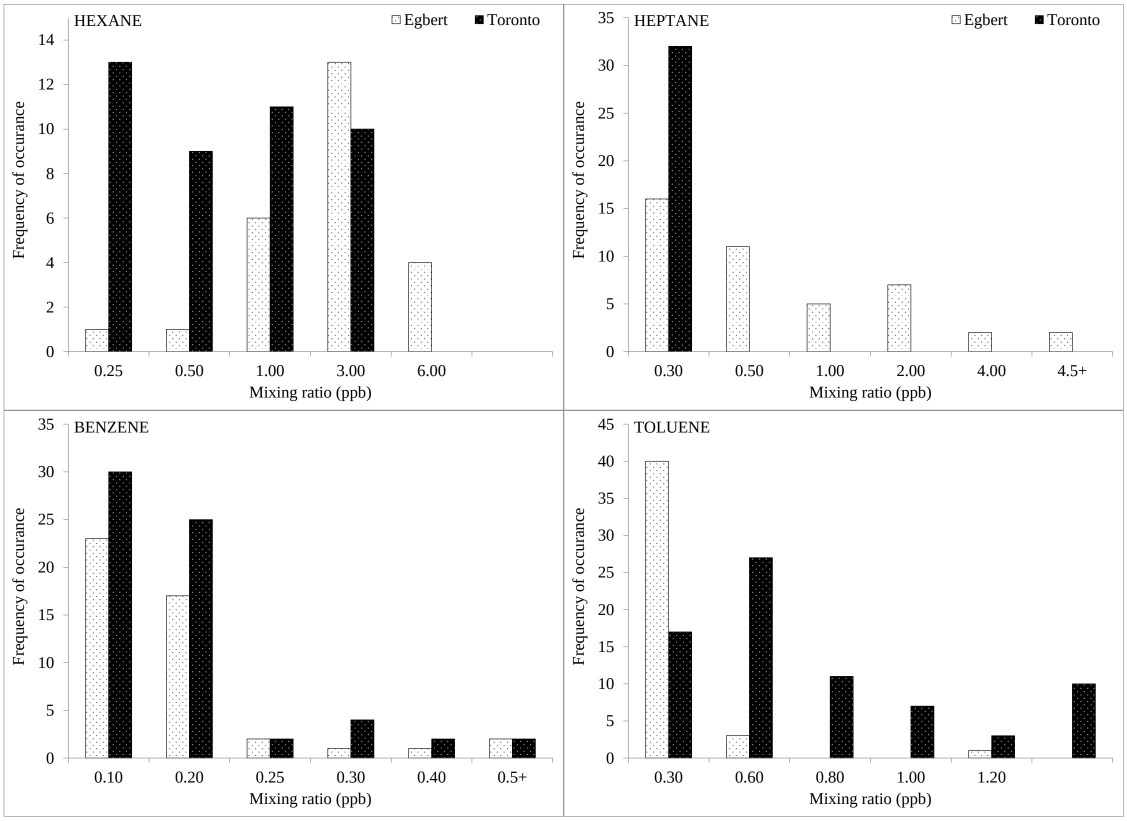


Figure 4.6: Frequency distribution of observed VOC mixing ratios (ppbv) in Egbert and Toronto samples.

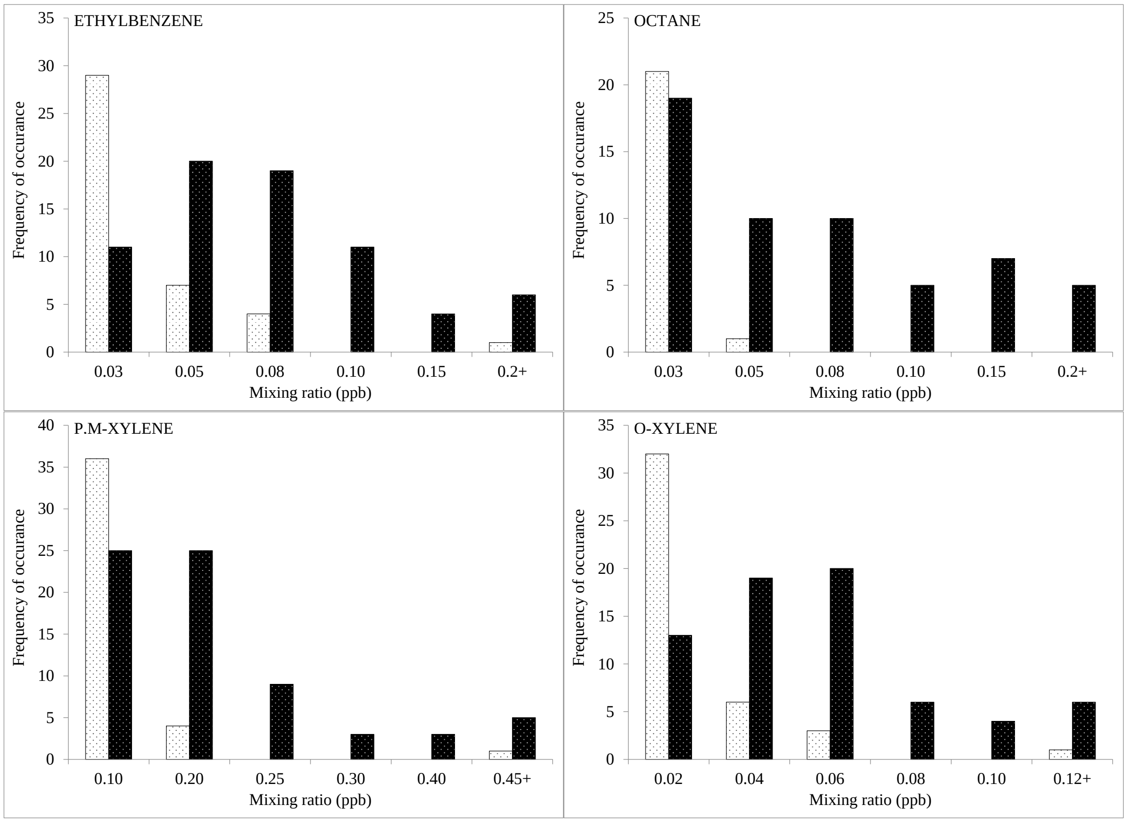


Figure 4. 6 (cont'd): Frequency distribution of observed VOC mixing ratios (ppbv) in Egbert and Toronto samples.

Seasonal averages and variability of VOC concentrations for Egbert and Toronto for fall (October-November), winter (December-January), spring (March), and summer (August-September) are shown in Figure 4.7.

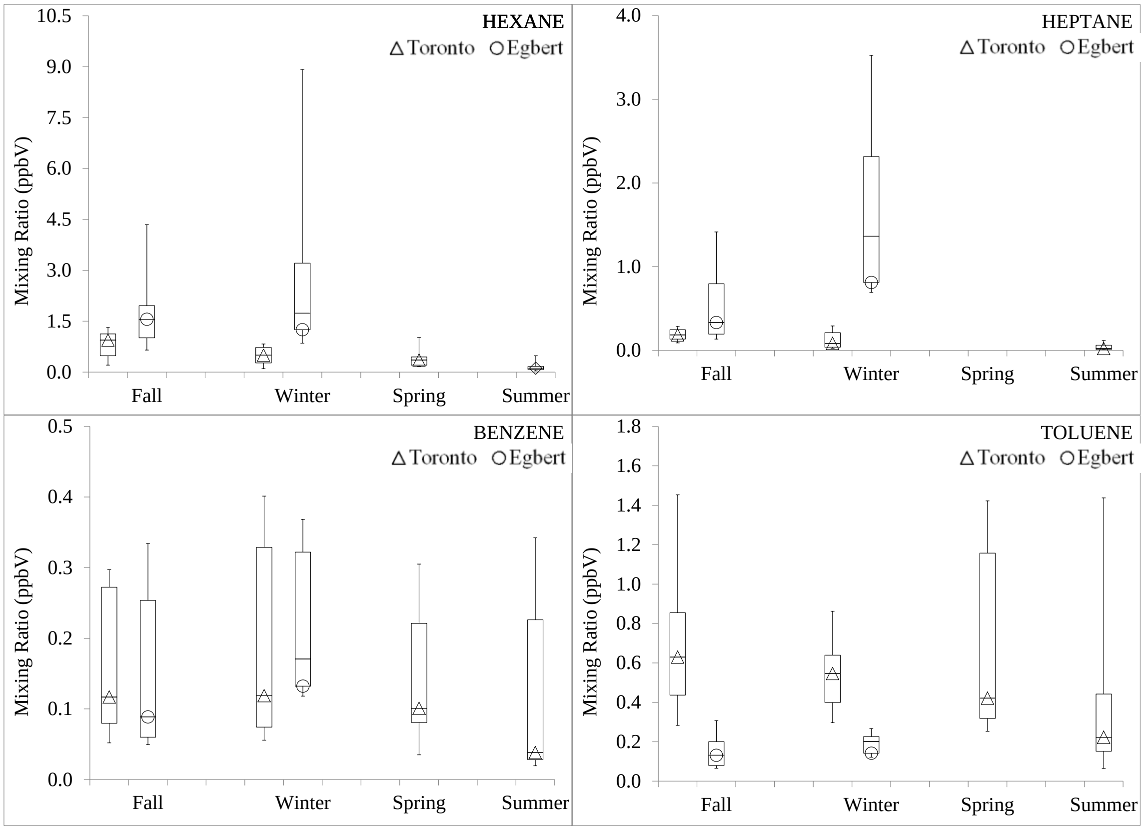


Figure 4.7: Box-and-whisker plots showing the distribution of values for ambient VOC concentrations observed during EC-YU campaign (Fall 2009-Summer 2010). Upper quartile (75%) and lower quartile (25%) are indicated by upper and lower ends of the boxes and medians by vertical bars within the boxes, 10% and 90% by the end points of the vertical lines. Triangles and circles are medians for Toronto and Egbert samples respectively.

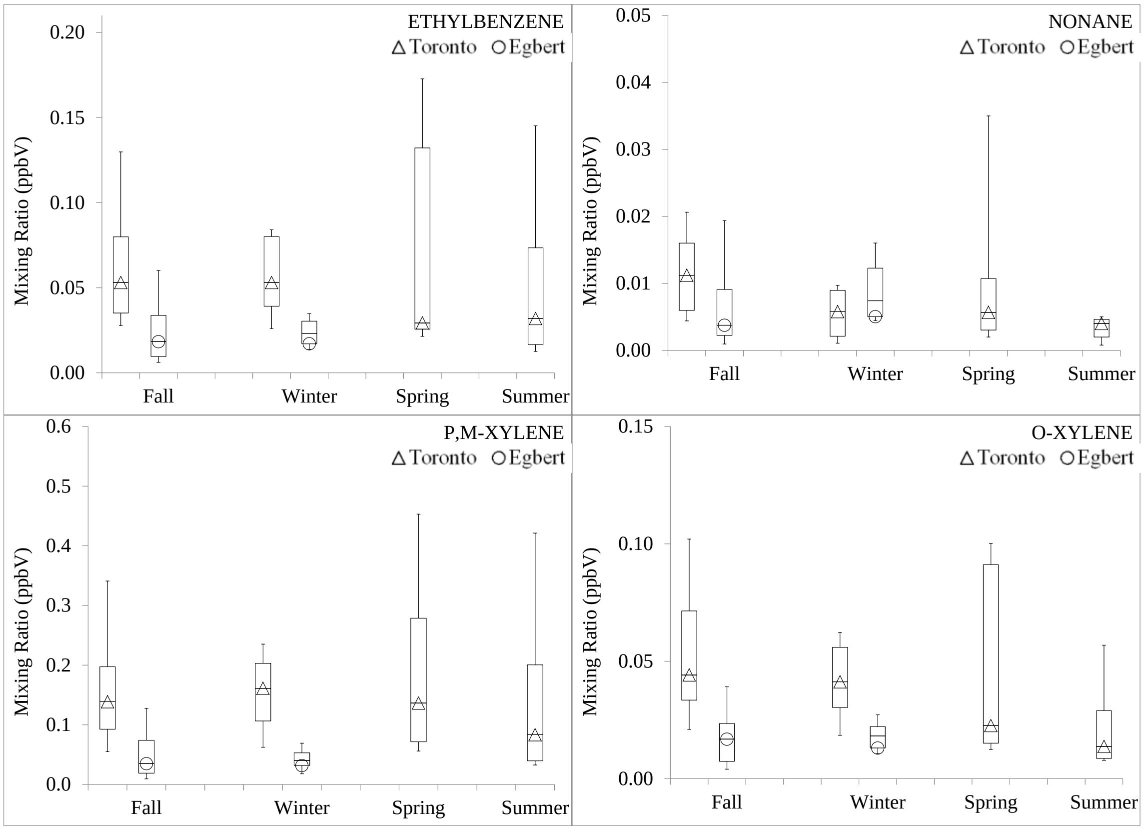


Figure 4.7 (cont'd): Box-and-whisker plots showing the distribution of values for ambient VOC concentrations observed during EC-YU campaign (Fall 2009-Summer 2010). Upper quartile (75%) and lower quartile (25%) are indicated by upper and lower ends of the boxes and medians by vertical bars within the boxes, 10% and 90% by the end points of the vertical lines. Triangles and circles are medians for Toronto and Egbert samples respectively.

While sinusoidal curves of concentrations with maxima values in winter and minima in summer [*Helmig et al.*, 2008; *Rudolph*, 1995] are not clearly observed for Toronto due to the high variability of data, generally the median concentrations for all compounds were lower in summer than winter (Figure 4.7).

Some VOC were highly correlated in concentrations, while others did not show any visible dependencies (Table 4.24, Appendix D)

Table 4.24: Correlation in concentrations of some VOC from Egbert and Toronto samples.

| Location | | Egbert | Toronto |
|---|---|---|---|
| Compound 1 | Compound 2 | $R^2$ | $R^2$ |
| heptane | hexane | 0.87 | 0.24 |
| benzene | hexane | 0.06 | 0.04 |
| benzene | ethylbenzene | 0.13 | 0.003 |
| toluene | benzene | 0.25 | 0.07 |
| toluene | hexane | 0.005 | 0.12 |
| toluene | ethylbenzene | 0.87 | 0.52 |
| toluene | p,m-xylene | 0.88 | 0.51 |
| toluene | o-xylene | 0.87 | 0.61 |

### 4.3.5 Stable carbon isotope composition of atmospheric VOC from BAQS and EC-YU campaigns

Though being from different sampling sites, results of the stable carbon isotope ratios determined for Harrow, Ridgetown, Egbert and Toronto compounds were somewhat similar to each other. However the spread was larger for most of the VOC from Toronto samples (Figure 4.8 B and Figure 4.8 C). Due to the limited data available, results for Ridgetown and Harrow were not combined and are presented as individual points (Figure 4.8 A), but it is visible that all of the Harrow delta values were heavier than those observed in Egbert and Toronto samples.

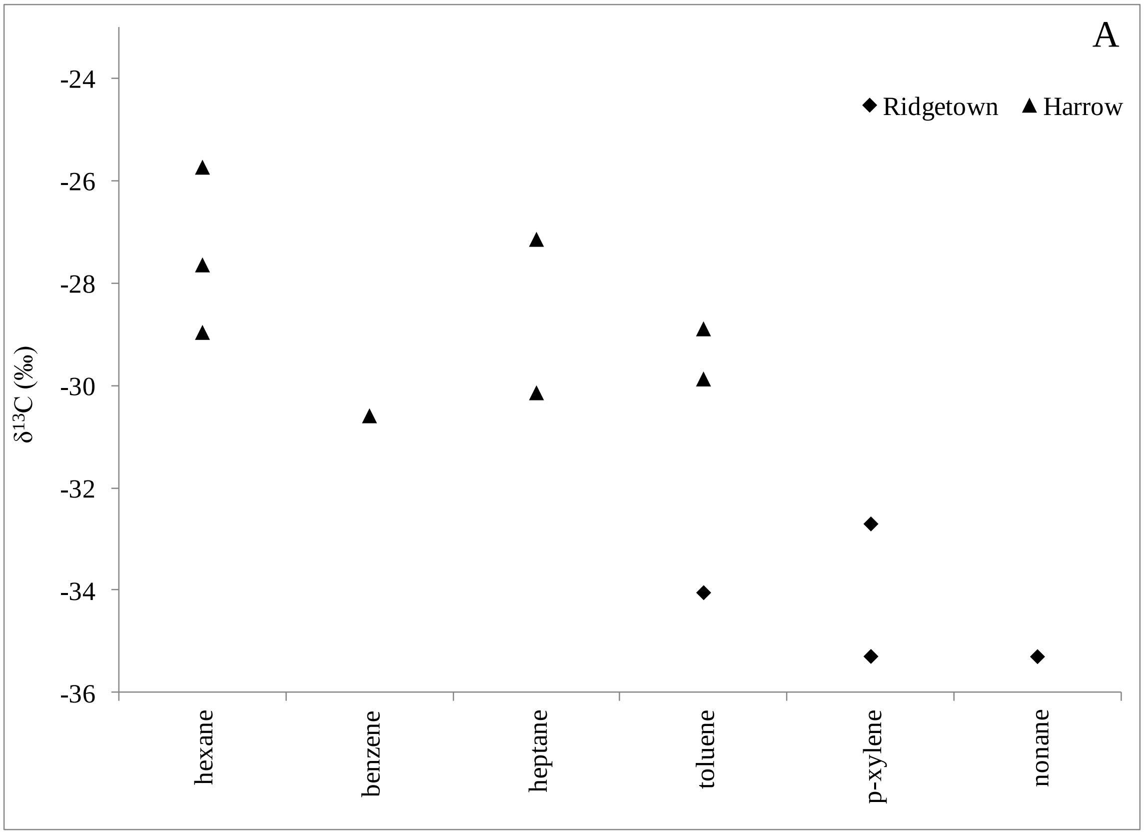


Figure 4.8: Stable carbon isotope ratios for BAQS and EC-YU samples. (A) Harrow and Ridgetown samples. Delta value for toluene from one Ridgetown sample (-41.2‰) is not shown. (B) and (C) Box-and-whisker plots representing statistical overview of delta values for VOC samples (Egbert (B), Toronto (C)). Upper quartile (75%) and lower quartile (25%) are indicated by upper and lower ends of the boxes and medians by vertical bars within the boxes, 10% and 90% by the end points of the vertical lines.

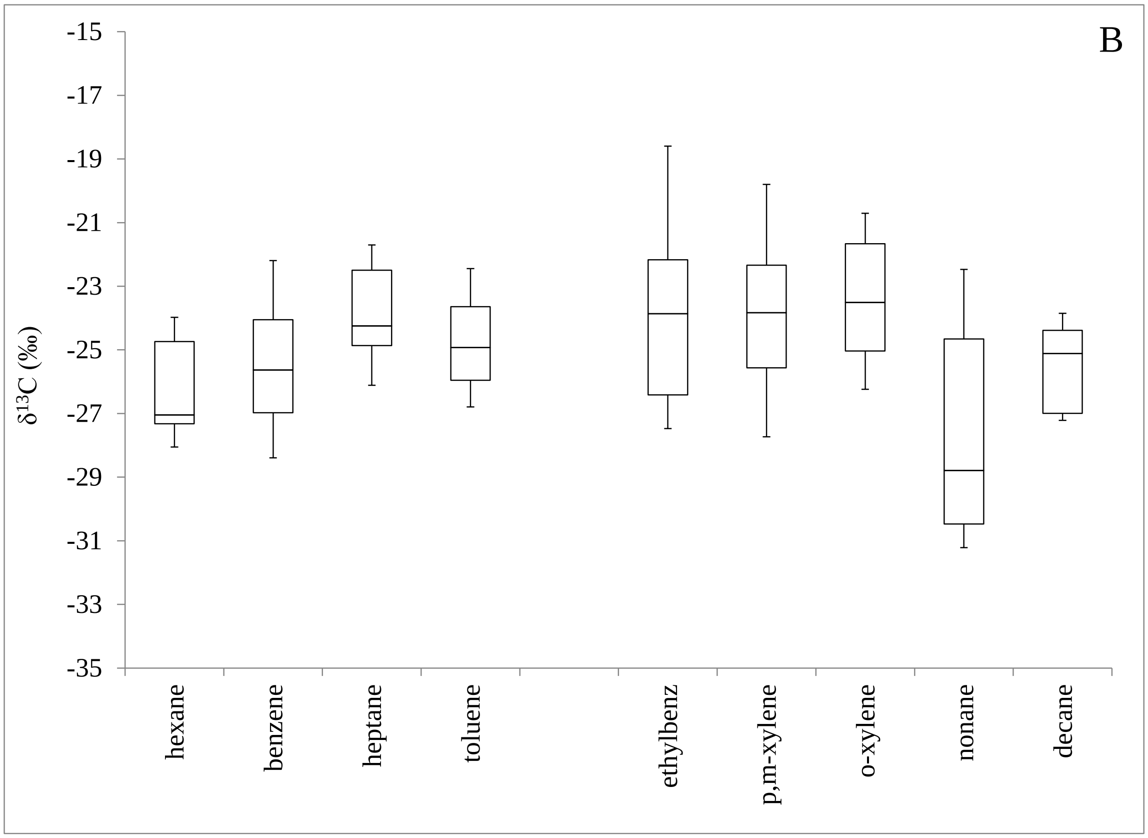


Figure 4.8 (cont'd): Stable carbon isotope ratios for BAQS and EC-YU samples. (A) Harrow and Ridgetown samples. Delta value for toluene from one Ridgetown sample (-41.2‰) is not shown. (B) and (C) Box-and-whisker plots representing statistical overview of delta values for VOC samples (Egbert (B), Toronto (C)). Upper quartile (75%) and lower quartile (25%) are indicated by upper and lower ends of the boxes and medians by vertical bars within the boxes, 10% and 90% by the end points of the vertical lines.

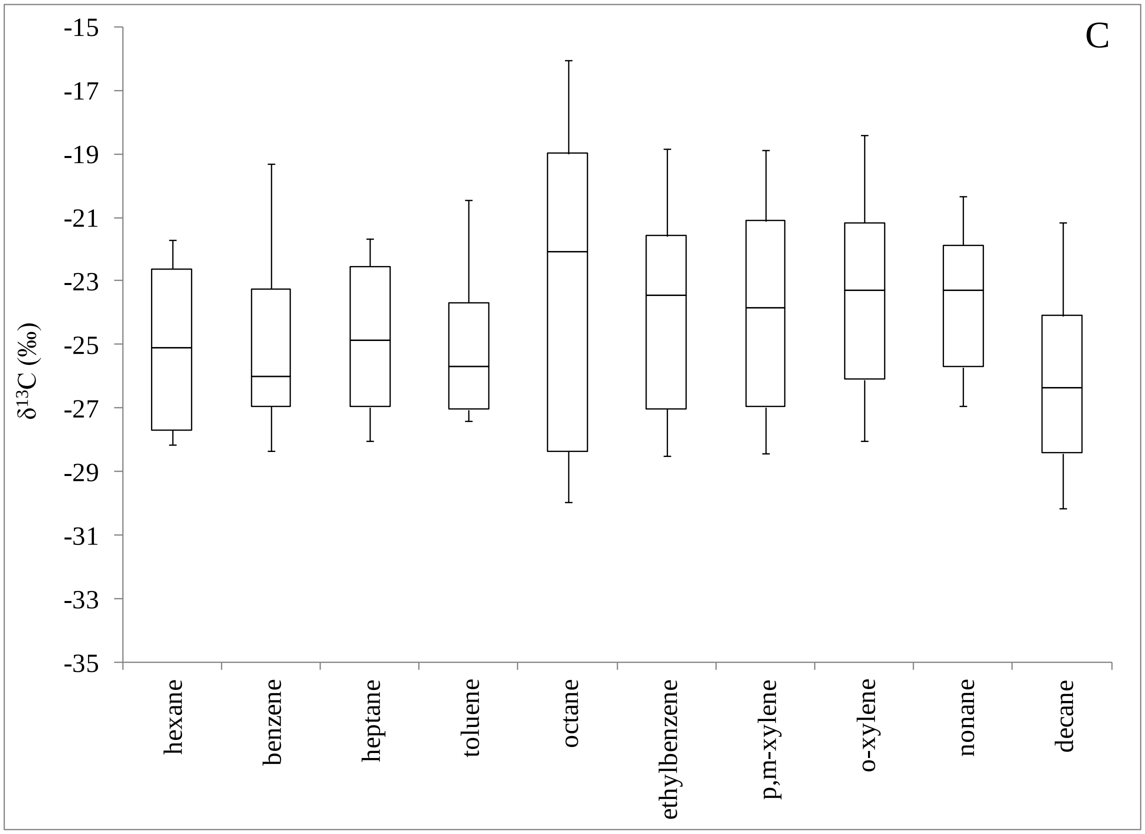


Figure 4.8 (cont'd): Stable carbon isotope ratios for BAQS and EC-YU samples. (A) Harrow and Ridgetown samples. Delta value for toluene from one Ridgetown sample (-41.2‰) is not shown. (B) and (C) Box-and-whisker plots representing statistical overview of delta values for VOC samples (Egbert (B), Toronto (C)). Upper quartile (75%) and lower quartile (25%) are indicated by upper and lower ends of the boxes and medians by vertical bars within the boxes, 10% and 90% by the end points of the vertical lines.

Seasonal variations of the isotope ratios of VOC are given for Toronto by combining available data into four seasonal subsets: fall (October-November), winter (December-January), spring (March), and summer (August-September) in Figure 4.9.

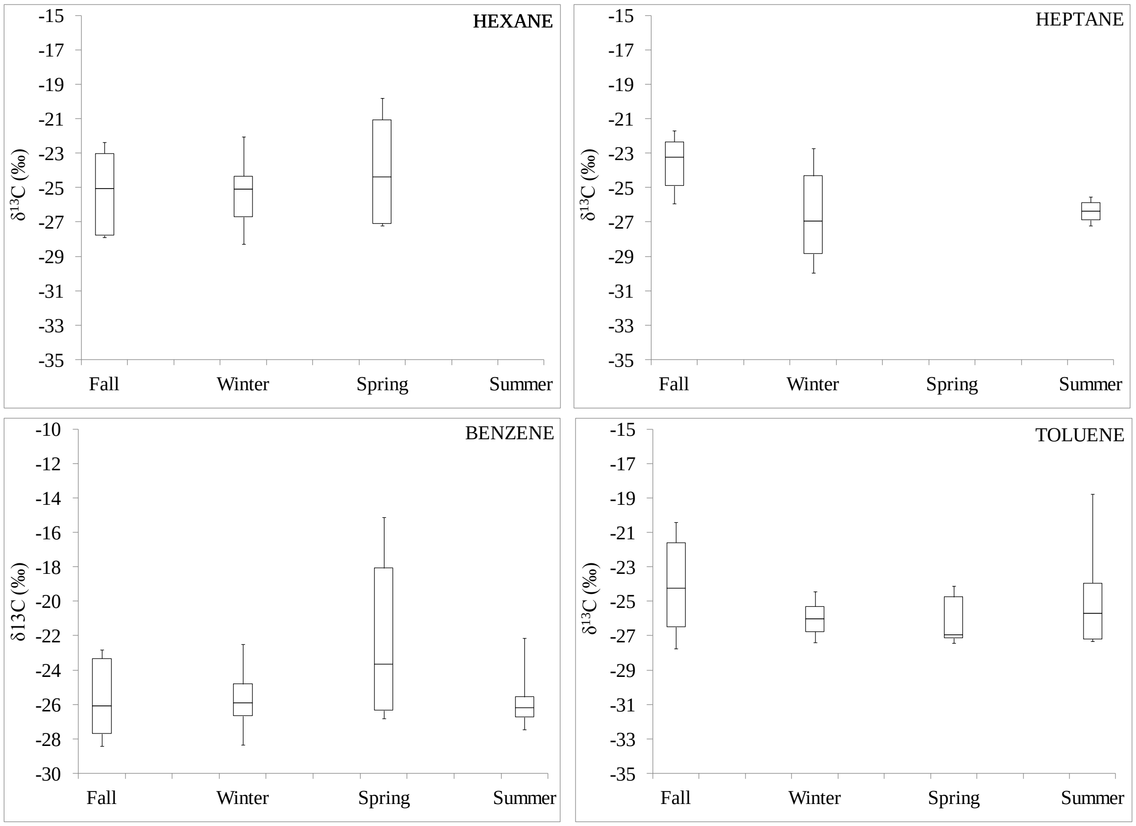


Figure 4.9: Box-and-whisker plots showing the season variation in distribution of delta values for ambient VOC for Toronto samples (Fall 2009-Summer 2010). Upper quartile (75%) and lower quartile (25%) are indicated by upper and lower ends of the boxes and medians by vertical bars within the boxes, 10% and 90% by the end points of the vertical lines.

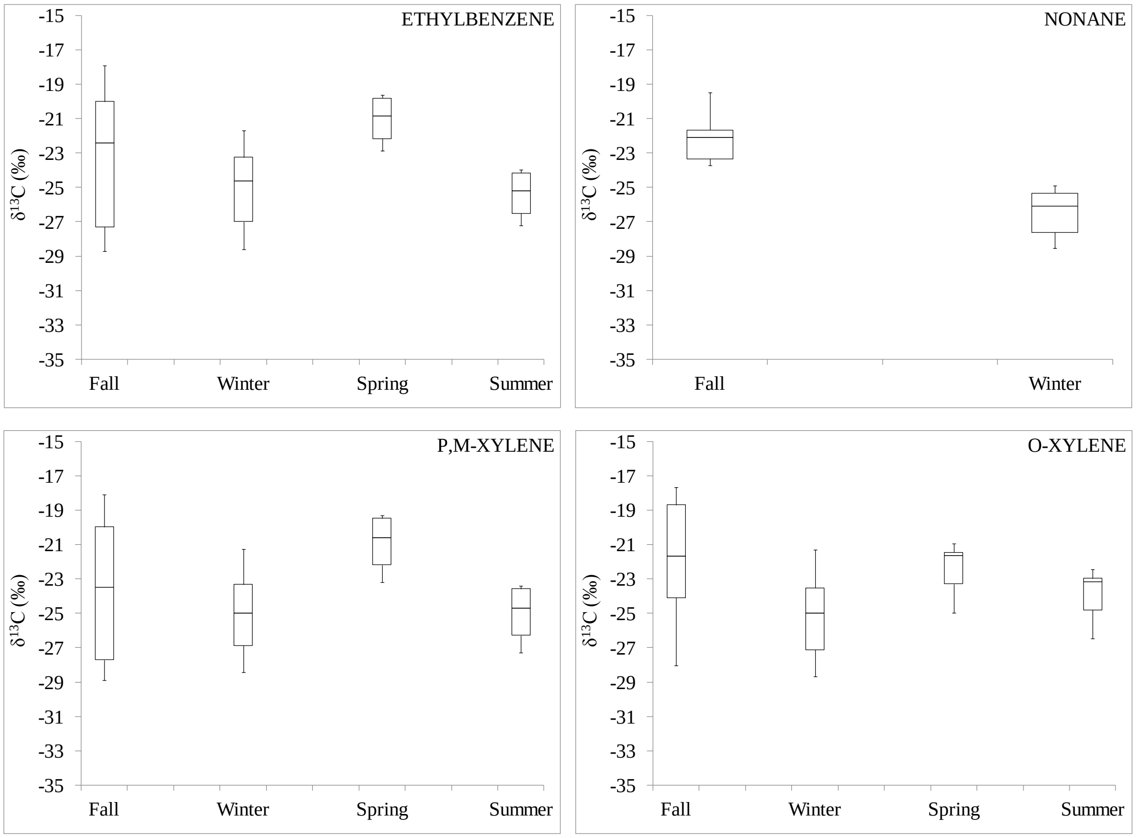


Figure 4.9 (cont'd): Box-and-whisker plots showing the season variation in distribution of delta values for ambient VOC for Toronto samples (Fall 2009-Summer 2010). Upper quartile (75%) and lower quartile (25%) are indicated by upper and lower ends of the boxes and medians by vertical bars within the boxes, 10% and 90% by the end points of the vertical lines.

Higher medians of delta values in fall and spring and lower in winter were observed for the compounds of high reactivity: toluene, ethylbenzene and xylenes. There was also a decrease in variability in the spring and summer data subsets of some aromatics compared to fall and winter.

Similarly as for concentrations, correlations of delta values were examined and are provided in Appendix E. However no strong correlations were observed. While delta values for some compounds were somewhat correlated (i.e toluene and hexane for

Egbert; toluene and ethylbenzene, p,m-xylene and o-xylene for Toronto samples), for others correlation was completely absent (benzene and hexane, toluene and ethylbenzene for Egbert; benzene and ethylbenzene, toluene and benzene for Toronto) (Table 4.25).

Table 4.25: Correlation in isotope composition of some VOC from Egbert and Toronto samples.

| Location | | Egbert | Toronto |
|---|---|---|---|
| Compound 1 | Compound 2 | $R^2$ | $R^2$ |
| heptane | hexane | 0.04 | N/A |
| benzene | hexane | 0.07 | 0.30 |
| benzene | ethylbenzene | 0.04 | 0.02 |
| toluene | benzene | 0.10 | 0.003 |
| toluene | hexane | 0.41 | 0.05 |
| toluene | ethylbenzene | $10^{-6}$ | 0.36 |
| toluene | p,m-xylene | 0.02 | 0.33 |
| toluene | o-xylene | 0.04 | 0.36 |

### 4.3.6 Photochemical Ages

*4.3.6.1 PCA determined from hydrocarbon clock*

Mixing ratios of VOC were used to determined PCA by regression analysis of $\ln\frac{[VOC]_t}{[VOC]_o}$ versus $k_{OH}$ (equation 2.9) (as described in 2.3.1). Two different reference samples were assigned for BAQS and EC-YU samples. For Ridgetown and Harrow, the average of 21 samples measured in June-July of 2007 in downtown Windsor (Courtesy of Ministry of Environment) and for Toronto and Egbert, the average of 4 samples measured in winter of 2002 in downtown Toronto were used [*Thompson*, 2003] (Table 4.26).

Compounds with low background concentrations, wide reactivity range, high ambient concentrations and known emission sources [*Kleinman et al.*, 2003b] were chosen for the VOC-$k_{OH}$ correlation analysis. These VOC and their rate constants ($k_{OH}$) for reactions with OH radicals used in the PCA calculations for BAQS and EC-YU data are listed in Table 4.26. More VOC were available for BAQS analysis since results from canister samples were available, while for EC-YU only cartridge sampling was used (3.2). Figure 4.10 contains an example of the regression plot for one of the Harrow samples.

Table 4.26: VOC and OH rate constants used for the PCA calculations for Harrow and Ridgetown (BAQS[c]) and Toronto and Egbert (EC-YU)

| Compound | $10^{12}$ x $k^a$ (298K) $cm^3 molec^{-1} s^{-1}$ | Compound used[b] BAQS | EC-YU |
|---|---|---|---|
| 2-methylbutane | 3.6 | √ | |
| 2-methylpentane | 5.2 | √ | |
| 3-methylpentane | 5.2 | √ | |
| acetylene | 0.912 | √ | |
| benzene | 1.22 | √ | √ |
| cyclohexane | 6.97 | √ | |
| ethylbenzene | 7 | √ | √ |
| isobutane | 2.12 | √ | |
| butane | 2.36 | √ | |
| hexane | 5.2 | √ | √ |
| pentane | 3.8 | √ | |
| o-xylene | 13.6 | √ | √ |
| p,m-xylene | 18.7 | √ | √ |
| toluene | 5.63 | √ | √ |
| heptane | 6.76 | | √ |
| octane | 8.11 | | √ |
| nonane | 9.7 | | √ |

(a) The rate constants were taken from Atkinson [2003a]and Finlayson-Pitts and Pits [2000], (b) Compounds used (√) in the PCA calculations, (c) For BAQS calculations data from canister samples was used

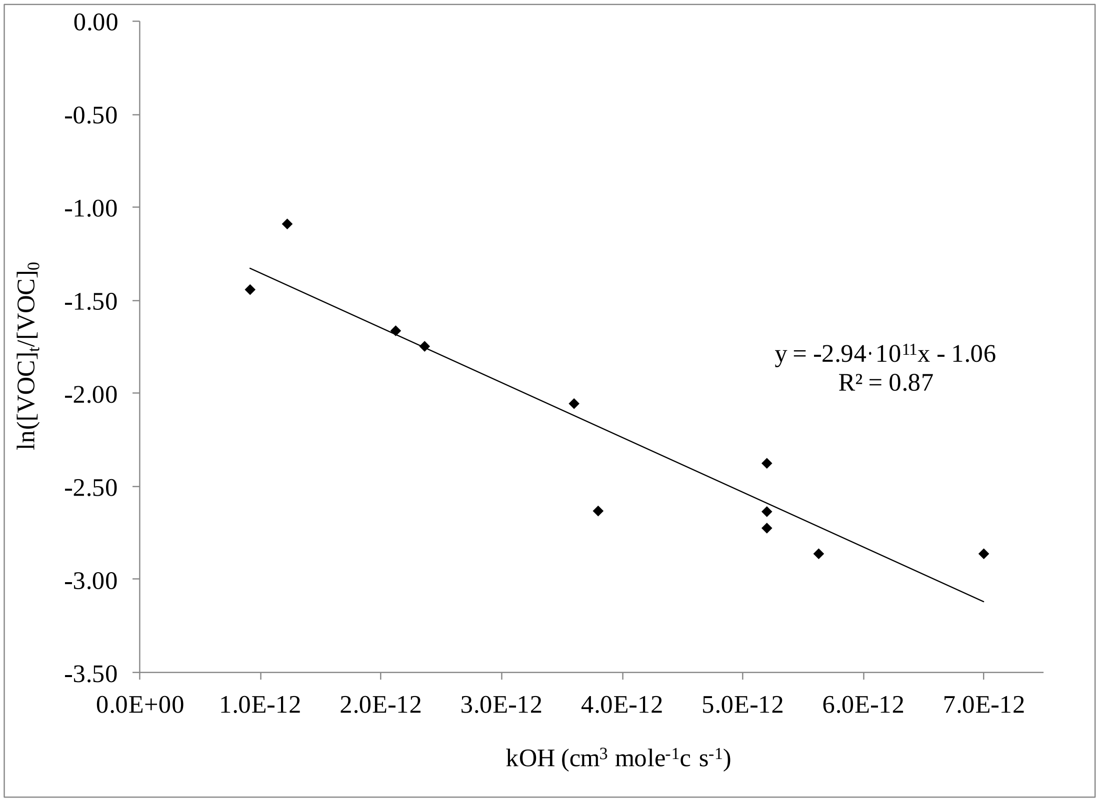


Figure 4.10: Regression plot of $\ln\frac{[VOC]_t}{[VOC]_o}$ versus $k_{OH}$ for Harrow sample (6/21/2007 12:48PM)

A summary of photochemical age values and dilution factors determined from the least square analysis and their statistical analyses is given in Table 4.27 and Table 4.28. A complete data set is provided in Appendix F. For some samples certain compounds were not used in the analysis to maintain linearity of the regression line. Apparent outliers contained abnormal concentration values (due to unusual source or measurement error) and were visible on regression plots. Removal of such a value usually changed the correlation coefficient ($R^2$) from less than 0.2-0.3 to more than 0.5-0.6.

Table 4.27: Photochemical Ages and their statistical analysis for Harrow, Ridgetown, Egbert and Toronto data sets.

| Parameter | N[a] | Photochemical Age (s molecules cm$^{-3}$) | | | | | |
|---|---|---|---|---|---|---|---|
| Location | | Average | σ[b] | min | max | 50 pct[c] | 75 pct |
| Harrow[d] | 34 | $1.41\times10^{11}$ | $0.85\times10^{11}$ | $-0.25\times10^{11}$ | $3.01\times10^{11}$ | $1.40\times10^{11}$ | $1.96\times10^{11}$ |
| Ridgetown[d] | 88 | $1.14\times10^{11}$ | $0.67\times10^{11}$ | $-0.79\times10^{11}$ | $3.12\times10^{11}$ | $1.17\times10^{11}$ | $1.50E\times10^{11}$ |
| Egbert[e] | 38 | $0.66\times10^{11}$ | $0.47\times10^{11}$ | $0.06\times10^{11}$ | $2.17\times10^{11}$ | $0.48\times10^{11}$ | $0.87\times10^{11}$ |
| Toronto[e] | 61 | $0.57\times10^{11}$ | $0.36\times10^{11}$ | $0.01\times10^{11}$ | $1.42\times10^{11}$ | $0.56\times10^{11}$ | $0.81\times10^{11}$ |

(a) Number of measurements, (b) σ- standard deviation, (c) - percentile. PCA calculations were performed using concentrations determined from canister samples (d) and cartridge samples (e).

Table 4.28: Dilution factors and their statistical analysis for Harrow, Ridgetown, Egbert and Toronto data sets.

| Parameter | N[a] | Dilution Factor | | | | | |
|---|---|---|---|---|---|---|---|
| Location | | Average | σ[b] | min | max | 50 pct[c] | 75 pct |
| Harrow[d] | 34 | 0.48 | 0.24 | 0.17 | 1.00 | 0.41 | 0.57 |
| Ridgetown[d] | 88 | 0.33 | 0.23 | 0.04 | 1.16 | 0.28 | 0.46 |
| Egbert[e] | 38 | 0.17 | 0.16 | 0.03 | 0.72 | 0.11 | 0.21 |
| Toronto[e] | 61 | 0.53 | 0.28 | 0.05 | 1.11 | 0.56 | 0.71 |

(a) Number of measurements, (b) σ-standard deviation, (c) - percentile. PCA calculations were performed using concentrations determined from canister samples (d) and cartridge samples (e).

Complete time series for the determined photochemical ages and dilution factors are illustrated in Appendix F. Overall, lower PCA values were observed in Toronto and Egbert compared to Harrow and Ridgetown (Table 4.27). Similarly, less dilution was observed in Toronto compared to Egbert, and Harrow compared to Ridgetown (Table 4.28).

PCA and correlation coefficient ($R^2$) of VOC-$k_{OH}$ graphs are compared in Figure 4.11.

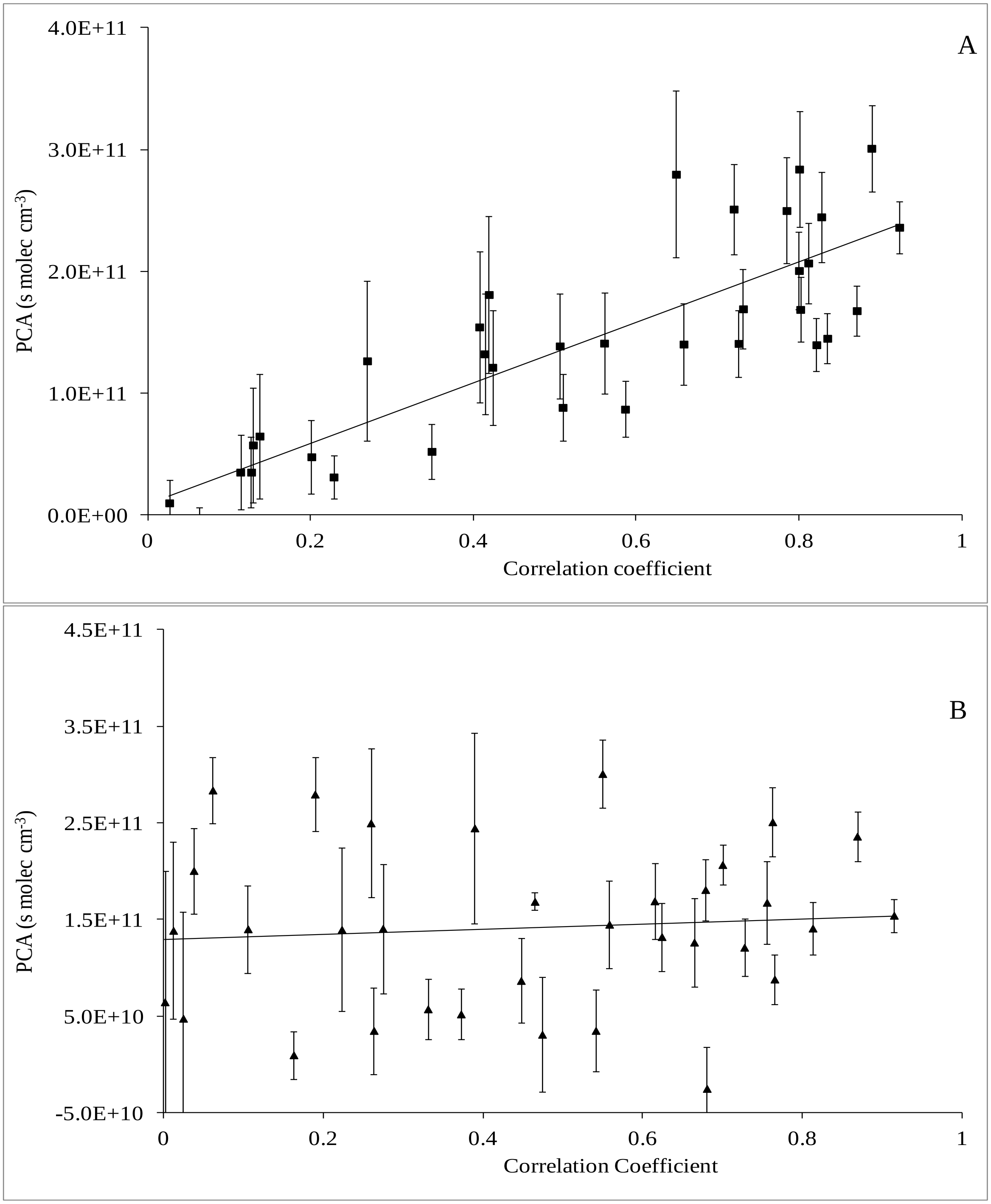


Figure 4.11: Dependence between photochemical Age and correlation coefficient for Harrow (A), Ridgetown (B), Egbert (C) and Toronto (D) samples

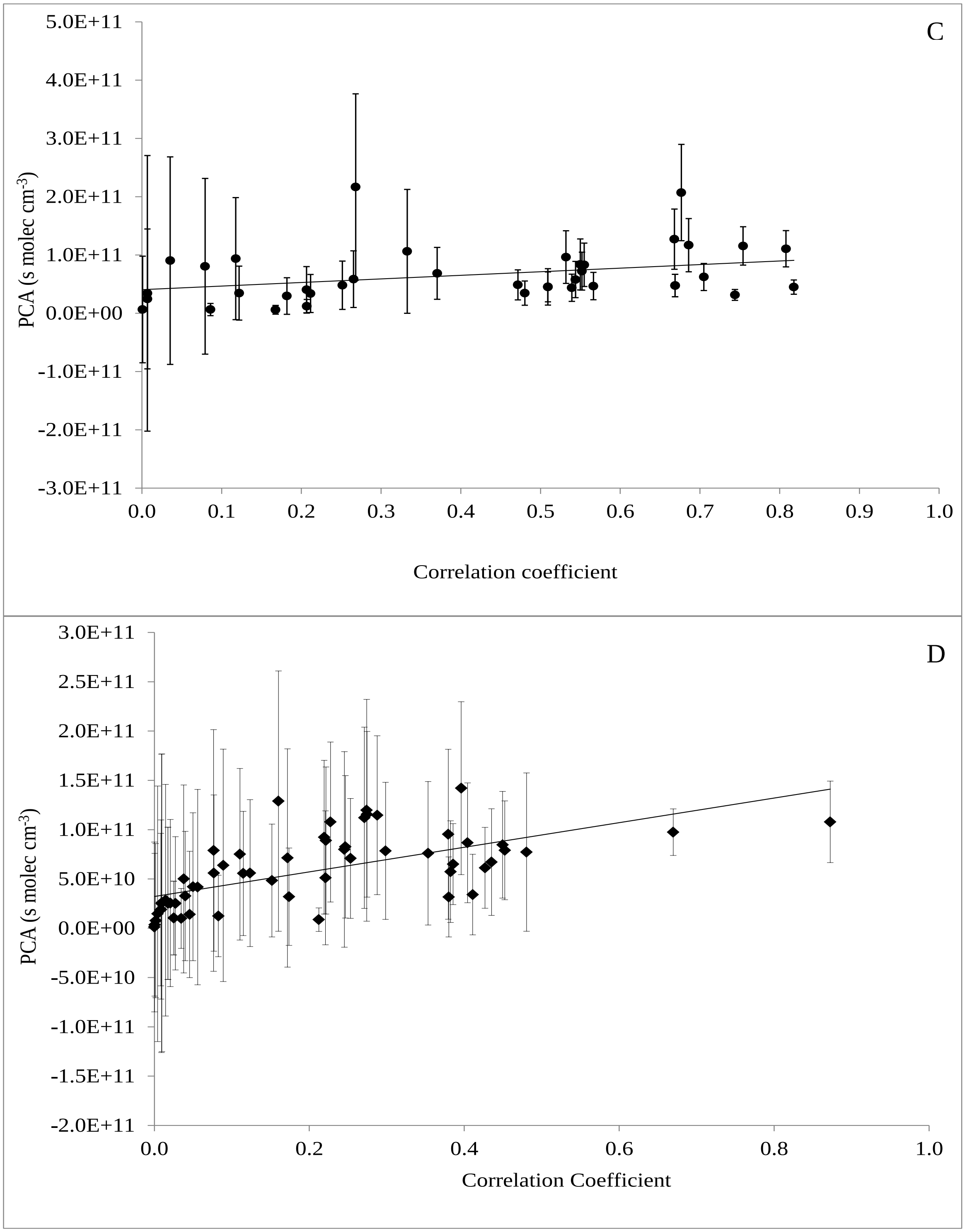


Figure 4.11 (cont'd): Dependence between photochemical Age and correlation coefficient for Harrow (A), Ridgetown (B), Egbert (C) and Toronto (D) samples

Another approach for the determination of photochemical ages used was based on concentration ratios of a specific pair of VOC (described in Section 2.3.1). A reference zero-time point sample that defines road-related emissions was determined by combining several tunnel studies (1993-2009) (Table 4.29), where reported values included not only direct emissions from a tailpipe, but also accounted for gasoline evaporation.

Table 4.29: Previously reported road-related emission ratios of toluene and benzene

| **Location** | **Date** | Toluene/Benzene (ppbv/ppbv) | Reported by |
|---|---|---|---|
| Zurich (Switzerland) | 1993, September | 1.24 | [*Staehelin et al.*, 1998] |
| Budapest (Hungary) | 1990, Summer | 2.05 | [*Haszpra and Szilagyi*, 1994] |
| Sydney (Australia) | 1994, October-November | 1.50 | [*Duffy and Nelson*, 1996] |
| San Francisco (USA) | 1994-1997, Summer | 2.24 | [*Kirchstetter et al.*, 1999] |
| Austria | 1997, October | 1.97 | [*Schmid et al.*, 2001] |
| Wuppertal (Germany) | 1997, 1998 | 1.58 | [*Kurtenbach et al.*, 2002] |
| Seoul (Korea) | 2000 | 2.90 | [*Na et al.*, 2002] |
| Taipei (Taiwan) | 2000, July | 2.01 | [*Hwa et al.*, 2002] |
| Zurich (Switzerland) | 2002, September - October | 2.27 | [*Stemmler et al.*, 2005] |
| Gubrist (Switzerland) | 2004, Winter | 1.99 | [*Legreid et al.*, 2007a] |
| Hong Kong (China) | 2003, Summer, Winter | 2.27 | [*Ho et al.*, 2009] |
| Toronto (Canada) | 2000, 2001, Fall, Winter | 1.64 | [*Thompson*, 2003] |

The average (1.97 ± 0.44) of listed studies (Table 4.29) was chosen as a good representative of a “true value” for mobile on-road emissions. A complete data set and time series for the ratio-determined photochemical ages are provided in Appendix G. Photochemical ages and their statistical analysis are listed in Table 4.30.

Table 4.30: Statistical analysis of PCA determined for BAQS and EC-YU samples using toluene benzene ratios.

| Parameter | | Photochemical Age (s molecules cm$^{-3}$) | | | | | |
|---|---|---|---|---|---|---|---|
| Location | N[a] | Average | σ[b] | min | max | 50 pct[c] | 75 pct |
| Harrow[d] | 34 | $0.43\times10^{11}$ | $1.50\times10^{11}$ | $-2.49\times10^{11}$ | $3.25\times10^{11}$ | $0.16\times10^{11}$ | $1.73\times10^{11}$ |
| Ridgetown[d] | 88 | $-0.97\times10^{11}$ | $1.15\times10^{11}$ | $-2.86\times10^{11}$ | $2.30\times10^{11}$ | $-1.08\times10^{11}$ | $-0.31\times10^{11}$ |
| Egbert[e] | 38 | $1.09\times10^{11}$ | $1.40\times10^{11}$ | $-1.92\times10^{11}$ | $4.78\times10^{11}$ | $0.87\times10^{11}$ | $2.15\times10^{11}$ |
| Toronto[e] | 61 | $0.57\times10^{11}$ | $3.60\times10^{11}$ | $-17.7\times10^{11}$ | $6.80\times10^{11}$ | $0.81\times10^{11}$ | $2.55\times10^{11}$ |

(a) Number of measurements, (b) σ- standard deviation, (c) - percentile. PCA calculations were performed using concentrations determined from canister samples (d) and cartridge samples (e).

#### *4.3.6.2 PCA determined from the isotope hydrocarbon clock*

The isotope hydrocarbon clock concept described in 2.3.2 [*Rudolph and Czuba*, 2000] was applied (equation 2.10) for determination of PCA for individual ambient VOC collected during BAQS and EC-YU campaigns. Since no studies of stable carbon isotope ratios of various VOC emission sources in the campaign region were conducted prior to the sampling campaign, the averages of previously published data for samples collected in Toronto were used as the reference point (Table 4.31, Table 4.32) [ *Rudolph et al.*, 2002; *Thompson*, 2003].

Table 4.31: Stable carbon isotope ratios of the main VOC emission sources

| Source | hexane | benzene | heptane | toluene | octane | ethyl-benzene | p,m-xylene | o-xylene |
|---|---|---|---|---|---|---|---|---|
| Fresh gasoline[a] | -23.85[e] | -25.83 | -22.79 | -25.96 | | -23.36 | -26.42 | -25.98 |
| Gasoline/Condensate[b] | -27.7 | -25.6 | | -27.5 | | | | |
| | (2.3)[f] | (3.7) | | (4.8) | | | | |
| Tunnel (Toronto,Winter)[b] | | -26.1 | -26.9 | -27.2 | -26.2 | -24.3 | -27.3 | -24.9 |
| | | (0.8) | (2.5) | (0.3) | (1.4) | (0.5) | (0.1) | (0.2) |
| Tunnel (Toronto, Fall)[b] | | -24.5 | -24.1 | -25.7 | -26.5 | -25.4 | -26.6 | -23.5 |
| | | (1.2) | (2.7) | (1.5) | (1.4) | (1.2) | (0.5) | (1.0) |
| Tunnel (New Zeland, Summer)[b] | -25.7 | -25.0 | -23.5 | -25.1 | -33.1 | -24.4 | -25.2 | -25.8 |
| | (1.3) | (1.1) | (3.8) | (0.7) | (11.8) | (1.4) | (1.1) | (1.9) |
| Tunnel (Toronto, Winter and Fall)[c] | -26.3 | -26.5 | -25.8 | -27.5 | -25.8 | -27.4 | -26.9 | -27.3 |
| | (1.3) | (1.0) | (0.8) | (1.0) | (2.6) | (0.9) | (2.0) | (0.4) |
| Gas Station (Toronto, Winter)[c] | -26.6 | -29.1 | -25.4 | -27.4 | -27.7 | -28.2 | -27.7 | -27.1 |
| | (0.4) | (0.3) | (1.2) | (0.6) | (1.5) | (0.4) | (0.5) | (0.6) |
| Underground garage (Toronto, Winter, | -27.3 | -27.7 | -27.9 | -27.1 | -27.6 | -27.5 | -27.7 | -27.2 |
| Spring)[c] | (0.8) | (0.7) | (1.3) | (0.7) | (0.5) | (1.1) | (1.0) | (1.1) |
| Refinery (Toronto, Winter)[c] | -26.5 | -28.6 | -26.3 | -28.4 | | | | |
| | (0.9) | (0.1) | (0.9) | (2.9) | | | | |
| Biomass burning (Mainz, laboratory)[d] | | -26.0 | | -26.5 | | | | |
| | | (0.1) | | (0.9) | | | -25.7 (0.5) | |

(a)[*Thompson*, 2003], (b) [*Smallwood et al.*, 2002], (c) [ *Rudolph et al.*, 2002], (d) [*Czapiewski et al.*, 2003], (e) error of the mean smaller than 0.5 ‰, (f) number in parenthesis is the error of mean.

Table 4.32: Isotope ratios and KIEs used for calculation of photochemical ages from VOC isotope ratios. The emission source isotope ratios are calculated based on the Table 4.30 data.

| Compound | $\delta^{13}C$ (‰) | $\sigma(\delta^{13}C)^a$ (‰) | $\varepsilon_{OH}{}^b$ (‰) | $\sigma(\varepsilon_{OH})^c$ (‰) |
|---|---|---|---|---|
| hexane | -26.68 | 0.43 | $2.2^d$ | 0.07 |
| benzene | -27.08 | 1.72 | $7.83^e$ | 0.42 |
| heptane | -26.07 | 1.30 | $1.96^d$ | 0.26 |
| toluene | -27.22 | 0.88 | $5.95^f$ | 0.28 |
| octane | -26.76 | 0.85 | $2.13^d$ | 0.39 |
| ethylbenzene | -26.56 | 1.64 | $4.34^f$ | 0.28 |
| p,m-xylene | -27.24 | 0.49 | $4.83^{f,j}$ | 0.05 |
| o-xylene | -26.00 | 1.72 | $4.27^f$ | 0.05 |

(a) the standard deviation of δ (‰), (b) carbon kinetic isotope effects for reaction of VOC with OH-radicals, (c) error of $\varepsilon_{OH}$, (d)[*Anderson*, 2004] (e) average ε calculated from 8.13 (0.8) [*Anderson et al.,* 2004] and 7.53 (0.5) [*Rudolph et al.*, 2002], (f) [*Anderson et al.,*2004], (j) KIE value (‰) is for p-xylene.

The uncertainty of the calculated photochemical age was determined using Gaussian error propagation analysis [ *Rudolph et al.*, 2003; *Thompson*, 2003]:

$$\Delta t[OH] = \sqrt{\left(\left(\frac{\sqrt{(\Delta\delta^{13}C_s)^2 + (\Delta\delta^{13}C_r)^2}}{\delta^{13}C_r - \delta^{13}C_s}\right)^2 + \left(\frac{\Delta\varepsilon}{\varepsilon_{OH}}\right)^2\right)} \times t[OH]$$

where Δ indicates the uncertainty of the variable. Errors are associated with analysis method ($\Delta\delta^{13}C_r$), sources ($\Delta\delta^{13}C_s$), and uncertainty in the KIE ($\Delta\varepsilon_{OH}$). Uncertainty in the rate constants ($\Delta k_{OH}$) is negligible compared to other sources of uncertainty and therefore not considered (Table 4.31 and Table 4.32) [*Anderson*, 2004; *Rudolph, 2007; Rudolph et al., 2002]*. Measurement error was set to 0.5‰ for all compounds, the uncertainties in the source composition and KIE are listed in Table 4.31 and Table 4.32.

Time series for photochemical ages per compound are given in Appendix H. The mean photochemical ages and their standard deviation for each compound individually are listed in Table 4.33.

Table 4.33: Mean photochemical ages and standard deviation determined for VOC from BAQS and EC-YU samples

| Location | Number of data points | Compound | PCA | σ(PCA)[a] | Max | Min |
|---|---|---|---|---|---|---|
| | | | $10^{11}$ s molecules $cm^{-3}$ | | | |
| Egbert | 26 | hexane | -0.35 | 8.31 | 5.65 | -35.44 |
| | 45 | benzene | 1.52 | 2.88 | 12.39 | -5.13 |
| | 43 | heptane | 1.34 | 4.36 | 6.31 | -23.38 |
| | 44 | toluene | 0.68 | 0.50 | 1.90 | -0.38 |
| | 39 | ethylbenzene | 0.89 | 1.18 | 5.40 | -0.44 |
| | 39 | p,m-xylene | 0.38 | 0.33 | 1.11 | -0.25 |
| | 40 | o-xylene | 0.43 | 0.45 | 1.71 | -0.41 |
| Toronto | 25 | hexane | 1.38 | 2.47 | 6.73 | -2.02 |
| | 43 | benzene | 1.14 | 3.59 | 14.08 | -2.43 |
| | 13 | heptane | 0.90 | 2.17 | 3.43 | -3.52 |
| | 73 | toluene | 0.46 | 0.97 | 5.82 | -0.39 |
| | 21 | octane | 2.72 | 5.20 | 15.49 | -2.96 |
| | 59 | ethylbenzene | 1.05 | 1.66 | 8.74 | -2.70 |
| | 57 | p,m-xylene | 0.38 | 0.57 | 3.02 | -0.81 |
| | 44 | o-xylene | 0.47 | 0.61 | 1.64 | -0.68 |

(a) standard deviation of PCA values

### 4.3.7 Origins and histories of the air parcels

Recent histories of the air samples were investigated based on 2 or 4-day back trajectories using HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory Model) by Air Resources Laboratory (NOAA). Examples of rose plots of origin, VOC concentrations and VOC isotope composition are given in Figure 4.12, Appendix L and Appendix M while the overview and the statistical analysis of the rose plot data are provided in Appendix N and Appendix O.

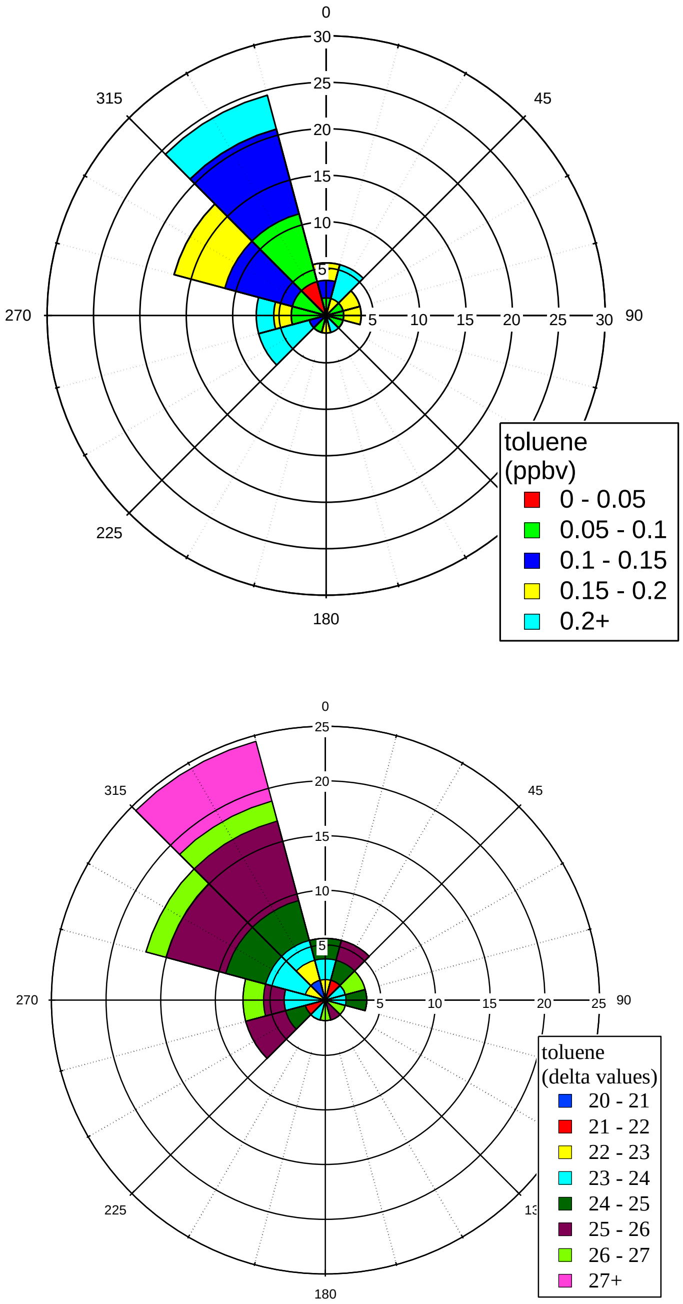


Figure 4.12: Rose diagram of air parcel origins showing the number of occurrences of VOC concentrations and isotope composition as function of wind direction (Egbert).

# 5. DISCUSSION

## 5.1 Sampling and Analysis

### 5.1.1 Adsorbents and their trapping efficiency

The selection of the adsorbent to be used for sampling was based on the examination of a few of their qualities such as adsorption strength and thermal stability.

Adsorption strength of the most commonly used materials: Carbopack B, Carboxene 569, and Tenax TA [*Buszewski et al.*, 2007; *Kroupa et al.*, 2004; *Tolnai et al.*, 1999]) was tested by the examination of the percentage breakthrough applying the frontal chromatography technique (Part 4.1.1.1). The percentage breakthrough for every compound was calculated as

$$\%Breakthrough = \frac{m_{back}}{m_{front}} \times 100\% \qquad (5.1)$$

where $m_{back}$ and $m_{front}$ are VOC mass found on the back and front cartridges respectively. The results obtained for cartridges filled with different adsorbents are presented in Table 4.1.

Results demonstrated (Table 4.1) that both Carbopack B and Tenax TA were inefficient in trapping of VOC, since the breakthrough for most of the compounds occurred only after 3.4 L sampled (per 0.55 g) and 15.12 L (per 0.36 g) respectively, even though the BTV recommended by the manufacturers and in some recent publications for n-pentane, n-hexane, benzene, toluene and octane were significantly higher (Table 2.1). Only insignificant breakthrough had occurred on Carboxene 569, ranging from 1-4 % for most of the compounds at 37 L and 82 L sampled, that coincided with previously published values for BTV (Table 2.1).

Since the BTV represents the maximum volume above which compound is no longer trapped by the adsorbent, there is a clear direct relation between the strength of the adsorbent and the BTV. However, this relation is not linear, since there are multiple factors such as temperature, concentration of compound, presence of the other chemicals in the sample, the flow rate, the trap dimensions and physical properties of the adsorbent that can affect the BTV (Table 5.1) [*Kroupa et al.*, 2004; *Simon et al.*, 1995].

Table 5.1: Summary of physical and chemical characteristics of Carbopack B, Carboxene 569 and Tenax TA.

| Adsorbent | Carbopack B/carbotrap B | Carboxene 569 | Tenax TA |
|---|---|---|---|
| Material Type | Graphitized carbon black | Carbon molecular sieve | Porous organic polymer |
| Monomer | - | - | Diphenyl-p-phenylene oxide (DPPO) |
| Particle Size[a] | 20/70 | 20/45 | 60/80 |
| Surface Area[a] $m^2/g$ | 100 | ~ 485 | 35 |
| $T_{max}$ ($^0C$) | 400 | >400 | >350 |
| Artefacts | Polar groups on the surface can attract polar molecules. A catalyst in some surface reactions at high ozone concentrations [e] | Low artifacts | Upon reaction with $O_3$ and $NO_x$ forms artefact compounds (e.g. cacetophenone, benzealdehyde)[b, c] |
| Water Affinity | Highly hydrophobic | Highly hydrophobic | Hydrophobic |
| Adsorption | Shape-selective [c], based on London dispersion forces [d, e] | Non-specific interactions | Non-specific, size and shape selective, based on Wander Waals forces |

a. [*SIS*, 1996-2010], b. [*Harper*, 2000], c. [*Dettmer and Engewald*, 2002], d. [*Rothweiler et al.*, 1991], e. [*Lee et al.*, 2006].

Carbopack B consists of the agglomerated fine-grained powders of graphitized carbon (99%). Since carbon is highly hydrophobic, the enrichment of the sorbent occurs only by the non-specific interactions, strength of which determined by the sizes and shapes of the molecules [*Dettmer and Engewald*, 2002]. And indeed, based on the obtained results (Table 4.1), the percentage breakthrough for n-hexane (C6) was lower than for n-pentane (C5) (4% versus 21%), lower for toluene (C7) than for benzene (C6) (2% versus 10%); and lower for n-hexane (free chain molecule) than benzene (condensed ring) due to the different number of contacts with the surface of the adsorbent. However, the percentage breakthrough for n-octane was much higher than that of six or seven carbon-containing molecules (40%), indicating a problem with sampling or sample processing (discussed elsewhere). While the surface of Carbopack B is considered to be inert (Table 5.1), it has been suggested that some polar groups can be found on its surfaces [*Di Corcia et al.,* 1981]; in addition, it was found that at high ozone concentrations the graphite can be catalytically active that can result in decomposition of some ambient compounds [*Lee et al.*, 2006]. While this should have no direct effect on the stability of the target HC and ArHC, it may still affect the overall performance of the adsorbent, which was observed in the lower than expected BTV (Table 2.1 and Table 4.1).

Tenax TA is made of a porous organic polymer and since the manufacturing process is highly controlled, its purity is usually very high. Absence of polar groups on the surface results in high hydrophobicity and thermal stability [*Dettmer and Engewald*, 2002]. However, since its surface area is low (Table 5.1), compounds with lower carbon number might not be trapped efficiently, which was indeed observed for benzene compared to toluene (12% breakthrough versus 8%, respectively) and benzene compared to hexane (12% breakthrough versus 8%, respectively) (Table 4.1). However, similarly to Carbopack B, breakthrough percentage values obtained identified lower than expected BTV (Table 2.1 and Table 4.1) indicating the presence of additional artifacts. While thermally stable, Tenax TA can chemically decompose in the presence of ozone, $NO_x$ and other atmospheric reactive species, that can result in changes of its adsorption properties and in a chemical breakdown of compounds adsorbed [*Dettmer and Engewald,* 2002; *Lee et al.*, 2006].

The combination of both Carbopack B and Tenax was used for a creation of the multitrap with a better performance (Table 4.1), however the contradictory results (more than 20% breakthrough for n-pentane, n-hexane and benzene) were obtained, suggesting possibility of preconcentration of some other highly concentrated compounds that occupied most of the active surface of the adsorbent [*Buszewski et al.*, 2007].

Carboxene 569 belongs to the class of carbon molecular sieves adsorbents that are characterized by a high specific surface area and sharply distributed pore sizes [*Dettmer and Engewald*, 2002]. Similarly to Carbopack B and Tenax TA, the adsorption occurs as a result of the non-specific interactions between the surface and VOC molecules. Since particles with different pore sizes are present, Carboxene 569 is capable of trapping both small and large molecules (Table 4.1) (1% breakthrough of pentane and 0.8% of toluene). However, dependence of the trapping efficiency on the molecular size and shape is still noticeable (breakthrough of 4% of benzene versus 0.4% of n-hexane). Due to the elaborate manufacturing process the surface is considered to be pure, though the oxides of some trace elements have been found in the micropores that resulted in higher than expected water uptake [*Dettmer and Engewald*, 2002; *Fastyn et al.*, 2003; *Gawlowski et al.*, 1999]. Based on the results obtained (Table 4.1) it was concluded that Carboxene 569 was the strongest among all the tested adsorbents, with the highest breakthrough volumes for target VOC, with capacity of trapping wider range of VOC (C-5 and higher) and with small possibility of surface-associated artifacts formation; thus it was used as a material in preparation of all the cartridges used in this work.

### 5.1.2 Background levels

Blank values of all cartridge materials (stainless steel tubes, silanized glass and quartz wool, and Carboxene 569) were determined individually to examine possible interferences with target compounds (Table 4.2, Table 4.3 and Table 4.4). Silanized glass wool at high temperatures produced high blank values : >10 ng for benzene, >5 ng for toluene and xylenes (Table 4.2). On the contrary, under similar test conditions, quartz wool showed better thermal stability and absence of any blank values (Table 4.3). While both of these materials are produced similarly, there are a few details that may explain the differences in their performance.

Glass wool is produced from natural ores such as quartz sand, feldspar and limestone that are first melted at 1000 °C into a glass fluid with an addition of calcined soda and borax, and then blown into very thin fibers [*HiSuccessInternational*, 2001-2011]. Silane ($SiH_4$) is used as a coupling agent to facilitate adhesion, fiber formation and to create a hydrophobic fiber coating [*3M*, 2006]. The quartz wool production process is very similar to the one used for the silanized wool. However, the fibers are produced from high purity quartz (99.95%-99.99% $SiO_2$) [*Lubin*, 1998] at high temperatures (1200 °C) and then a resin binder (mostly polyurethane adhesive) and oil are sprayed on the strands to solidify and bind them together [*Knauf Insulation*, 2004]. Consequently, the significant differences between the glass and quartz wool are the purity of the starting material, their thermostability and post-production treatment. Indeed, tests performed (Table 4.2 and Table 4.3) have confirmed that the untreated quartz wool is thermally more stable than silan-treated glass wool (Table 4.2).

No severe background disturbances at the retention times of target compounds were observed in the chromatograms for Carboxene 569 at different temperatures (Table 4.4, Figure 4.1) proving it to be suitable as an adsorbent; while traces of benzene and toluene were detected for some cartridges, their magnitudes were insignificant to affect the data. Since Carboxene 569 is made out of carbon sieves with 93.7% of C and 0.3% of H in elemental composition [*Dettmer and Engewald*, 2002], these detected small traces could be a result of incomplete graphitization of the starting material.

### 5.1.3 Desorption condition

Desorption of VOC from the adsorbent is a kinetically controlled process, thus finding correct desorption conditions: time, temperature, carrier gas flow rate, dimensions of the furnace is essential. Since the adsorption of VOC on Carboxene 569 occurs due to the non-specific interactions and the possibility of the irreversible adsorption is minimal (Table 2.2), all compounds adsorbed onto the sorbent during sampling are expected to be recovered completely at the correct experimental settings.

Since the target VOC compounds are all non-polar hydrocarbons their recovery is highly temperature dependent (Table 4.5 and Table 4.6). Indeed, lower desorption temperatures (Table 4.5 Test 1, 2, 3 and Table 4.6 Test 1, 2) have resulted in poor recovery of compounds with low volatility. Unfortunately, the option to increase temperature is limited since a prolonged exposure to higher temperatures resulted in a degradation of the cartridge materials (Table 4.2, 4.4). Thus temperatures above 590 K could not be used. 553 K was chosen as an optimum temperature that allows maximum recovery and does not result in the thermal decomposition of VOC or adsorbent (Table 4.8 Test 8).

In order to avoid uneven heat distribution along the cartridge, a 30 cm furnace instead of 15 cm was used, which ensured that the 13 cm long cartridge is positioned right in the middle of the furnace where any temperature gradient is minimal. Results of desorption tests with the modified furnace are given in Table 4.8. Depending on flow rate and temperature desorption efficiencies close to 100% were achieved for most of compounds (Table 4.8).

Desorption time is another critical parameter that ensures completeness of the desorption [*Kuntasal et al.*, 2005], thus the dependence of recoveries (R) on 15, 20, 30 and 40 min time intervals were examined (Table 4.5 Test 1, 2, 4, 6, 7 and Table 4.6 Test 3, 4, 5). While for lighter VOC short desorption was suitable (Table 4.5 Test 2, 3 and Table 4.6 Test 5), the heavier compounds required significantly longer time (Table 4.5 Test 6, 7); thus 40 min was selected as the optimum desorption time (Table 4.8, Test 8). Only a small influence of the carrier gas flow rate on the analyte recovery was determined in the range of 50-150 mL/min (Table 4.5 Test 1, 2, 3, 5), thus the flow rates of 60-80 mL/min were used for most of the tests (Table 4.8). Overall, with optimized desorption conditions, the recoveries for the most analytes ranged between 90-100% (Table 4.8 Test 7 and 8).

### 5.1.4 Analyte stability during storage

It was established that tightly closed sample-containing cartridges could be stored both at room temperature for a short period and in a freezer for longer time with no significant loss of VOC (4.1.1.4, Figure 5.1A).

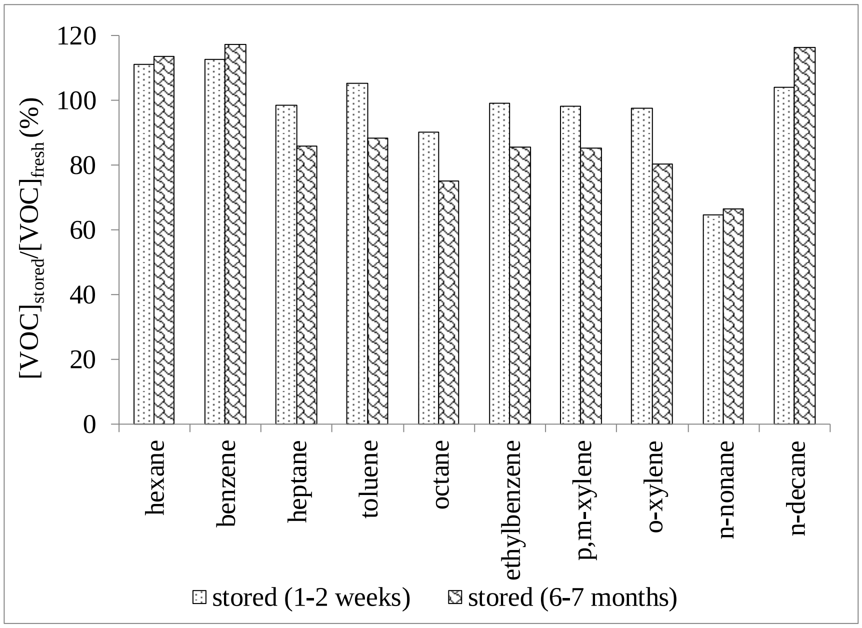


Figure 5.1A: Averaged results of sample recoveries (%) for fresh, 1-2 weeks and 6-7 months stored samples.

Similarly, no significant isotopic fractionation due to storage was observed for both sets of conditions (Figure 5.1B). However, there were fewer discrepancies if the samples were stored in a colder environment.

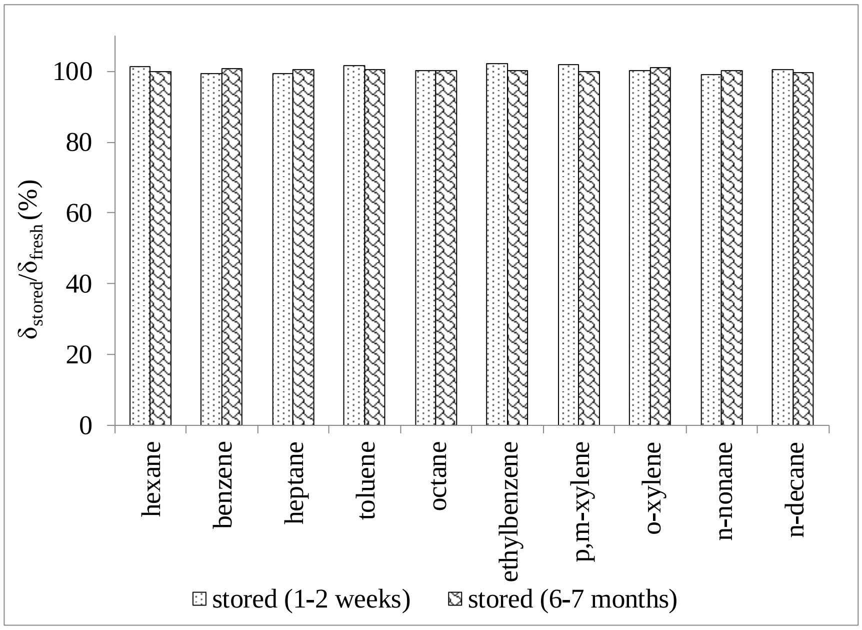


Figure 5.1B: Averaged results for 1-2 weeks and 6-7 months stored samples versus fresh sample recoveries (stable carbon isotope composition). Data points correspond to a target compound listed in Table 4.10.

### 5.1.5 Experimental parameters for the preconcentration systems

The experimental parameters for re-concentration of thermally desorbed compounds were selected based on the reproducibility results of the trapping and desorption tests (described in 4.1.2). Glass beads were used as a trapping material in Trap-1 to increase its adsorption surface; use of any adsorbent was avoided to prevent interferences that could occur due to its thermal degradation with time [*Camel and Caude*, 1995]. A capillary trap (Trap-2) was selected for the second preconcentration step, since the combination of the packed trap with a chromatographic column could result in an incomplete transfer of the analytes due to the significant differences in the carrier gas flow rates in the trap and the column [*Cao and Hewitt*, 1992].

The use of the cryogenic liquids for VOC preconcentration in conjunction with thermal desorption is quite common [*Camel and Caude*, 1995; *Harper*, 2000], thus both Trap-1 and Trap-2 were set to be cooled with liquid nitrogen. It was established that the temperature of both should be as low as possible to trap VOC efficiently during two preconcentration stages (Table 4.10). While cryogenic trapping is a well known technique each cryogenic trap is developed individually based on reproducibility tests, and it is usually configured so that there is no gradient cooling of the cryofocusing tube [*Kohno and Kuwata*, 1991]. The presence of a temperature gradient was visible for original Tekmar 5010 setup where traps were soldered onto the liquid-nitrogen containing tubes (described in 3.2.1.1), and reproducibility of the signal was affected, especially for lighter VOC (Table 4.11 and Table 4.12). Another temperature gradient was detected due to the inefficient automatic cooling of the Trap-1 in Tekmar 5010 (Figure 3.6). In the default setup, this trap was temperature controlled by the internal microprocessor with cooling dependant on the flow rate of liquid nitrogen introduced into the system at a limited rate from a solenoid valve. With this setup, there was a possibility of the production of a temperature differential between the trap and temperature monitor due to the poor heat conductance across the wall of the liquid-nitrogen carrier tube and/or disturbances of the thermocouple sensors by the cryogen droplets [*Kohno and Kuwata*, 1991]. Hence introduction of immersed-trap configuration ensured elimination of gradient cooling of the cryo-traps and significantly improved the analytical precision (Table 4.11 and Table 4.12). Desorption temperature of Trap-1 and injection temperature of Trap-2 were set high enough (513K) to ensure complete release of heavier VOC (Table 4.10 and Table 4.12). With the chosen parameters, a precision of below 5% for most of the compounds was reached (Table 4.11 and Table 4.12).

## 5.2 Method Evaluation

The evaluation of the performances of Tekmar 5010-GC-FID/IRMS and TSPS-GC-FID/IRMS was based on an analysis of a statistic (Relative Standard Deviation, RSD) and closeness of off-line and on-line delta values for each individual compound in different samples (4.2.1 and 4.2.2). In general, results for TSPS were better than for the earlier developed Tekmar 5010 due to the further improvements.

### 5.2.1 Sensitivity

Usually sensitivity of an analytical system is limited by the sensitivity of its detector (FID or IRMS in this case). FID is sensitive to mass and theoretically can detect substances present in as low as pg masses, while IRMS sensitivity for isotope ratios is determined by the smallest difference in $\delta^{13}C$ values that can be detected for a given sample mass or the sample mass needed to measure a given difference in $\delta^{13}C$ values. Based on the natural abundance of $^{13}C$, and the instrumental limitations of the IRMS used, a theoretical detection limit of 1.1 ngC was determined by Thompson (2003). However, the actual IRMS sensitivity is also limited by the data evaluation. The original peak integration software incorporated into an IRMS operating system did not allow accessing each peak individually and did not provide a manual peak evaluation option. While it was sufficient for a preliminary analysis of highly concentrated samples, it was not suitable for many other samples. Consequently, each peak was integrated manually using a Microsoft Excel based software. To minimize bias due to the subjective peak evaluation, each peak was integrated ten times with varying starting and ending points by 5 units (1 unit = 0.1 second), this allowed to obtain averaged delta values with little bias from the original choice of peak boundaries.

While the detection limit (DL) is relevant for concentration measurements and usually set at $3\sigma_{blank}$, there is no universal definition of DL for delta values. Consequently, DL for IRMS has to be based on the desired reproducibility and established dynamic range (Table 4.18, Figure 4.4). For this work the IRMS error due to integration was accepted to be not more than 0.3 ‰ and peaks with lower reproducibility in integrations (more than 0.5 ‰) were rejected and their delta values were not used. Usually these were small peaks with decreased signal to noise ratios. The detection limit for IRMS was set based on the accuracy of the results from analysis of reference mixtures and data evaluation generally was in the range of 3-5 ng for the VOC studied here. In summary, these detection limits for isotope ratios were set based on a targeted reproducibility and accuracy of 0.5 ‰. It should be noted that for the heavier n-alkanes the systematic bias maybe higher based on comparison between the isotope ratio of artificial mixtures and GC-IRMS measurement of these mixtures. However, since it can presently not be ruled out that this is the result of problems in the off-line analysis of n-alkanes no corrections for this bias were made (a more detailed discussion of this can be found in Chapter 5.3.2).

### 5.2.2 Linearity

The working range for any analytical method is usually established based on linearity analysis, where linearity is evaluated based on the linear regression results for multi-point calibration. Linearity is considered to be acceptable when linear regression square coefficients are ≥0.99, signal to noise ratios are high and peaks have a Gaussian distribution shape [*Ribes et al.*, 2007]. Based on the regression analysis for calibration curves (Table 4.14) maximum and minimum masses of the linearity ranges were established for individual VOC and are provided in Table 5.2.

Table 5.2: The upper end of the linearity range (ng) for concentration analysis of target VOC. The lower end of the range is the detection limit (provided in 4.2.3).

| Compound | FID | IRMS2007 | IRMS2011 |
|---|---|---|---|
| pentane | 75 | 30 | N/A |
| hexane | 78 | 26 | 28 |
| benzene | 160 | 50 | 25 |
| heptane | 181 | 67 | 50 |
| toluene | 263 | 137 | 62 |
| octane | 262 | N/A | 57 |
| ethylbenzene | 155 | N/A | 48 |
| p,m,-xylene | 388 | N/A | 75 |
| o-xylene | 153 | N/A | 32 |
| p-xylene | N/A[a] | 97 | N/A |
| n-nonane | 146 | 91 | 39 |
| n-decane | 167 | 21 | 12 |

(a) N/A- not available

It should be mentioned that actual linearity ranges might be wider since the masses provided are only those that were tested experimentally. It did not cause any problem, since most of the values determined for ambient samples were within these limits (Table 5.3, Figure 5.2).

Table 5.3: Maximum masses (ng) of target compounds extracted from ambient samples that were collected during BAQS and EC-YU field campaigns.

| Compound | BAQS | EC-YU |
|---|---|---|
| | Max | Max |
| pentane | 435 | |
| hexane | 13 | 672.6 |
| benzene | 76 | 107.2 |
| heptane | 22 | 434.7 |
| toluene | 214 | 803.4 |
| octane | | 372.2 |
| ethylbenzene | | 106.2 |
| p,m,-xylene | | 106.2 |
| o-xylene | | 106.2 |
| p-xylene | 32 | |
| n-nonane | 18 | 128.2 |
| n-decane | 4 | 142.3 |

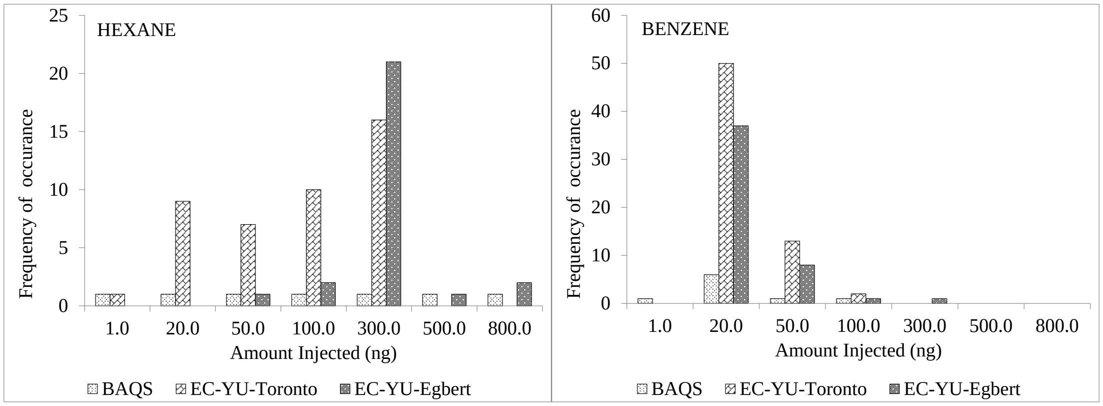


Figure 5.2: Distribution of VOC masses (ng) found in ambient samples (BAQS and YU-EC studies (for YU-EC campaign samples Toronto and Egbert samples are provided separately))

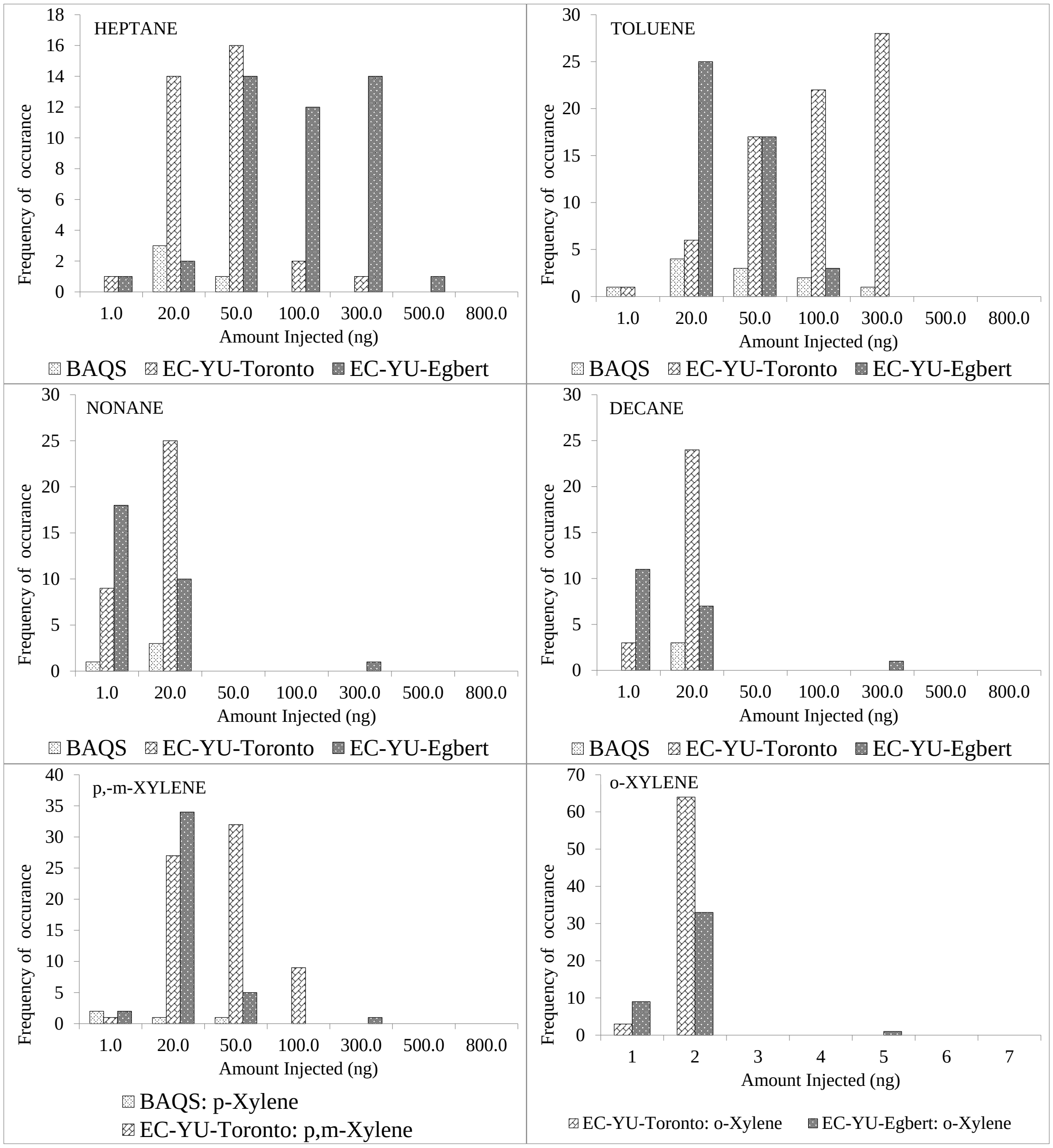


Figure 5.2 (cont'd): Distribution of VOC masses (ng) found in ambient samples (BAQS and YU-EC studies (for YU-EC campaign samples Toronto and Egbert samples are provided separately))

### 5.2.3 Precision and Accuracy

The precision of the method was evaluated using reproducibility tests described in 4.1.2. (Table 4.15). Values obtained with both FID and IRMS were well below 10% and most of the time lower than 5%, which is within an acceptable range for an analytical method. Typically, RSD values were lower for more concentrated samples, since the intensity of the signal increases with increase in concentration and it becomes less affected by noise (Table 4.15).

The accuracy of the method was examined using on-line and off-line delta values (4.2.2). An important factor for the quality of isotopic composition determination was the mass of hydrocarbon available for an individual measurement. In general, for ArHC off-line and on-line values usually coincided for mixtures with injected masses more than 3-5 ng per compound (Table 4.18). However, for many alkanes a significant bias between off-line and on-line data was observed, even though both off-line and on-line tests displayed a good reproducibility, with uncertainties well below the magnitude of the bias. One possibility is that for heavy alkanes isotopic fractionation might have taken place inside the stainless steel canisters where the mixtures were stored, as has been found in previous studies where the concentrations of heavy alkanes in stainless steel canisters can decrease with time. Since $^{12}C$ containing molecules are more reactive compared to $^{13}C$ molecules, it is expected that any loss of n-alkanes with time will result in enrichment of $^{13}C$. Indeed, the delta $^{13}C$ on-line measurements of alkanes in canisters gave higher $^{13}C$ values than the off-line values, which represent the $^{13}C$ of the alkanes at the time the mixtures were prepared. Another possible explanation for the bias between off-line and on-line is an incomplete oxidation during off-line combustion. This also would result in a decrease of the isotope ratio in the $CO_2$ formed, since $^{12}C$ will oxidize more readily than $^{13}C$. The closeness of off-line and on-line values of aromatics is compatible with both possibilities since these compounds are less affected by storage inside a stainless steel canister and are more efficiently oxidized during off-line combustion. Generally 0.5 ‰ difference between on-line and off-line values is acceptable for GC-IRMS method.

### 5.2.4 Overall Method Performance

While individual elements of the developed system are widely used, there were just a few attempts to use them for isotope ratio analysis of ambient VOC. Table 5.4 summarizes a few studies where some or all similar elements of the developed system were used.

Table 5.4: Summary of performances of the methods used for analysis of ambient VOC

| Compounds Investigated | System Details | Detection Limits (ng) | Performance | Reported by |
|---|---|---|---|---|
| ArHc | Multisorbent Adsorption/Thermal Desorption/GC/MS | 0.4-2 | 80-100 % [a] | [*Pankow et al.*, 1998] |
| HC, ArHC | Multisorbent Adsorption/Thermal Desorption/GC/MS | 0.001-0.005 | ≥75 % [a] | [*Ribes et al.*, 2007] |
| HC, ArHC | Multisorbent Adsorption/Thermal Desorption/GC/MS | 1-3 | > 90% [a] | [*Wu et al.*, 2004] |
| ArHC | Unisorbent Adsorption/Thermal Desorption/GC/FID/MS | 0.05-0.5 | > 90% [a] | [*Stacey and Wright*, 2001] |
| ArHC | Unisorbent Adsorption/Thermal Desorption/GC/IRMS | N/A[c] | ≥80% [a]<br>±0.3‰ [b] | [*Eckstaedt et al.*, 2011] |
| HC | Canister/GC/IRMS | > 1 | ≥95% [a] | [*Rudolph et al.*, 2002] |
| HC | Canister/GC/IRMS | N/A | > 2‰ [b] | [*Saito et al.*, 2002] |
| HC, ArHC | GC/IRMS | N/A | ±0.3‰-±0.5‰ [b] | [*Smallwood et al.*, 2002] |
| HC, ArHC | GC/IRMS | ≥ 1 | ≥70% [a] | [*Rudolph*, 2007] |

(a) Precision, (b) Accuracy, (c) N/A- not available

As can be seen, the performance of the developed method is in good agreement with previously published methods and techniques, even though not all of the systems include all of the parts used in our method (Table 5.5). One of the major advantages of this method is a broader range of low concentrated atmospheric HC and ArHC, which has not been done previously as to our knowledge. With the detection limit of 3-5 ng/C for on-line isotope ratio measurements and ≤3 ng/C for concentration measurements this method can be widely applicable for a wide range of ambient species.

## 5.3 Ambient volatile organic compounds

Residence time as well as the concentration of reactants such as the OH-radical or ozone are key parameters that directly affect the extent of chemical and physical transformation of VOC in the atmosphere. Since residence times cannot be directly measured, they are usually derived from back-trajectories or approximated based on the compound concentrations and their variability [*Junge*, 1973]. Consequently, it is possible theoretically to characterize study locations by the photochemical and physical histories of the air masses passing through the sampling locations using mixing ratios of VOC. As VOC are transported away from their sources, their concentration decreases due to the chemical reactions and dilution with background air. The extent of change due to removal depends on the residence time of the compound in the atmosphere, its reactivity and the concentration of the reaction partners; dilution depends on time as well as meteorological conditions. Both factors result in concentrations of primary VOC that are higher closer to the emission sources, and then decrease as the distance increases. If chemical loss reactions are the dominant factor, gradients and variability of concentration are expected to depend on VOC reactivity while in the case of dilution and mixing the steepness of the gradient and variability will mainly depend on meteorological conditions and background concentration of the VOC. Another factor that influences ambient concentrations of VOC is spatial and temporal variability of emission rates.

In this subchapter concentrations and isotope ratios of ambient VOC are discussed and compared with previously published data (5.3.1). They are used to derive information about emission sources and location (5.3.2) and study dependencies between mixing ratios and isotope composition of VOC (5.3.3). Photochemical ages determined using both the hydrocarbon and isotope hydrocarbon clocks are compared and similarities and differences explained (5.3.4). Finally applications of VOC isotopic composition measurements for understanding local and regional photochemistry are examined and discussed.

### 5.3.1 Comparison of concentrations and carbon isotope composition with literature data

To classify each sampling location as urban, semi-urban and rural, and to examine the effect of local emission sources and long-range transport on regional air quality in the common “classical” way, the detected mixing ratios of VOC (Table 4.20, 4.21, 4.22 and Figure 4.5) and isotope ratios (Table 4.20A, 4.21, 4.22 and Figure 4.8) are compared with previously published data from urban and rural field campaigns (Table 5.6 and Table 5.7).

Mixing ratios in medium to high pptv ranges detected in Ridgetown samples (Table 4.20, Figure 4.5 A) are comparable with those found by Hagerman [1997], Riemer [1998], Pankow [2003], and Thompson [2003], and indicate a rural area, with local emission sources having low impact on air quality (Table 5.6). Low $\delta^{13}C$ observed in Ridgetown (Table 4.20A, Figure 4.8A) differ from all previously reported data (Table 5.7). However, since the mass of VOC injected for these measurements were lower than 3 ng it is possible that these results are biased by linearity problems (discussed in 5.2.2).

Both Harrow and Egbert (Table 4.20, 4.21, Figure 4.5 B and Figure 4.5 C) can be considered semi-rural locations based on the elevated mixing ratios for some VOC that are relevant to semi-urban or suburban environment (low to medium pptv ranges) (Table 5.6) except hexane and heptane from Egbert samples (Table 4.21) [*Jobson et al.*, 2004;

*Legreid et al.*, 2007b; *Pankow et al.*, 2003; *Roberts et al.*, 1984]. The majority of the determined $\delta^{13}$C (Table 4.20, 4.21, Figure 4.8 A,B) are also comparable with those observed in sub-urban locations. However, there are some data points that match those of both urban and remote rural areas *[Czuba, 1999; Rudolph et al., 2002; Thompson, 2003]*. These observations suggest that both Harrow and Egbert experience air masses that are impacted by the presence of local sources and both short range and long range transported air parcels, but the contribution of long-range transported air towards the overall air mass is very small for reactive VOC compared to the locally emitted compounds and thus generally local emissions dominate. Significantly higher levels of hexane and heptane suggest the presence of a substantial local source with a constant hexane to heptane emission ratio. This is unusual for most types of locations and will be discussed elsewhere (5.3.3).

Concentrations and $\delta^{13}$C observed for Toronto samples (Table 4.22, Figure 4.5 D, Figure 4.8C) were comparable with those found in semi-urban and urban locations [*Czuba*, 1999; *Guo et al.*, 2004; *Legreid et al.*, 2007b; *Pankow et al.*, 2003; *Roberts et al.*, 1984; *Rudolph et al.*, 2002; *Thompson*, 2003]. Since the Toronto sampling site was located about 19 km north of downtown in a suburban, mixed industrial and residential area, these concentrations and isotope composition are not surprising, as the air masses in this area most probably consist of a mixture of freshly emitted air parcels from a variety of urban sources that are diluted with background air.

Table 5.6: VOC concentrations (ppbv) for various urban and rural areas previously reported

| Reference | Location | Type of emission | Date | hexane | benzene | toluene | octane | p,m-xylene | o-xylene | ethyl-benzene |
|---|---|---|---|---|---|---|---|---|---|---|
| Thompson, 2003[a] | New Zeland, Baring Head | background | 1999-2000 | | 0.009 | | | | | |
| | Canada, Alert | background | 1999-2001 | | 0.088 | | | | | |
| | Canada, Fraserdale | background | 2000-2001 | | 0.095 | 0.05 | | 0.028 | 0.009 | 0.009 |
| | Canada, Vancouver | suburban | 2000 | | 0.522 | 3.489 | | | 0.318 | 0.259 |
| | New Zeland, Hamilton | suburban | 1999 | 0.278 | 0.803 | 1.484 | 0.024 | 0.584 | 0.218 | 0.168 |
| | Canada, North York | urban | 2000 | 0.247 | 2.899 | 1.127 | | 0.454 | 0.154 | 0.149 |
| Pankow, 2003[b] | USA | | | | | | | | | |
| | Turnerswille, NJ | urban | 1998-2002 | | 0.43 | 0.85 | | 0.42 | 0.16 | 0.12 |
| | Western Springs, IL | semi-urban | | | 0.17 | 0.23 | | 0.01 | 0.03 | 0.03 |
| | Coles Farm, NJ | rural | | | 0.23 | 0.29 | | 0.12 | 0.05 | 0.04 |
| Roberts, 1985[c] | USA, Rocky Mountains | rural | 1981-1982 | 0.013-0.82 | 0.020-0.85 | 0.005-1.28 | 0.004-0.11 | | | |
| Hagerman, 1997[d] | Southeastern US | | | | | | | | | |
| | Centerville, Alabama | rural | 1992-1994 | 0.53 | 0.91 | 1.26 | 0.14 | 0.70 | 0.18 | 0.21 |
| | Oak Grove, Mississippi | rural | | 0.59 | 0.93 | 1.67 | 0.22 | 0.64 | 0.23 | 0.28 |
| | Yorkville, Georgia | rural | | 0.64 | 1.23 | 2.83 | 0.18 | 1.23 | 0.42 | 0.48 |
| | Candor, North Carolina | rural | | 0.58 | 1.16 | 2.12 | 0.30 | 0.89 | 0.39 | 0.32 |
| Riemer, 1998[e] | USA, Nashville, Tenessee | rural | 1995 | | 0.26-0.69 | 0.19-0.47 | | 0.021-0.18 | 0.03-0.11 | 0.028-0.091 |

Table 5.6 (cont'd): VOC concentrations (ppbv) for various urban and rural areas previously reported

| Reference | Location | Type of emission | Date | hexane | benzene | toluene | octane | p,m-xylene | o-xylene | ethyl-benzene |
|---|---|---|---|---|---|---|---|---|---|---|
| | Canada | | | | | | | | | |
| Courtesy of J.Rudolph. 2003[f] | Toronto | urban | 2002-2003 | 0.45 (±0.23[k]) | 0.61 (±0.38) | 2.32 (±1.12) | | 0.58 (±0.35) | 0.20 (±0.12) | 0.21 (±0.12) |
| | North York | urban | 2002-2003 | 0.39 (±0.14) | 0.48 (±0.16) | 2.18 (±1.56) | | 0.0.89 (±0.48) | 0.27 (±0.14) | 0.31 (±0.17) |
| | Etobicoke | urban | 2002-2003 | 0.21 (±0.18) | 0.35 (±0.05) | 0.997 (±0.62) | | 1.03 (±0.48) | 0.23 (±0.09) | 0.33 (±0.18) |
| Courtesy of the Ontario Ministry of Environment, 2007[g] | Windsor (Downtown) | urban | 2007 | 0.18 (±0.17) | 0.25 (±0.11) | 0.997 (±0.62) | | 0.31 (±0.19) | 0.10 (±0.06) | 0.101 (±0.05) |
| Jobson, 2003[h] | USA, Houston | urban | 2000 | 0.29-0.41 | 0.32-0.34 | 0.40-0.42 | | 0.16 | 0.06 | 0.06 |
| Guo, 2004[i] | China, Hong Kong | urban | 2001 | | 2.1-2.5 | 13.1-13.5 | | 1.6-1.8 | 0.5-0.6 | 1.2-1.3 |
| | Switzerland | | | | | | | | | |
| Legreid, 2007[j] | Gubrist Tunnel | road transport | 2004 | | 0.53-21.5 | 0.81-59.8 | | 0.59-26.3 | 0.21-11.4 | |
| | Zurich | urban | 2005 | | 0.26-0.62 | 0.74-2.42 | | 0.33-1.14 | 0.13-0.42 | |

Table 5.6 (cont’d): VOC concentrations (ppbv) for various urban and rural areas previously reported

| Reference | Location | Type of emission | Date | 2-methyl-butane | 2-methyl-pentane | 3-methyl-pentane | acetylene | iso-butane | butane | pentane |
|---|---|---|---|---|---|---|---|---|---|---|
| Thompson, 2003 | New Zeland, Baring Head | background | 1999-2000 | | | | | | | 0.005 |
| | Canada, Alert | background | 1999-2001 | | | | | | | 0.055 |
| | Canada, Fraserdale | background | 2000-2001 | | | | | 0.098 | 0.195 | 0.063 |
| | Canada, Vancouver | suburban | 2000 | | | | | | 2.657 | 2.063 |
| | New Zeland, Hamilton | suburban | 1999 | | | | | 3.365 | 7.499 | 4.143 |
| | Canada, North York | urban | 2000 | | | | | | 2.995 | 0.702 |
| Hagerman, 1997 | Southeastern US | | | | | | | | | |
| | Centerville, Alabama | rural | 1992-1994 | 2.45 | 1.5 | 0.72 | 1.18 | 1.16 | 2.64 | 1.25 |
| | Oak Grove, Mississippi | rural | | 3.0 | 1.23 | 0.84 | 1.19 | 1.43 | 2.98 | 1.25 |
| | Yorkville, Georgia | rural | | 4.12 | 1.86 | 0.88 | 1.65 | 1.32 | 3.44 | 2.16 |
| | Candor, North Carolina | rural | | 2.69 | 1.43 | 0.59 | 1.3 | 0.99 | 2.73 | 1.19 |
| Riemer, 1998 | USA, Nashville, Tenessee | rural | 1995 | 0.19 | 0.041 | 0.015 | | 0.11 | 0.19 | 0.075 |
| Courtesy of J.Rudolph | Canada, Toronto (Downtown) | urban | 2002-2003 | 1.38 (±0.62) | 0.48 (±0.31) | 0.35 (±0.20) | 1.65 (±0.96) | 0.86 (±0.29) | 3.05 (±1.2) | 0.78 (±0.38) |
| | Canada, North York | urban | 2002-2003 | 1.28 (±0.74) | 0.40 (±0.16) | 0.30 (±0.11) | 1.40 (±0.39) | 0.91 (±0.44) | 2.43 (±1.24) | 0.74 (±0.38) |
| | Canada, Etobicoke | urban | 2002-2003 | 0.53 (±0.17) | 0.20 (±0.15) | 0.09 (±0.03) | 1.17 (±0.25) | 0.39 (±0.11) | 0.98 (±0.0.28) | 0.31 (±0.10) |
| Courtesy of the Ontario Ministry of Environment | Canada, Windsor (Downtown) | urban | 2007 | 0.98 (±0.53) | 0.26 (±0.14) | 0.19 (±0.09) | 0.59 (±0.31) | 0.43 (±0.22) | 0.79 (±0.43) | 0.62 (±0.35) |

Table 5.6 (cont'd): VOC concentrations (ppbv) for various urban and rural areas previously reported

| Reference | Location | Type of emission | Date | 2-methyl-butane | 2-methyl-pentane | 3-methyl-pentane | acetylene | iso-butane | butane | pentane |
|---|---|---|---|---|---|---|---|---|---|---|
| Jobson, 2004 | USA, Houston | urban | 2000 | 0.91-1.23 | | | 0.41 | 1.21 | 1.11 | 0.37 |
| Guo, 2004 | China, Hong Kong | urban | 2001 | | | | 4.0 | 2.75-3.63 | 5.55-8.83 | 1.48-2.17 |
| Legreid, 2007 | Switzerland | | | | | | | | | |
| | Gubrist Tunnel | road transport | 2004 | | | | | | 7.41 | |
| | Zurich | urban | 2005 | | | | | | 0.73-1.97 | |

a. [*Thompson,* 2003]b [*Pankow*, 2003] , c. [*Roberts et al.*, 1984], d. [*Hagerman et al.*, 1997], e. [*Riemer et al.*, 1998], f. [*Rudolph and Harvanova*, 2003], g. [*Environment*, 2007], h. [*Jobson et al.*, 2004], i. [*Guo et al.*, 2004], j.[*Legreid et al.*, 2007b], k. standard deviation.

Table 5.7: Reported data on stable carbon isotope composition of ambient VOC.

| VOC | $\delta^{13}$C (‰) | Georgaphic Location | Type of location | Months |
|---|---|---|---|---|
| hexane | -32.6 (1.5)[a, b] | Toronto | suburban | Mar (00) |
| | -25.9 (2.7)[c] | North York | suburban | Dec (97) |
| | -27.0(2.5)[c] | North York | suburban | Jun (99) |
| | -26.8 (2.2)[b] | Houston | urban | Aug-Sep (00) |
| | -27.4 (3.0)[d] | Belfast | urban | Annual (03-04) |
| benzene | -25.1 (2.4)[b] | Alert | remote rural | All year (99-01) |
| | -22.95 (1.1)[b] | Fraserdale | remote rural | All year (00-01) |
| | -27.4 (1.3)[b] | Baring Head | remote rural | All year (99-00) |
| | -24.6 (2.5)[b] | North York | suburban | Nov (00) |
| | -23.8 (2.5)[c] | North York | suburban | Dec (97) |
| | -24.6 (2.3)[c] | North York | suburban | Jun (99) |
| | -25.05 (0.8)[b] | Toronto | suburban | Oct-Nov (00) |
| | -24.7 (2.3)[b] | Vancouver | suburban | Mar (00) |
| | -23.9 (2.8)[b] | Houston | urban | May-Jun (00) |
| | -26.3 (4.8)[b] | North York | urban | Aug-Sep (01) |
| | -24.1 (2.5)[b] | Vancouver | urban | May-Jun (00) |
| | -22.7 (2.5)[b] | Houston | urban | Aug-Sep (00) |
| | -28.3 (1.7)[d] | Belfast | urban | Annual (03-04) |
| heptane | -26.3 (4.8)[b] | North York | suburban | Oct-Nov (97) |
| | -19.3 (1.0)[b] | Hamilton | urban | Mar-Apr (99) |
| | -24.1 (2.5)[b] | Vancouver | urban | May-Jun (00) |
| | -22.7 (4.7)[b] | Houston | urban | Aug-Sep (00) |
| | -24.3(6.5)[e] | North York | suburban | Dec (97) |
| | -27.2(3.9)[d] | Belfast | urban | Annual (03-04) |
| toluene | -25.3 (0.5)[b] | Alert | remote rural | Nov (99-01) |
| | -26.8 (0.6)[f] | N Germany | costal site | Aug-Sep |
| | -23.7 (1.5)[b] | North York | suburban | Oct-Nov (00) |
| | -26.9 (0.9)[c] | North York | suburban | Dec (97) |
| | -25.01(1.1)[c] | North York | suburban | Jun (99) |
| | -27.1 (1.0)[b] | Toronto | suburban | Mar (00) |
| | -24.1 (1.2)[b] | Vancouver | urban | May-Jun (00) |
| octane | -24.0 (2.7)[b] | Houston | urban | Aug-Sep (00) |
| | -20.7 (1.1)[b] | North York | suburban | Oct-Nov (00) |
| ethylbenzene | -24.5 (2.1)[b] | Vancouver | urban | May-Jun (00) |
| | -29.8 (1.0)[b] | Toronto | suburban | Mar (00) |
| | -26.4 (3.7)[b] | North York | suburban | Oct-Nov (00) |
| | -26.37 (3.0)[c] | North York | suburban | Dec (97) |

Table 5.7 (cont'd): Reported data on stable carbon isotope composition of ambient VOC.

| VOC | $\delta^{13}C$ (‰) | Georgaphic Location | Type of location | Months |
|---|---|---|---|---|
| p,m-xylene | -26.5 (0.5)$^{b}$ | Alert | remote rural | Nov (99-01) |
| | -24.3 (8.1)$^{b}$ | North York | suburban | Oct-Nov (00) |
| | -27.4 (1.7)$^{c}$ | North York | suburban | Dec (97) |
| | -25.6 (1.0)$^{c}$ | North York | suburban | Jun (99) |
| | -25.4 (0.5)$^{b}$ | Vancouver | urban | Jun (00) |
| o-xylene | -23.8 (0.5)$^{b}$ | Alert | remote rural | Annual (99-01) |
| | -19.7 (2.0)$^{b}$ | North York | suburban | Oct-Nov (00) |
| | -26.3 (3.3)$^{c}$ | North York | suburban | Dec (97) |
| | -24.9 (1.5)$^{c}$ | North York | suburban | Jun (99) |
| | -23.9 (0.5)$^{b}$ | Vancouver | urban | Jun (00) |
| nonane | -32.9 (1.0)$^{b}$ | Alert | remote rural | Nov (01) |
| | -29.7 (3.0)$^{b}$ | North York | suburban | Oct-Nov (00) |
| | -28.26 (3.8)$^{c}$ | North York | suburban | Dec (97) |
| | -20.4 (1.0)$^{b}$ | Hamilton | urban | Mar (99) |
| | -30.4 (1.0)$^{b}$ | Vancouver | urban | May-Jun (00) |
| decane | -25.2 (2.9)$^{c}$ | North York | suburban | Dec (97) |
| | -24.8(3.2)$^{c}$ | North York | suburban | Jun (99) |

(a) the number in brackets are the standard deviation of δ (‰). (b) [*Thompson*, 2003] (c) [*Rudolph et al.*, 2002], (d)[*Redeker et al.*, 2007], (e) [*Czuba*, 1999], (f) [*Bahlmann et al.*, 2011].

Based on the comparison of mixing ratios and stable carbon isotope composition of individual VOC with the literature, Ridgetown could be classified as rural, Harrow and Egbert as semi-rural and Toronto as semi-urban areas. However, it should be noted that the isotope data might be biased towards concentrated samples (mostly local) with lower delta, since for low concentration samples delta values might not have been determined due to the detection limit constrains of IRMS (Table 4.20A, 4.21, 4.22, 5.8, Figure 4.6 and Figure 4.9). Theoretically, if photochemical processing is present, VOC are expected to become heavier in isotope composition and their concentrations will decrease; however at the same time low sample mass can result in the bias towards lighter measurements, sometimes creating an opposite effect on the overall δ. However the presence of delta values substantially heavier than those of emissions for low concentration samples (Figure 5.3) demonstrate that in many cases photochemical processing results in isotope fractionation significantly larger than potential bias from measurement (2.2.3).

Table 5.8: Number of data points available for atmospheric VOC in Egbert and Toronto samples

| Compound | Location | Total samples | Number of data points | Location | Total samples | Number of data points |
|---|---|---|---|---|---|---|
| hexane | Egbert | 54 | 26 | Toronto | 79 | 25 |
| benzene | | | 45 | | | 44 |
| heptane | | | 43 | | | 13 |
| toluene | | | 44 | | | 73 |
| octane | | | 1 | | | 19 |
| ethylbenzene | | | 39 | | | 58 |
| p,m-xylene | | | 39 | | | 24 |
| o-xylene | | | 40 | | | 44 |
| nonane | | | 16 | | | 14 |
| decane | | | 7 | | | 17 |

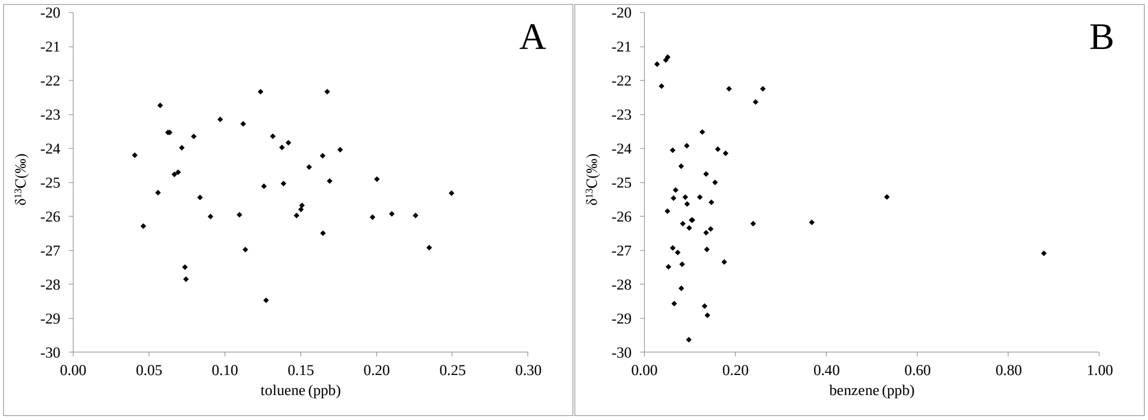


Figure 5.3: Mixing ratio versus stable carbon isotope ratio plots for toluene (A) and benzene (B) from samples collected at Egbert. Each data point has an uncertainty of ±0.5‰.

### 5.3.2 Use of concentrations and stable carbon isotope composition in the determination of possible emission sources and their proximity

It is expected that samples collected close to their emission sources will exhibit isotope composition similar to their sources, and samples collected further will be enriched in $\delta^{13}C$, displaying isotope fractionation as a result of the photochemical processing in the atmosphere (Section 2.2.2, and Section 2.3.2). Stable carbon isotope ratios of the main VOC emission sources has been widely studied and quantified; a summary of reported data is provided in Table 4.31.

Isotope ratios of many Toronto and Harrow samples are generally compatible with those of transport-related emissions (Table 4.31, Figure 4.8, Figure 5.4). However, there are some important details. Observed differences of $\delta^{13}C$ are within uncertainties of the source composition and are not statistically significant for hexane (Egbert, Toronto), heptane (Toronto) and benzene (Egbert, Toronto). Differences in $\Delta\delta^{13}C$ between Egbert and Toronto aromatics are lower than 0.5‰ and thus statistically not significant. $\delta^{13}C$ determined for Harrow benzene and heptane were lower than fossil fuel emissions (Figure 5.4), indicating possible emission with lighter isotope composition (lower $\delta^{13}C$). For the remaining compounds differences higher than the source uncertainty (0.5‰-2‰) are observed (2.5‰ for toluene, 2.9‰ for ethylbenzene, 3.3‰ for p,m-xylene and 2.7‰ for o-xylene) indicating the presence of ambient VOC enriched in $^{13}C$ compared to their sources (Figure 5.4).

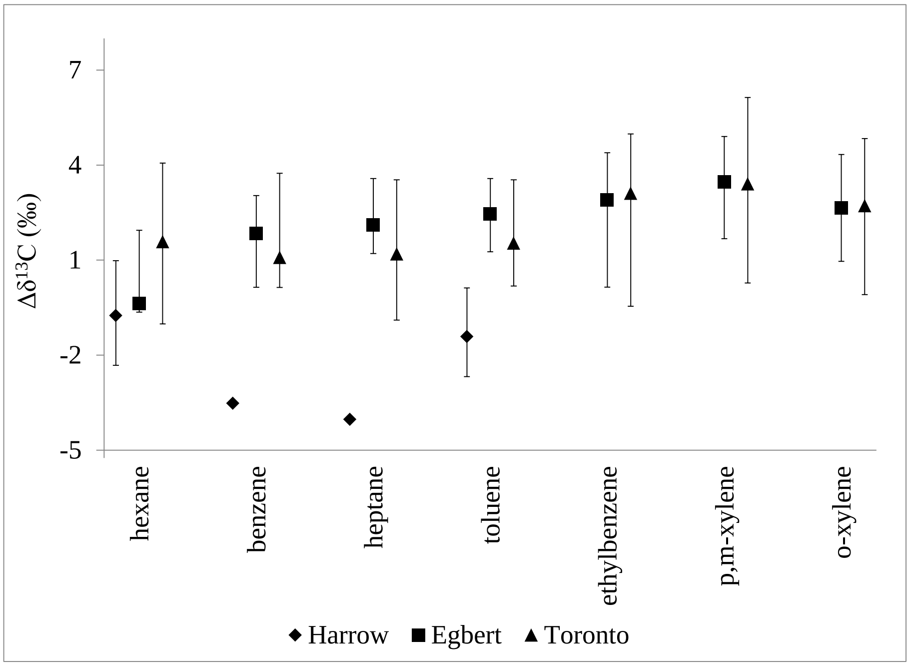


Figure 5.4: Differences in medians of source isotope composition (Table 4.32) and averages from ambient VOC ($\delta_{ambient}$-$\delta_{source}$, ‰). Upper quartile (75%) and lower quartile (25%) are indicated by the end points of the vertical lines.

Frequency distributions of $\delta^{13}C$ determined from Egbert and Toronto samples are shown in Figure 5.5.

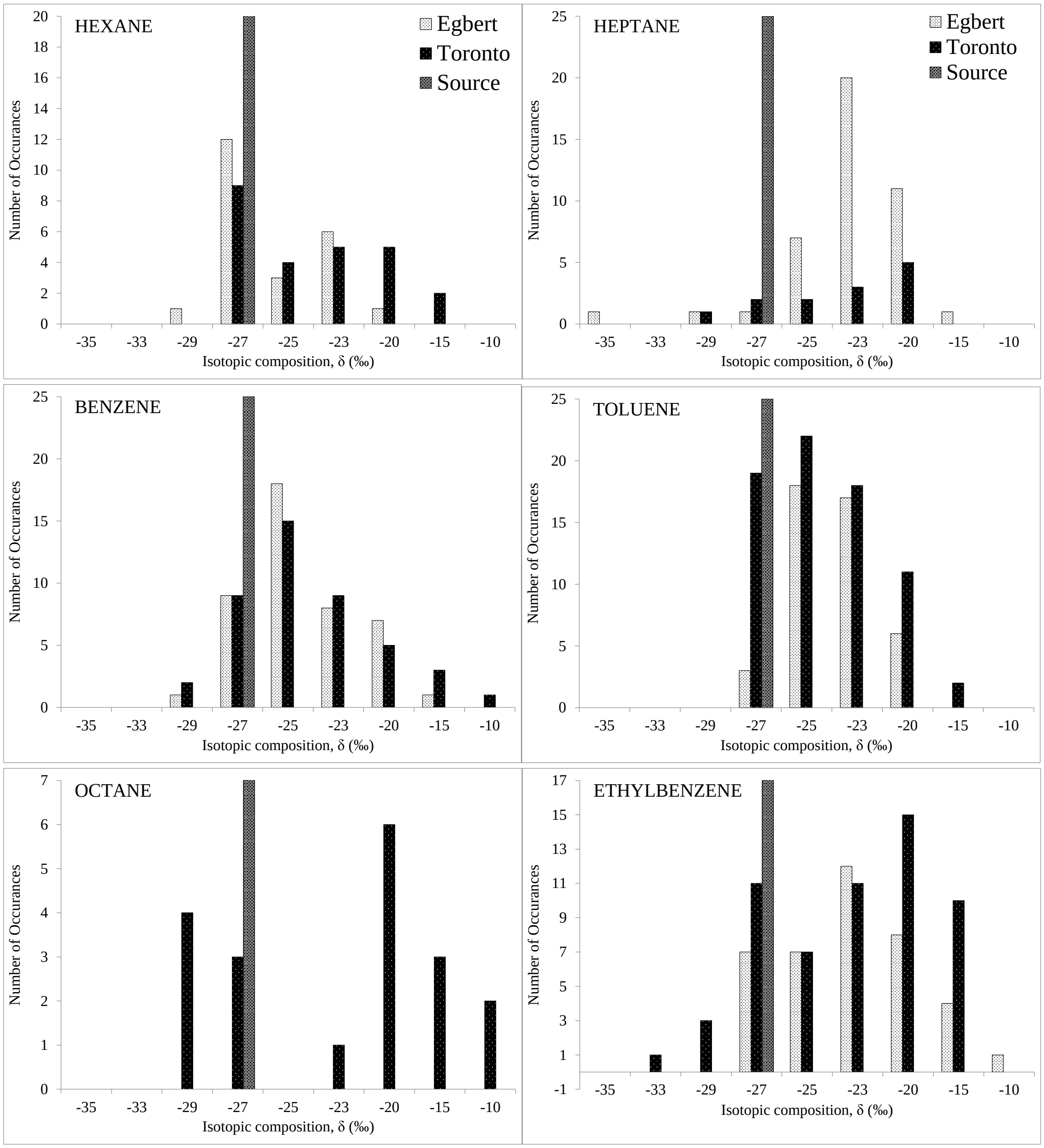


Figure 5.5: Frequency distribution of the isotope ratios comparing to fossil fuel derived emissions (source) for Egbert and Toronto. Uncertainty in $\delta^{13}$C for the source signatures is 0.5‰-1.7‰.

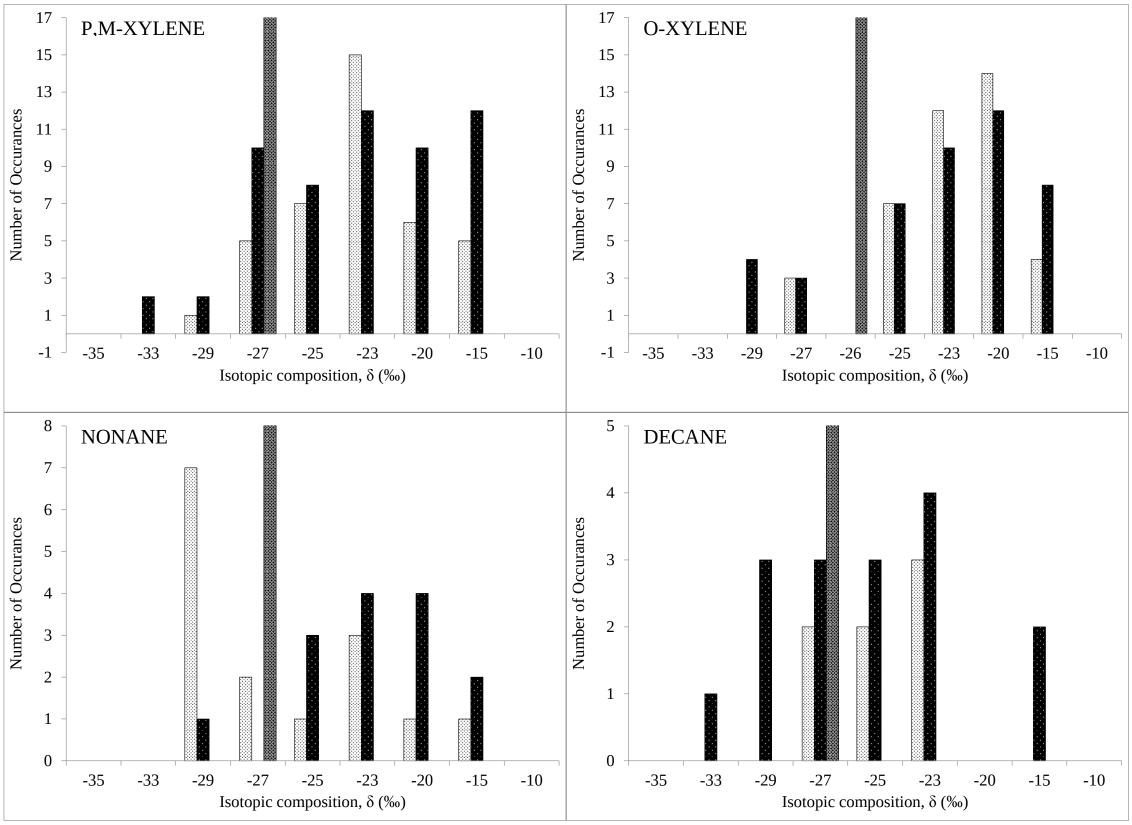


Figure 5.5 (cont'd): Frequency distribution of the isotope ratios comparing to fossil fuel derived emissions (source) for Egbert and Toronto. Uncertainty in $\delta^{13}$C for the source signatures is 0.5‰-1.7‰.

While hexane, benzene and toluene have the majority of their data clustered close to the $\delta^{13}$C of the source, other aromatics (ethylbenzene, p-,m-,o-xylenes) exhibit higher variability and are sometimes significantly enriched compared to their sources (ethylbenzene, p- m-,o-xylenes). For nonane and decane there are also a few substantially enriched data. However the number of data points for these compounds is insufficient for reliable frequency distribution analysis (Table 5.8). For ethylbenzene, p-, m-, o-xylenes there is a substantial number of data points which are heavier by 4‰ - 7‰ while for alkanes, benzene and toluene data that are more than 2‰-4 ‰ heavier than their emission sources are rare (Figure 5.5). This may be due to lower reactivity of toluene and benzene compared to xylenes and the lower KIE for reaction of alkanes compared to reactions of aromatics.

Comparison between data from Toronto and Egbert may be biased by the fact that there were data available for all seasons for Toronto but only for fall and winter for Egbert. Unfortunately the number of data points for spring and summer from Toronto are rather small and do not allow a detailed comparison of frequency distributions between spring + summer and fall+ winter. Nevertheless, when comparing the seasonal frequency distribution for Toronto no significant differences are noticed (Figure 5.6). This and the relatively small number of data points for spring and summer makes it unlikely that comparison between the Toronto and Egbert data set is biased by the spring and summer data from Toronto. Thus combining of the data for Toronto is justified.

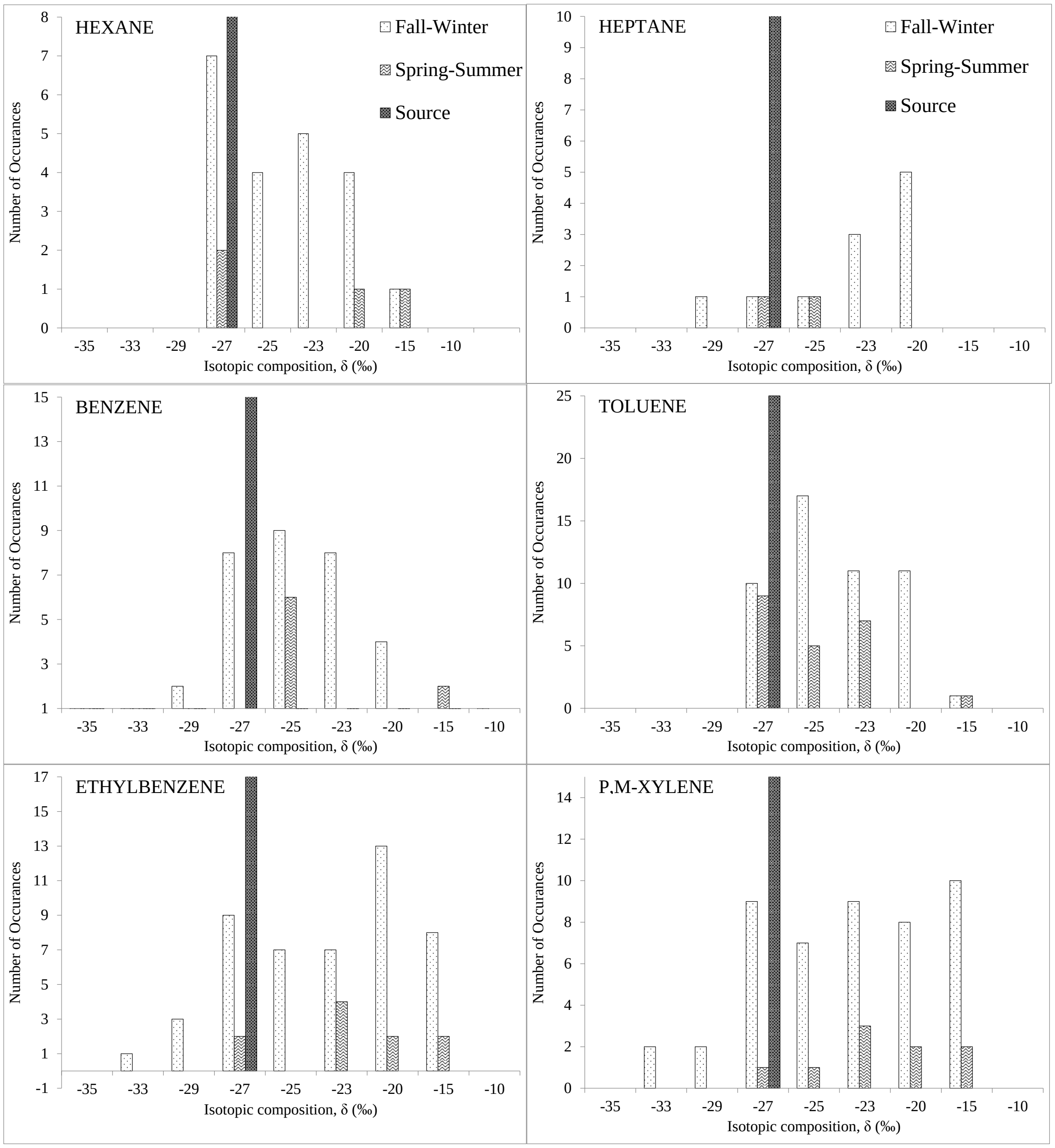


Figure 5.6: Seasonal frequency distribution of the isotope ratios for Toronto samples.

The proximity of the emission sources can be characterized using mixing ratios as an indicator. Closeness of strong sources accounts not only for higher levels in concentrations but at the same time for their high variability; this variability decreases with increasing distance from a source [*Jobson et al.*, 1999; *Jobson et al.*, 1998; *Junge*, 1973; *Parrish et al.*, 1992]. The residence time of the compound in the atmosphere has been shown to display linear behavior when plotted against the variability of VOC concentrations in a double-logarithmic plot [*Helmig et al.*, 2008; *Jobson et al.*, 1999; *Jobson et al.*, 1998]:

$$\ln(\sigma_{\ln x}) = -b\ln\tau + \ln A = b\ln k + \ln A \qquad (5.1)$$

where $\sigma_{\ln x}$ is the relative standard deviation of the logarithm of the atmospheric concentrations, $\tau$ the atmospheric residence time of the trace gas, k is the rate constant for the reaction with OH and A and n are semi-empirical constants [*Jobson et al.*, 1999; *Jobson et al.*, 1998].

It should be mentioned that due to the limited number of data from cartridge sampling for the BAQs campaign, canister samples were used for the data analyses described above. Since canister samples were taken as “grab samples” they represent a single point in time and space. These values should not be considered to be representatives of daily concentration levels of VOC that are obtained from the cartridge samples. Due to the much longer averaging time for cartridge samples lower variability is expected compared to point samples. This bias needs to be considered when comparing variability for BAQS samples with EC-YU. In addition, since both Egbert and Toronto data are based on 24 hour cartridge samples, they can be compared directly and the expected finding that VOC concentrations at Egbert are significantly less impacted by local sources than at Toronto is not biased by differences in sampling strategies. Since Toronto analysis includes data points from fall, winter, spring and summer and Egbert from wall and winter possible higher variability of concentrations due to the seasonal changes should be considered. However, no significant variation throughout the seasons is observed (Figure 4.7) and thus the seasonal data sets for both Egbert and Toronto can be reasonably combined into one.   Similarly the results for Harrow and Ridgetown can be compared directly without undue risk of bias. The disadvantage of a 24 hour sampling was reduced variability of concentration and isotope composition values that otherwise may be observed throughout the day.

The linear regression plots of the variability in concentrations versus lifetime for BAQS and EC-YU samples are provided in Figure 5.7.

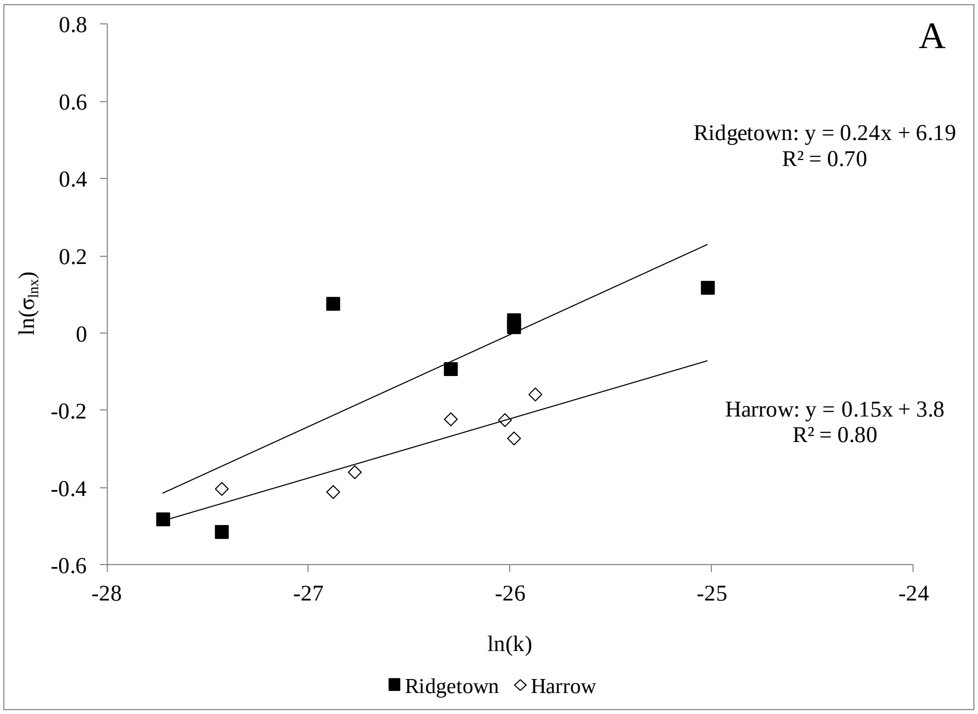


Figure 5.7: The double-logarithmic plot of the standard deviation of VOC mixing ratios versus their rate constants in reactions with OH radicals (A for Harrow and Ridgetown, B for Egbert and Toronto). Compounds used are listed in Table 5.9

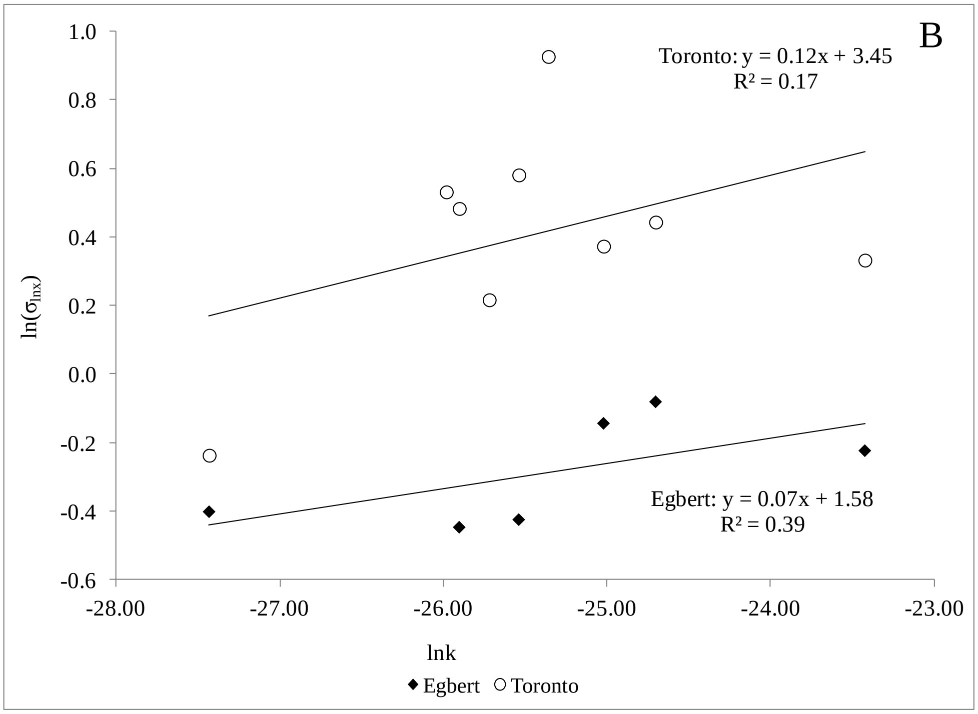


Figure 5.7 (cont'd): The double-logarithmic plot of the standard deviation of VOC mixing ratios versus their rate constants in reactions with OH radicals (A for Harrow and Ridgetown, B for Egbert and Toronto). Compounds used are listed in Table 5.9

Values of $\sigma_{\ln x}$ for target compounds and results of the regression fits (b values) are summarized in Table 5.9.

Comparing the data from 4 sampling sites, the highest $\sigma_x$ values per compound for most VOC are observed for the Toronto sampling site indicating expectedly the variability determined by local emission sources with limited averaging due to mixing. The decrease in variability in Egbert and Harrow samples (Table 5.9) suggests that these sites are generally less impacted by strong local sources. The Ridgetown data show even less impact from nearby sources.  A similar conclusion can be drawn based on the frequency distribution of VOC at Egbert compared to Toronto (Figure 4.6). For most compounds the distributions are very narrow for Egbert, but wide, and often very similar for different VOC in Toronto. However some species displayed higher than anticipated variability (for example propane in Ridgetown and Harrow, 2-methylbutane and butane in Ridgetown (Table 5.9), heptane and hexane in Egbert (Table 5.9 and Figure 4.6), the most probable cause of these discrepancies is an impact of a strong local emission source, and thus these compounds were not included in the regression analysis (Figure 5.7). Overall, it is evident that the further away from emission sources the observations are made, the higher the degree of correlation between lifetime and variability of concentration (for example, Ridgetown $R^2$=0.70 and Harrow $R^2$=0.80) (Table 5.9, Figure 5.7).

Table 5.9 Variability statistics ($\sigma^c$) for target compounds and results (b) of the linear regression fits for Ridgetown, Harrow, Egbert and Toronto samples

| Location/Compound | $10^{11}\times k_{OH}$ [a] | Ridgetown | Harrow | Egbert | Toronto |
|---|---|---|---|---|---|
| p,m-xylene | 1.87[b] | 1.07 | 0.87 | 0.92 | 1.56 |
| o-xylene | 1.36 | 3.95 | 0.85 | 0.87 | 1.45 |
| heptane | 0.68 | 0.89 | 0.69 | 1.54 | 1.24 |
| octane | 0.81 | N/A | N/A | 0.65 | 1.79 |
| toluene | 0.56 | 0.50 | 0.73 | 0.64 | 1.62 |
| 2-methylpentane | 0.52 | 0.27 | 0.76 | N/A | N/A |
| 3-methylpentane | 0.52 | 0.21 | 0.80 | N/A | N/A |
| n-hexane | 0.52 | 0.35 | 0.80 | 0.93 | 1.70 |
| pentane | 0.38 | 0.52 | 0.70 | N/A | N/A |
| 2-methylbutane | 0.36 | 1.09 | 0.66 | N/A | N/A |
| butane | 0.24 | 1.12 | 0.67 | N/A | N/A |
| 2-methylpropane | 0.21 | 0.96 | 0.80 | N/A | N/A |
| benzene | 0.12 | 0.54 | 0.35 | 0.67 | 0.79 |
| propane | 0.11 | 2.70 | 0.66 | N/A | N/A |
| acetylene | 0.09 | 0.38 | 0.45 | N/A | N/A |
| b-coefficient | | 0.24 | 0.15 | 0.07 | 0.12 |
| $R^2$ (correlation) | | 0.70 | 0.80 | 0.39 | 0.17 |

N/A- data is not available

(a) k is the rate constant for the reaction with the OH-radical. The rate constants were taken from Atkinson [2003a] and Finlayson-Pitts and Pits [2000].

(b) The average of rate constants for p-xylene and m-xylene (14.3 and 23.1 $cm^3 molec^{-1} s^{-1}$ respectively) was used for $\tau$ calculation

(c) $\sigma$ is standard deviation in the data set per each compound

The slope of the correlation (coefficient b) can also be used to examine impact of local and regional emissions on the air masses [*Helmig et al.*, 2008]. It has been shown that b is close to zero for locations with variable local emission sources and close to one for photochemically processed air masses from remote confined locations ([*Helmig et al.*, 2008; *Jobson et al.*, 1999; *Jobson et al.*, 1998] .b-coefficients obtained for all four locations are closer to zero than one, indicating strong influence of local sources on the air quality in all these areas.

While fresh emission sources dominated local air quality in Toronto, lower median concentrations (Figure 4.7) and higher isotope ratios (Figure 4.9) of VOC in summer indicate presence of some photochemical processing. However, these changes are not significant, suggesting that photochemistry is not the only factor that has strong impact on VOC concentration levels in Toronto. One possible reason is that, due to the close vicinity of the sampling location to the sources, chemical processing is limited and therefore has only a small direct impact on VOC levels. This hypothesis can be tested using isotope ratios. And indeed, for most samples collected in Toronto the VOC isotope ratios are very close to that of VOC emissions (see 5.3.1.)

The relative impact of the photochemical processing on VOC concentrations can be derived using the change in isotope ratios:

$$\frac{[VOC]_{initial}}{[VOC]_{processed}} = \exp^{\frac{\Delta\delta}{\varepsilon}} \tag{5.1}$$

although this approximation neglects long range transport and mixing, and ascribes all photochemistry to processing within one uniform air mass (Figure 5.8).

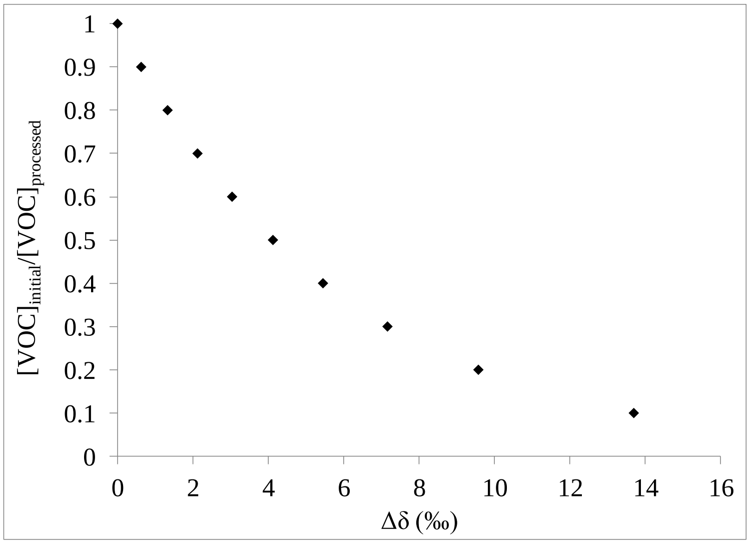
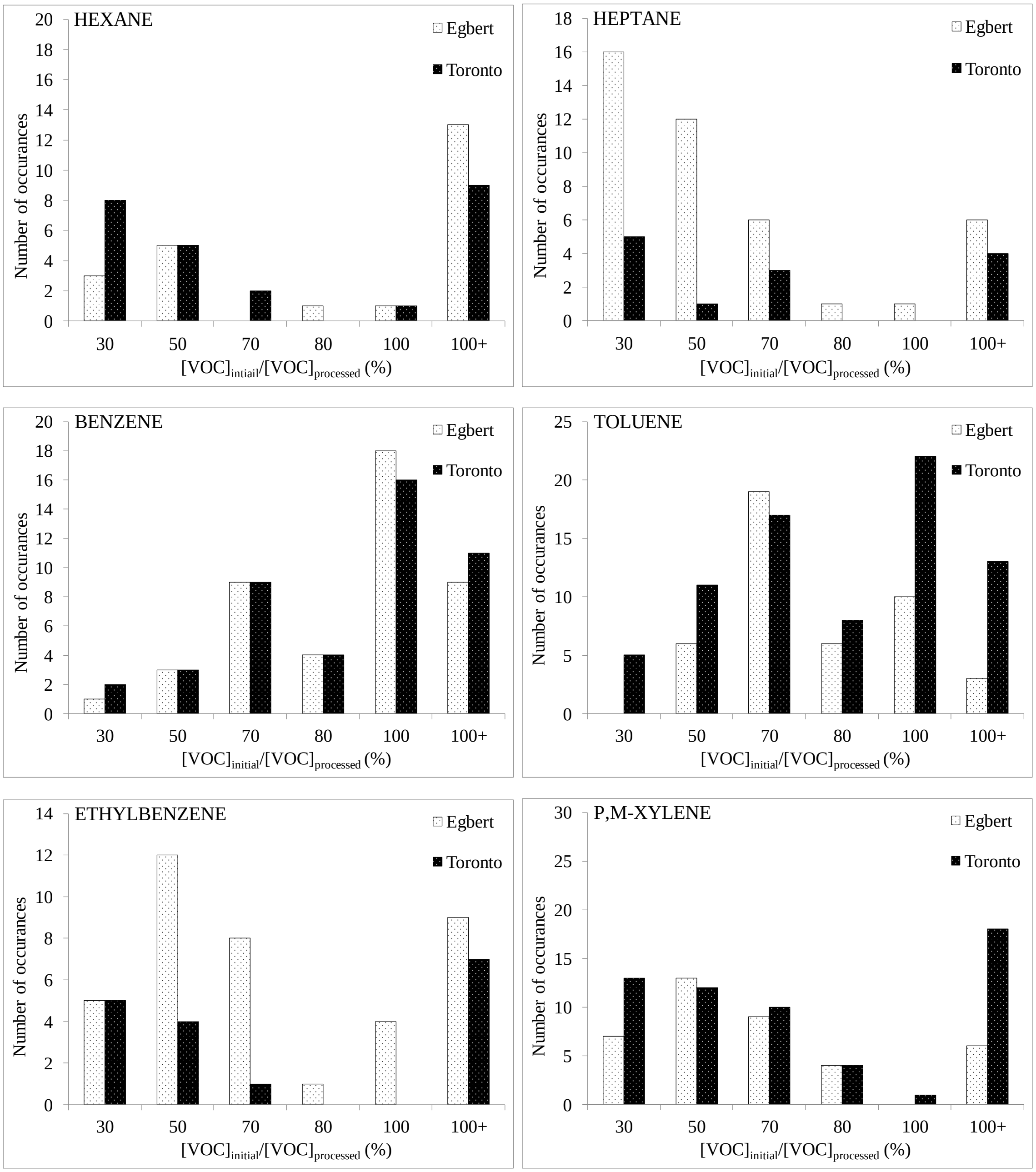


Figure 5.8: Impact of the isotope ratio change due to processing on VOC concentration (theoretical calculations are based on toluene)

Based on this simplification Δδ can be converted into percent reduction by reaction (Figure 5.9) and provide quantitative determination of processing (Eq.5.1).

Based on the results shown in Figure 5.9, there is a significant number of occurrences where chemical processing substantially contributes to changes in concentrations. As expected this is most frequently observed for the most reactive VOC and at Egbert.



<u>Figure 5.9:</u> % Reduction by reaction ($[VOC]_{initial}/[VOC]_{processed}$)

### 5.3.3 Correlation of concentrations and isotope composition

Correlations between compound concentrations can result from physical processing of the air mass such as dilution and mixing as well as processing, although in the latter case the correlation is not linear. Correlation in delta values can be explained by the photochemical processing or by the differences of the isotope ratios of emission sources. Correlation coefficients for concentrations are provided in Table 4.24 and for isotope ratios in Table 4.25 and Appendixes D and E).

For Egbert, strong correlation of concentrations is clearly visible for heptane and hexane, toluene and ethylbenzene, p,m-xylene and o-xylene. If two outliers are omitted there is also good correlation between toluene and benzene. This implies common or co-located source for these compounds, and since VOC with C6 and higher are usually connected with vehicle emissions and fuel evaporation, it seems likely that VOC at Egbert are mostly determined by gasoline-associated emission sources. However, there is no obvious correlation between alkanes and aromatics although hexane and heptane should be correlated with aromatics if vehicle exhaust is the dominant source. Sometimes very high concentrations of hexane and heptane and the very high correlation between these two compounds suggest there is an unusual source for these two substances. It should be noted that Egbert samples were collected in a trailer that contained other working chemical equipment and which was located next to a research building with several laboratories; hence it is quite possible that the VOC cartridge samples were contaminated since hexane and heptane are solvents widely used in laboratories. This could explain the higher levels of both of these VOC at Egbert comparing to other sites, as well as the presence of correlation between these compounds, and absence of correlation between them and aromatics (Tables 4.20, 4.21, 4.22, 4.24 and 4.25).

For Toronto, correlation of heptane and hexane is absent. Strong correlation between toluene and ethylbenzene, p,m-xylene and o-xylene as well as hexane in Toronto samples indicates the existence of a common source. However, for Toronto the correlation between benzene and toluene or other compounds is weaker than for Egbert. It is possible that while benzene is a regulated substance, there are still various benzene emission sources with emission patterns different from typical urban sources. Specifically, there is a large tank farm only a few kilometers away from Environment Canada. Mixing of emissions from sources with different emission patterns can significantly weaken the correlation between VOC mixing ratios.

Correlation in delta values can be caused by both photochemical processing and presence of emission sources with different isotope ratios. Based on published studies of the isotope ratio of VOC emissions (Table 5.7) there is only little variability and photochemical processing is only small for most samples (Figure 5.9). It is therefore not surprising that the measurements do not show strong correlation between VOC isotope ratios (Table 4.25).

The absence of an inverse relation between concentrations and $\delta^{13}C$ for VOC (Figure 5.3) is consistent with an overall dominance of dilution and mixing over processing as factor determining VOC concentrations. While the measurements show several data points with significant processing, the number of such points is too small to result in strong correlations between isotope ratios and VOC concentrations (2.2.3).

### 5.3.4 Photochemical ages determined from the hydrocarbon and isotope hydrocarbon clocks

While concentrations, stable carbon isotope composition, their trends, variability and correlations can be used for assessment of the local emission sources and photochemistry, often the analysis is qualitative (5.3.1, 5.3.2, 5.3.3). Alternatively, the photochemical age of the air masses determined by the methods described in 2.3 can be used to quantitatively classify sampling sites, as well as quantitatively predict the preceding photochemistry of the air masses. Results of different PCA determinations are provided in 4.3.6. All PCA determined by the different methods for four sampling locations (Harrow, Ridgetown, Egbert and Toronto) are combined in Figure 5.10. Due to the very limited number of data available for isotope hydrocarbon clock analysis of Harrow and Ridgetown samples PCA from these data are not included in Figure 5.10.

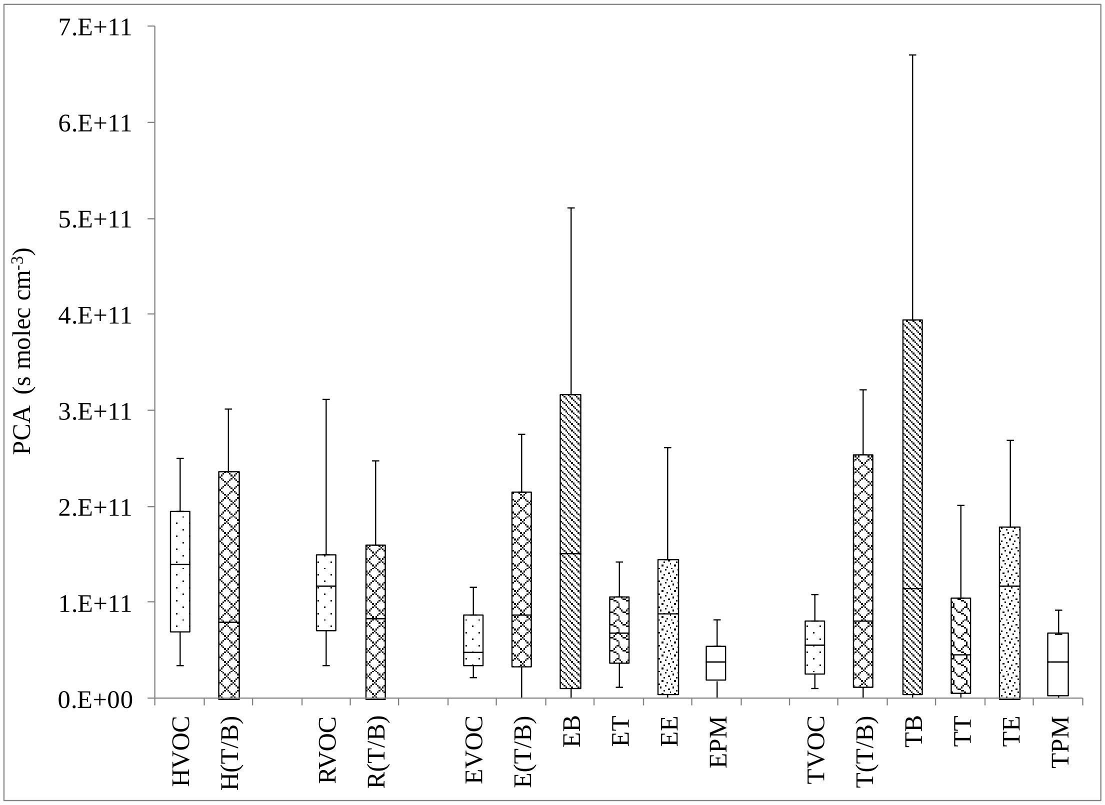


Figure 5.10: Box-and-whisker plot representing statistical analysis of photochemical ages determined using three different methods (mixing ratios of VOC and their rate constants (VOC), concentration ratios of toluene and benzene (T/B) and stable carbon isotope composition of benzene (B), toluene (T), ethylbenzene (E), p,m-xylene (PM)) for Harrow (H), Ridgetown (R), Egbert (E) and Toronto (T) samples. Upper quartile (75%) and lower quartile (25%) are indicated by upper and lower ends of the boxes and medians by vertical bars within the boxes, 10% and 90% by the end points of the vertical lines. Similarly determined PCA are depicted by the same pattern. The first letter on the horizontal scale identifies the location.

The PCA calculated by both hydrocarbon and isotope hydrocarbon clocks theoretically are subjects to several assumptions as discussed in 2.3.1 and 2.3.2.

However, the main factor that greatly affects PCA determination is the choice of the reference point. While in principle the choice of the reference sample is arbitrary, for practical reason samples with no substantial processing, with small variation of concentrations and isotope composition in emission patterns should be selected (4.3.6.1, 4.3.6.2). Hence for hydrocarbon clock analysis of BAQS and EC-YU data, the two closest industrial centers to the sampling sites with major emission sources were selected (down town samples of Windsor and Toronto). These samples were considered to represent time point zero with negligible photochemical aging and a dilution factor of unity (4.3.6.1, Table 4.26). While the assumption of an absence of photochemical processing is reasonable due to the closeness of measurement sites to emission sources, the dilution factor is somewhat arbitrary since it depends on the strength of nearby sources and atmospheric mixing and therefore on sampling location. The emission pattern, which is relevant for determination of processing, does not depend on source strength as long as the source types sampled are representative.

For the examination of vehicle associated emissions the averages of road-related emission ratios of toluene and benzene were used (Table 4.29). Since these studies were done over different time periods, seasons and included various types of vehicles in many countries, it was assumed that obtained average is a suitable reference point for the gasoline-related emissions.

Similarly, for the isotope hydrocarbon clock approach, the most critical point was the choice of the reference point. Due to the limited number of studies of the isotope composition for different emission sources, the reference point was estimated using the averages of all data available for Toronto (Table 4.31, 4.32).

Overall, while each differently calculated PCA included several sources of systematic errors, the major bias in these PCA is defined by the variability of their source ratios, which could range from 10%-55% (Table 5.10).

Table 5.10: Reference values and their uncertainties associated with the determination of the average concentrations

| Compound | BAQS | EC-YU | Source $\delta^{13}C$ Composition |
|---|---|---|---|
| | (ppbv) | | (‰) |
| 2-methylbutane | 0.98 (±0.53) | | |
| 2-methylpentane | 0.26 (±0.14) | | |
| 3-methylpentane | 0.19 (±0.09) | | |
| acetylene | 0.59 (±0.31) | | |
| benzene | 0.25 (±0.11) | 0.76 (±0.38) | -27.08 (±1.72) |
| cyclohexane | 0.05 (±0.03) | | |
| ethylbenzene | 0.101 (±0.05) | 0.26 (±0.12) | -26.56(±1.64) |
| isobutane | 0.43 (±0.22) | | |
| butane | 0.79 (±0.43) | | |
| hexane | 0.18 (±0.17) | 0.45 (±0.23) | -26.68(±0.43) |
| pentane | 0.62 (±0.35) | | |
| o-xylene | 0.10 (±0.06) | 0.26 (±0.12) | -26.00 (±1.72) |
| p,m-xylene | 0.31 (±0.19) | 0.73 (±0.35) | -27.24 (±0.88) |
| toluene | 0.997 (±0.62) | 2.89 (±1.18) | -27.22 (±0.88) |
| heptane | | 0.20 (±0.12) | -26.07 (±1.30) |
| octane | | 0.10 (±0.04) | -26.76 (±0.85) |
| nonane | | 0.03 (±0.01) | |

Clearly there is lower uncertainty in isotope composition of the source, thus PCA determined using isotope hydrocarbon clock are less biased comparing to those calculated using the hydrocarbon clock. Calculations of these uncertainties are described in 4.3.6.1 and 4.3.6.2.

The PCA determined with the hydrocarbon clock approach are provided in Table 4.27, 4.28, 4.30 and Appendix F. For the Egbert analysis hexane and heptane were not used due to the possibility of contamination discussed in 5.3.3. Low PCA values and their variability are all consistent with previously discussed observations (5.3.1 and 5.3.2) and imply that air of Harrow, Ridgetown, Egbert and Toronto is mostly influenced by local emissions, rather than long range transported air masses. The relation between PCA and the dilution factor (D) is examined using correlation coefficients of the regression plots in Figure 5.11. It is clear that dilution factors are quite variable with a majority of data points below 0.5. Since D compares VOC concentrations relative to the reference point, dilution values can only be used on a relative scale for values based on the same set of initial VOC mixing ratios.

Dilution of VOC can be distinguished from mixing based on the indirect dependence between PCA and D. For example, high sun intensity can increase photochemistry and at the same time increase convection resulting in the mixing of fresh, almost non-processed air masses (i.e. low PCA and low D). On the other hand, older air masses are more processed and are generally more diluted due to the longer residence time in the atmosphere (high PCA and low D). The increase of the correlation coefficient (R) can be used to confirm photochemical aging (Figure 4.11). If there is no change in ratios resulting in no spread in the data, random scatter dominates and $R^2$ is low. However if there is a substantial change in ratio due to processing, random scatter has a little impact and $R^2$ is high. Decrease in PCA with an increase in dilution factor is quite visible if some values with high dilution (<0.5) and small PCA ($<10^{11}$ s molec $cm^{-3}$) are omitted, indicating both photochemical and physical processing for Harrow and Ridgetown. However, only for Ridgetown, correlation coefficient increase with an increase of PCA indicating more photochemical processing (Figure 4.11). This trend was not observed for both Egbert and Toronto samples due to the high uncertainties of the dilution factors since only a limited number of VOC was available for the least squares analysis precluding any conclusions (Appendix F).

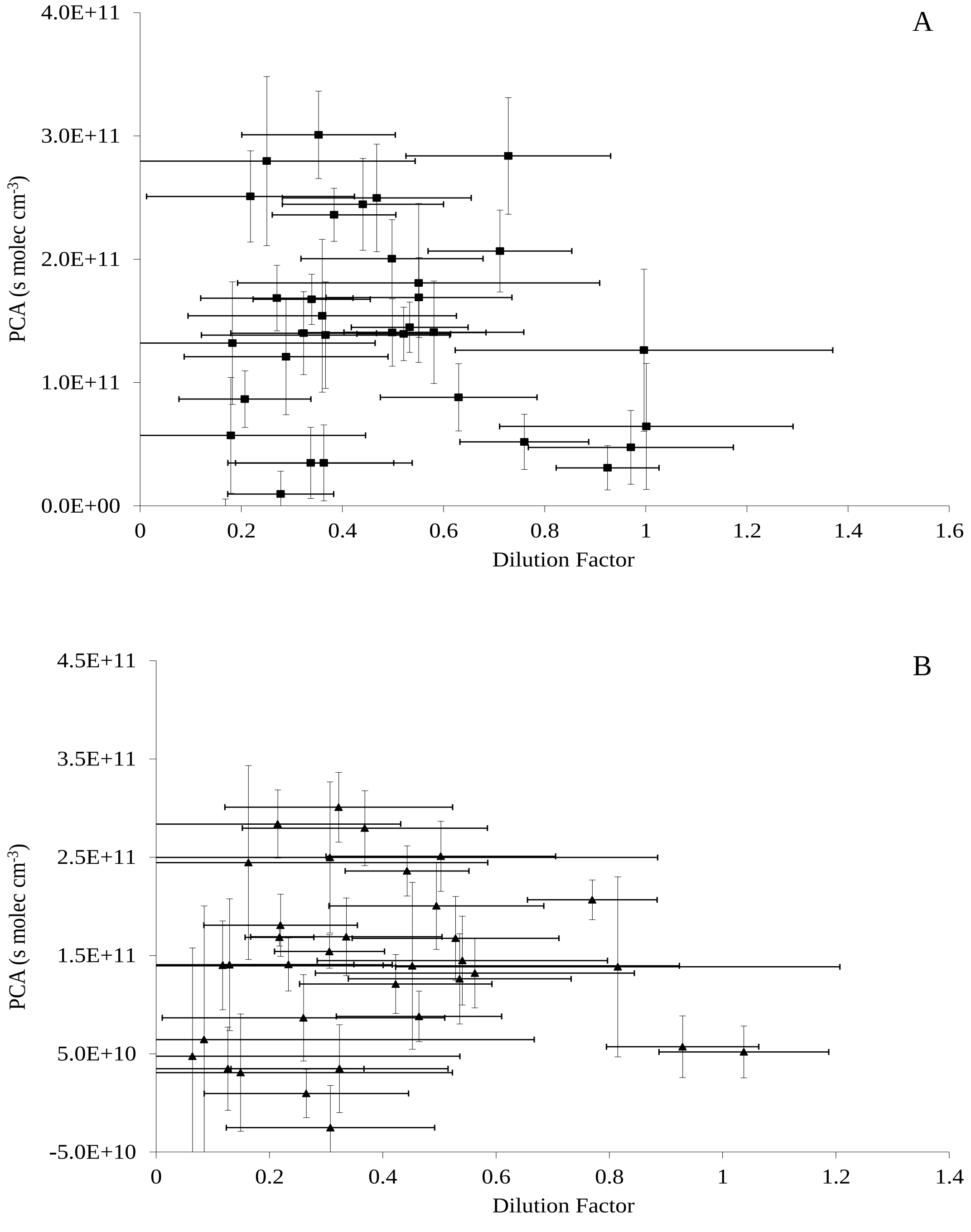


Figure 5.11: Plot of photochemical age versus dilution factor for Harrow (A) and Ridgetown (B) samples. Error bars represent uncertainties in the values determined using least squares regression analysis.

PCA determined from toluene benzene ratios are listed in Table 4.30 and Appendix G. While a somewhat higher variability of these values is observed (Table 4.30, Figure 5.8), values obtained are mostly within the uncertainty of PCA determined using VOC-$k_{OH}$ relation. The presence of some negative PCA (Appendix G) is due to the data scattering around the “true values”, which results in a negative value if PCA is low. Based on this analysis, it should be concluded that the use of VOC ratios specific for certain emission source could be utilized for the determination of PCA, but should be limited for samples collected in close proximity to their sources and serve more as a tool for source identification.

PCA determined from the isotope hydrocarbon clock are provided in Table 4.33 and Appendix H. While there is a higher variability in Toronto samples, the values are still comparable with those determined for Egbert (Figure 5.10). Since there was no inverse relation between concentrations and $\delta^{13}$C its absence for calculated PCA is not surprising (Figure 5.3, Appendix I). PCA determined for individual compounds when compared with each other (using both one and two variable analysis) showed correlation for the most of the VOC (Table 5.11, Figure 5.12, Appendix J). Correlation analysis was performed using the two-way regression option of IGOR Pro software (WaveMetrics, Inc). A few PCA values that were unrealistically negative or were highly affecting the linearity of the correlation line were eliminated in the two-way regression analysis. Unfortunately, the cause of the occurrence of these outliers could not be determined.

Table 5.11: PCA correlation of some VOC from Egbert and Toronto samples.

| Location | | Egbert | Toronto |
|---|---|---|---|
| Compound 1 | Compound 2 | $R^2$ | $R^2$ |
| heptane | hexane | 0.39 | 0.6 |
| toluene | benzene | 0.34 | 0.44 |
| toluene | hexane | 0.41 | 0.49 |
| ethylbenzene | toluene | 0.13 | 0.39 |
| p,m-xylene | toluene | 0.35 | 0.38 |
| p,m-xylene | ethylbenzene | 0.73 | 0.98 |
| p,m-xylene | o-xylene | 0.55 | 0.82 |

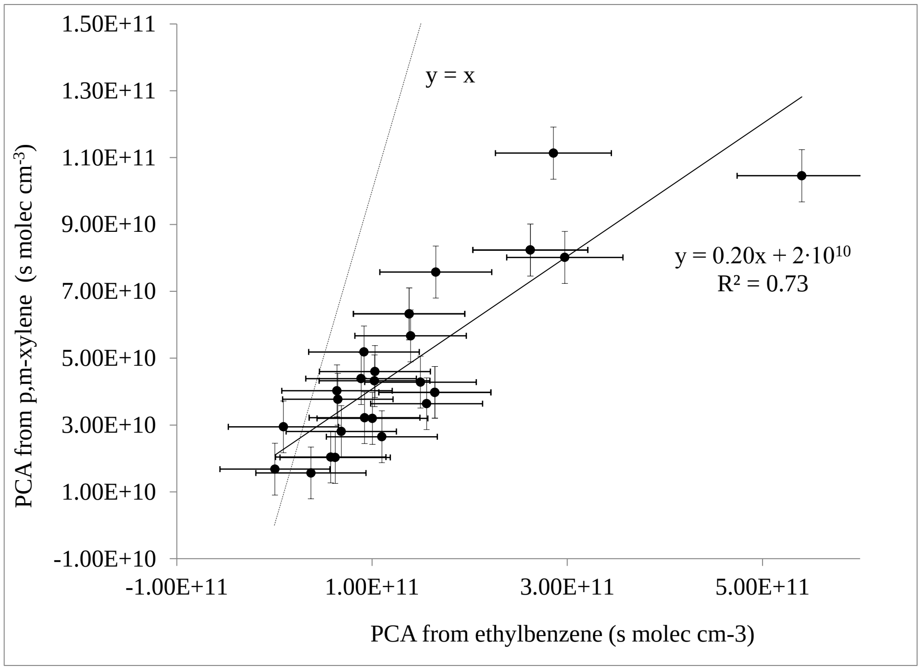
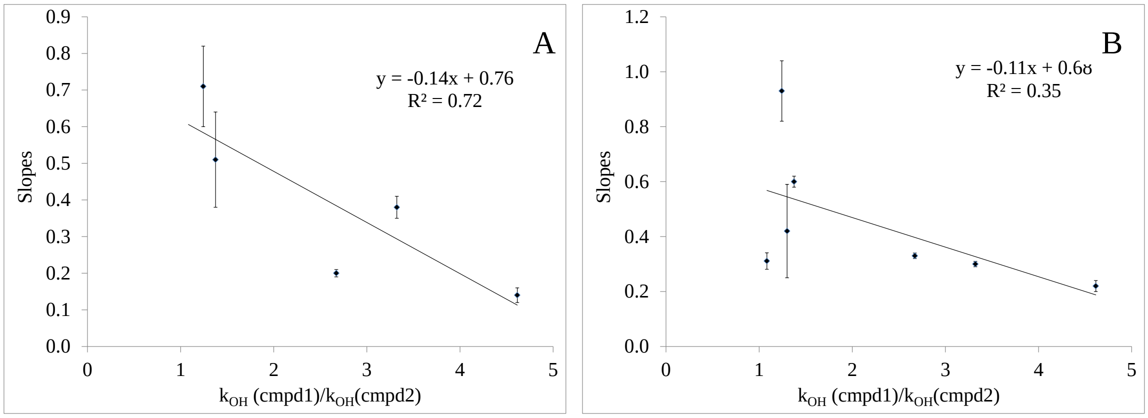


Figure 5.12: Example of correlation graph for PCA determined from stable carbon isotope ratios of p,m-xylene and ethylbenzene (Egbert samples).

Correlations of the determined slopes (Figure 5.9, Appendix J) versus compound reactivity are provided in Figure 5.13.



<u>Figure 5.13:</u> Correlation of slopes from the least square regression analysis of PCA determined from isotope composition for individual compounds versus compound reactivity (Egbert (A), Toronto (B). Error bars are uncertainties in the slopes calculated using two variable analysis by IGOR software. Cmpd1 and cmpd2 are compounds listed in Table 5.11. For Egbert plot correlation of hexane and heptane, toluene and hexane was excluded.

Significant correlation of the slopes (especially for Egbert samples) indicates that these compounds have similar photochemical history, with more reactive compounds depleting faster comparing to the less reactive one (Figure 5.13). Consequently, for more reactive VOC the contribution from remote sources (aged air parcels) is lower than for less reactive VOC.  Correlations of hexane and heptane, and toluene and hexane were removed for Egbert since hexane and heptane were considered to be contaminants in this location.

PCA determined from isotope composition of benzene showed highest variability and were significantly higher compared to other compounds (Figure 5.10, Table 4.33). The presence of some other unaccounted local sources with different $\delta^{13}$C can be ruled out based on the frequency distribution (Figure 5.5), since almost no data with lighter than the reference value isotope ratio were observed. However, high variability could be explained by the fact that since benzene is one of the longest-lived VOC in the set (Table 5.9) variable contributions from aged air parcels may be more important than for other

VOC. Such a trend is not detectable for other aromatics, since their atmospheric lifetime is smaller and thus their overall isotope composition is dominated by freshly emitted air masses in Egbert and Toronto. Due to the limited number of data points, and since data are available only for Fall and Winter seasons for Egbert, seasonal variations of PCA are not visible (Appendix H) and cannot be commented on. For Toronto, higher medians of delta values (which are directly related to PCA) were observed for the compounds of high reactivity VOC (toluene, ethylbenzene and p-,m-,o-xylenes) in fall and spring and lower in winter samples (Figure 4.10) although these differences were minor and statistically insignificant. Due to the limited number of isotope composition similar isotope hydrocarbon clock analysis was not performed for Harrow and Ridgetown compounds.

Correlation analysis of differently determined PCA was possible only for PCA determined from toluene benzene ratio and from stable carbon isotope ratios (Figure 5.14, Appendix K1.2 and K2.2), since PCA from VOC-$k_{OH}$ regression analysis contained high uncertainties that would make any conclusion invalid (Appendix K1.1 and K2.1).

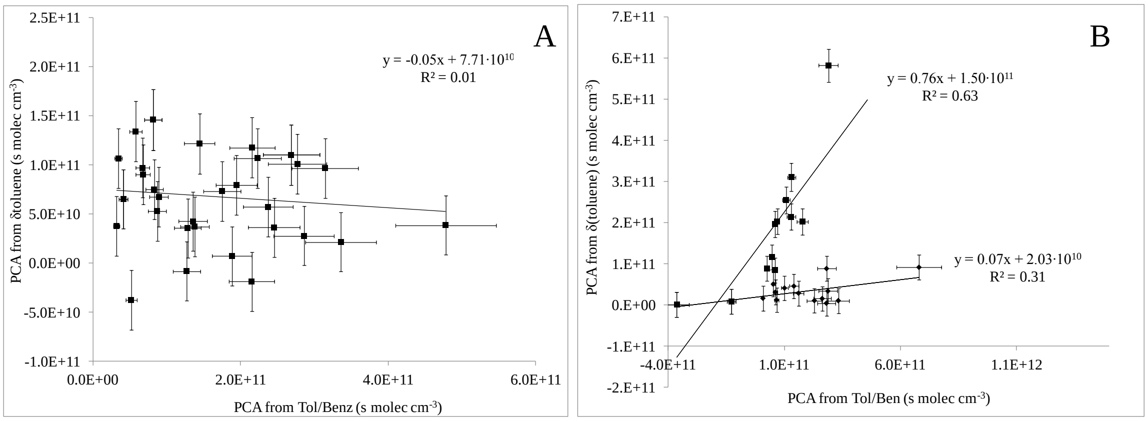


Figure 5.14: Correlations of PCA determined from toluene benzene ratio (using vehicle emission as a reference point) and PCA from stable carbon isotope composition of toluene (A- Egbert, B- Toronto)

Surprisingly there is little correlation between $PCA_{\delta toluene}$ and $PCA_{toluene/benzene}$ (Figure 5.14). The only exception is one cluster of data with similar ages that cannot be really called a correlation due to a limited number of points (Figure 5.14B). The absence of a correlation between PCA can be explained by the fact that the toluene benzene ratio is heavily impacted by “remote” benzene (consistent with the benzene age observations), while the toluene age is more sensitive to local emissions, with the exception of a little interference from local toluene or the impact of a strong aged (remote) source. For example, the expected close to unity “correlation” was observed in Toronto for PCA$\delta_{toluene}$ versus PCA from toluene benzene ratio (Figure 5.12B) formed by the samples with the air origins mainly from north and north west with toluene concentrations ranging from 0.7 ppbv to 1.5 ppbv (Appendix O), clearly indicating local fresh vehicle-associated emissions that are not affected much by the clean air masses from the north. Almost no correlation ($R^2$=0.07) was formed by the samples of various air origins (south, south west, north west and west), with low mixing ratios of toluene (from 0.03 to 0.25 ppbv) and benzene (0.02-0.20 ppbv). In principle, these might be somewhat photochemically aged air samples, however PCA$\delta_{toluene}$ values are still significantly influenced by the presence of freshly emitted non-processed toluene with lighter isotope composition.

In Egbert, the expected correlation of one is skewed even more (Figure 5.14A), possibly by mixing of fresh emissions with light delta values with background or aged air masses. Unfortunately no clear consistent dependencies of mixing ratio levels or isotope composition on the origins of air masses or any meteorological conditions were observed (Appendix L, M, N and O).

In conclusion, most of the PCA calculated using different approaches have resulted in PCA values that ranged from zero to about $3 \cdot 10^{11}$ molecules s $cm^{-3}$. While there were some differences and variations discussed above, the majority of the determined PCA were rather small, approximately 55-80 hrs if the diurnal average value of OH-concentration of $1 \cdot 10^6$ -$1.5 \cdot 10^6$ molecules $cm^{-3}$ are used. Conclusions made based on the concentrations, isotope composition and different PCA (the hydrocarbon and isotope hydrocarbon clocks) were consistent and indicated that Toronto and Egbert air quality is mostly affected by the strong local sources, emission from which occasionally gets diluted by fresh air parcels from the north and north west. However, photochemical processing indicated by the frequency distribution of $\delta^{13}C$ is still present to some extent; but it is usually overcomed by the fresh emissions from local sources.

## 5.4 Source study: Isotopic composition of benzene and toluene from diesel and biofuel samples

Stable carbon isotope composition of benzene and toluene from regular diesel (RD) and biodiesel (B) samples is presented in Table 4.23. Emissions from regular diesel samples for toluene on average were -27.4‰ with a standard deviation of ±1.2‰ and -25‰ (±1‰) for benzene. These $\delta^{13}C$ values are, as expected, close to the isotope composition of crude oil derived compounds (Table 4.31) [*Rudolph et al.*, 2002; *Smallwood et al.*, 2002; *Thompson*, 2003]. Emissions from biofuel samples were lighter, -44.49‰ (±0.28‰) for benzene and -30.29‰ (±0.28‰) and -32.31‰ (±0.17‰) for toluene. While for toluene, the difference is not large (less than 5 ‰), for benzene it is quite significant (almost 20‰) (Table 5.12).

The isotope ratios of toluene show some variations between the results obtained for different operating modes of the engine. For regular diesel with the idle engine mode toluene is more enriched than for all other modes, while for biofuel it is enriched less. Otherwise the data show no systematic dependence on speed of rotation (Table 5.12).

For regular diesel the isotope ratio of benzene is slightly higher than that for the tunnel samples that are dominated by tailpipe emissions, but since there is only one data point available this difference may not be significant. Toluene for idle and M2-M5 samples is comparable with those from the gas station, tunnel and underground garage samples, that are influenced by both evaporation of fuel and tailpipe emissions and overall are close to the refinery samples, that are dominated by unprocessed and processed fossil fuels [*Rudolph et al.,* 2002]. Since the difference between the parent fuel and emissions are due to the incomplete combustion in the engine, slight differences in $\delta^{13}$C for different M2-M5 tests are expected and can be explained by the preference of the removal of the lighter isotopologue.

Table 5.12: Stable carbon isotope composition of benzene and toluene in emissions, diesel and biofuel samples.

| **EMISSIONS** | | benzene | toluene |
|---|---|---|---|
| **Sources**[a] | | $\delta^{13}$C (‰) | $\delta^{13}$C (‰) |
| Underground garage (Toronto, Winter, Spring) | | -27.7 (0.7)[b] | -27.1 (0.7) |
| Tunnel (Toronto, Winter and Fall) | | -26.5 (1.0) | -27.5 (1.0) |
| Gas Station (Toronto, Winter) | | -29.1 (0.3) | -27.4 (0.6) |
| Refinery (Toronto, Winter) | | -28.6 (0.1) | -28.4 (2.9) |
| | | | |
| **Regular diesel** | RPM | | |
| RD-Idle | 900 | -24.99 (0.78) | -26.1 (0.1) |
| RD-M2 | 1700 | LDL | -27.47 (0.21) |
| RD-M3 | 2250 | LDL | -27.01 (0.11) |
| RD-M5 | 1200 | LDL | -28.98 (0.21) |
| Average | | N/A | -27.4 |
| Standard Deviation | | N/A | 1.2 |
| | | | |
| **Biofuel** | RPM | | |
| B100-Idle | 900 | -44.49 (0.28) | -32.31 (0.17) |
| B100-M2 | 1700 | LDL | -30.29 (0.28) |

(a) [*Thompson,* 2003], (b) standard deviation calculated from repeated measurements

$\delta^{13}$C values for toluene from biofuel experiments are not only lighter than toluene emissions for experiments using regular diesel, but also lighter than toluene from refinery emissions (-28.4‰ ± 2.9‰) and other fossil fuel derived emissions (Table 5.12) by several permil. While these differences are small, the two measured isotope ratios for toluene from biodiesel experiments are consistently and significantly lower than the typical $\delta^{13}$C of fossil fuel derived emissions (Table 5.12).

The isotope ratio of benzene observed in biofuel experiments is nearly 20‰ lighter than typical isotope ratios of fossil fuel derived benzene emissions (Table 5.12). Since there is only one measurement available for benzene emissions from biofuel experiments this result may not be representative. This difference is much higher than any other variability of isotope ratios observed in these experiments. Moreover, the benzene isotope ratio observed in the experiment using regular diesel is consistent with other isotope ratio measurements for fossil fuel derived benzene (Table 5.12).

Biodiesel is made out of a feedstock (in this case soy seeds) through trans-esterification of vegetable oils through an addition of alcohols (usually methanol) in the presence of catalyst[*IEA*, 2007; *USADE*, 2012] (Figure 5.15). While production processing of the soybean is a well developed process, the mixture of hydrocarbons derived from it is complex and still under investigation. It is known that the major fraction of the produced oil is made out of aliphatic hydrocarbons ($C_{12}$-$C_{35}$), steroidal hydrocarbons and terpene hydrocarbons [*Gunawan et al.*, 2012]. Propene that may be formed in the combustion process from terpenes can then form benzene, toluene and other aromatic compounds [*Choudhary et al.*, 2002]. Such complex reaction sequences may well result in significant isotope fractionation for individual products, even at the high temperatures typical for combustion engines.

Vegetable Oil and Fat → Transesterification → Crude Biodiesel →
Refining → Biodiesel

Figure 5.15: Biodiesel production pathway

Soybeans follow a C3 photosynthesis pathway, which was similarly followed by the plants that formed current fossil fuel in the past [*Reddy and Hodges*, 2000]. Due to the $^{13}C$ discrimination during methabolical processing the mean value of $\delta^{13}C$ for these plants is –28.5‰±2.5‰, which is about 20‰ less than $\delta^{13}C$ of ambient $CO_2$ [*Farquhar et* *al.*, 1989; *Farquhar et al.*, 1982; *O'Leary*, 1981]. Isotope composition of preindustrial $CO_2$ has been widely studied and was determined to vary from –7.6 ‰ to -6.5 ‰, while $\delta^{13}$ C of current $CO_2$ ranges from -11 ‰ to -8 ‰ depending on local emissions [*Brenninkmeijer et al.*, 2003; *Chmura et al.*, 2005; *Leuenberger et al.*, 1992; *Wahlen*, 2002]. Therefore, visible difference in toluene $\delta^{13}$C between fossil fuel and biofuel samples (2‰ and 4 ‰) could be explained by the differences in isotope composition of their precursor ($CO_2$) (up to 4‰).

# 6. CONCLUSIONS

Due to the complexity of the existing methods used for measurements, the number of publications containing stable carbon isotope composition of ambient VOC or their interpretation is still quite limited. However, in addition to the ambient mixing ratios, the isotope composition of any atmospheric VOC provides very valuable information that can be used to understand processes in atmosphere further. In this work it was shown that stable carbon isotope composition of VOC can be used along with or instead of other common methods not only to identify possible emission sources, but to approximate their proximity and determine the photochemical age of air masses.

Recently, application of stable carbon isotope in ambient studies has been limited by the absence of suitable sampling and analysis techniques for VOC present in pptv-ppbv levels. In this work reliable sampling and analysis methods were developed. Selective sampling from 20-100 L of ambient air onto an adsorbent filled cartridge allowed collection of suitable masses of VOC in a controlled time period with flow rates variable from 10-50 mL/min. Stainless steel cartridges packed with Carboxene 569 as adsorbent with quartz wool to hold the adsorbent in place showed no significant background signal and proved to be acceptable for the collection of both alkanes and aromatic VOC. The desorption procedure used a small furnace for thermal desorption of sampled VOC and a two-stage preconcentration system to recover the VOC. Two preconcentration systems developed (Tekmar 5010 and TSPS ) showed at least 90% reproducibility using a trapping temperature of 93 K and a subsequent desorption at 513K for 15-20 min. An improved cryogenic trap allowed the increase of reproducibility up to 95% and a significant decrease in the consumption of liquid nitrogen. Absence of any fractionation during the sampling and analysis stages was proven by the comparison between on-line and off-line measurements. On-line measurements of artificial VOC test mixtures were done using all sampling and analysis stages, followed by the GC separation and combustion in the oxidation furnace. The stable carbon isotope ratio of the bulk VOC, which were used to prepare the mixtures, were determined using conventional off-line IRMS measurements. Good agreement for aromatic VOC proved good accuracy of the method; however there were some discrepancies for alkanes, which still require further investigation.

Overall, the simplicity and affordability of the proposed sampling and sample processing systems is a valuable step towards the possibility of a wider application of stable carbon isotope measurements of ambient VOC. However, it has to be remembered that GC-IRMS instrumentation currently still is demanding and expensive. Nevertheless, due to the option to collect VOC from large volumes of air and the resulting larger sample masses reduces the need for GC-IRMS instrumentation with extreme sensitivity. This is an important step towards establishing VOC isotope ratio measurements as standard technique in atmospheric chemistry.

One of the consequences of a lack of simple and inexpensive measurement techniques for VOC isotope ratios is the lack of substantial sets of ambient observations. This limits the possibility of isotope ratio data collected as part of this thesis comparison with other data sets and requires development of methodologies to extract new insight into atmospheric VOC chemistry from isotope ratio measurements.

In this work the possibility of using VOC isotope ratios to distinguish between the impact of local emissions and long range transport was explored. Consistent with their location mixing ratios classified the sampling sites as rural (Ridgetown), semi-rural (Harrow and Egbert) and semi-urban (Toronto) areas. Nevertheless, based on the frequency distributions of delta values, it was determined that for most of the analyzed samples VOC are freshly emitted and have been subject to little photochemical processing. While this is expected for the semi-urban Toronto site, this observation is surprising for a semi-rural location such as Egbert. Although the isotope ratios for the semi-rural site show that there are more occurrences with significant VOC processing than at the suburban location, for a large fraction of measurements at Egbert the VOC processing derived from isotope ratios show that most VOC were not or only marginally processed. This demonstrates that for this semi-rural location local emissions very often dominate over the impact of long range transport.

The limited extent of processing is also consistent with the absence of strong systematic annual variability in both concentrations and isotope ratios for any of the compounds in Toronto. With the possible exception of one observation at Ridgetown all measured VOC isotope ratios are fully consistent with emissions resulting from the use of petroleum, i.e. have a fossil fuels origin.

Differentiation between local sources of VOC and impact of long range transport is, in principle, based on the assumption that photochemical processing occurs during transport. The more direct measure, the extent of photochemical processing can be derived from VOC concentration ratios as well as VOC isotope ratios. The results of the EC-YU study (Egbert and Toronto) were used for hydrocarbon and isotope hydrocarbon clock analyses. Unfortunately the number of isotope ratio measurements conducted successfully during the BAQs campaign (Ridgetown and Harrow) was too small to justify meaningful comparisons.

One of the limitations of the observations at Egbert and Toronto was the generally low extent of variability in VOC isotope ratios and thus of the photochemical age of VOC. Although there were several data points which demonstrated that there was substantial VOC processing, most of the VOC isotope ratios were within a few permil identical to that of emissions. For these small changes experimental uncertainties as well as uncertainties in the isotope ratio of emissions result in substantial uncertainty of PCA derive from isotope ratios. Nevertheless, PCA derived from the isotope ratios of different VOC show a substantial degree of correlation. This supports the concept that meaningful PCA can be derived from VOC isotope ratios. Surprisingly, the slope of correlations between PCA derived from different VOC depends on VOC reactivity. The most likely explanation is simply that due to the longer atmospheric residence time less reactive

VOC, on average, will be exposed to processing for longer time periods. This strongly suggests that the widely used term “photochemical age of an air mass” should be modified to reflect the fact that in many cases substances with different reactivity will have different PCA. One of the potential advantages of the differences in PCA for VOC with different reactivity is the possibility to study atmospheric transport at different timescales and therefore different spatial scales.

As a future application for this method, VOC with both shorter and longer lifetimes could be monitored. Other locations should be selected to determine if conclusions made in this work are applicable for other similar sampling sites; for longer photochemical processing, remote sites should be selected. In addition, shorter sampling time periods could be used to study diurnal variability. Furthermore, proposed experimental technique could be developed further by including measurements of isotope ratios of hydrogen (D/H). Since hydrogen atoms are present in every VOC, combining both carbon and hydrogen isotope ratios should provide even more details on possible chemistry of the VOC degradation pathways in the atmosphere. The sampling methodology developed as part of this work allows for collection of samples that contain sufficient mass for measurement of stable hydrogen isotope ratios of VOC.

The interpretation of stable carbon isotope ratios in this work is based on conceptual models. Numerical model simulations of carbon isotope ratios would be a very valuable, extremely promising alternative to interpret the observations and a viable option to validate numerical model simulations of atmospheric VOC. However, numerical models which allow prediction of VOC isotope ratios are scarce and the few currently available published models do not have the spatial resolution required for a meaningful interpretation of measurements very close to major sources.

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# APPENDIX A: Sample Information

## A1.1: Concentrations (ppbv) of VOC in Harrow Samples (canisters)

| Date | 20/06/07 | 20/06/07 | 21/06/07 | 21/06/07 | 21/06/07 | 22/06/07 | 22/06/07 | 23/06/07 | 23/06/07 | 23/06/07 | 24/06/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | 13:57 | 17:19 | 10:09 | 12:48 | 17:39 | 9:19 | 12:24 | 9:57 | 12:43 | 18:20 | 10:02 |
| propane | 0.340 | 0.309 | 0.752 | 0.353 | 0.267 | 0.589 | 0.623 | 0.425 | 0.179 | 0.337 | 0.944 |
| i-butane | 0.062 | 0.033 | 0.115 | 0.082 | 0.076 | 0.187 | 0.197 | 0.050 | 0.028 | 0.132 | 0.189 |
| acetylene | 0.136 | 0.160 | 0.421 | 0.140 | 0.114 | N/A | 0.126 | 0.105 | N/A | 0.138 | 0.325 |
| butane | 0.173 | 0.075 | 0.288 | 0.138 | 0.155 | 0.271 | 0.242 | 0.152 | 0.108 | 0.259 | 0.381 |
| t-2-butene | 0.007 | 0.003 | 0.006 | 0.002 | 0.006 | 0.002 | 0.004 | 0.001 | 0.001 | 0.016 | 0.002 |
| 1-butene | 0.016 | 0.014 | 0.010 | N/A | 0.020 | N/A | 0.011 | N/A | 0.003 | 0.009 | 0.001 |
| 2-methylpropene | 0.042 | 0.072 | 0.038 | 0.049 | 0.051 | 0.059 | 0.037 | 0.019 | 0.041 | 0.043 | 0.022 |
| 2,2-dimethylpropane | 0.002 | 0.001 | 0.003 | 0.001 | 0.002 | 0.003 | 0.003 | 0.001 | 0.002 | 0.001 | 0.005 |
| c-2-butene | 0.004 | 0.003 | 0.005 | 0.003 | 0.006 | 0.003 | 0.003 | 0.002 | 0.002 | 0.015 | 0.002 |
| cyclopentane | 0.049 | 0.072 | 0.082 | 0.053 | 0.045 | 0.047 | 0.047 | 0.047 | 0.062 | 0.141 | 0.058 |
| i-pentane | 0.232 | 0.091 | 0.389 | 0.126 | 0.184 | 0.242 | 0.231 | 0.180 | 0.111 | 0.316 | 0.359 |
| pentane | 0.096 | 0.042 | 0.214 | 0.045 | 0.081 | 0.100 | 0.095 | 0.096 | 0.058 | 0.168 | 0.173 |
| propyne | 0.009 | 0.004 | 0.012 | 0.005 | 0.004 | 0.006 | 0.004 | 0.004 | 0.007 | 0.004 | 0.015 |
| 1,3-butadiene | 0.004 | 0.003 | 0.009 | 0.002 | 0.003 | 0.009 | 0.002 | 0.001 | 0.003 | 0.006 | 0.007 |
| t-2-pentene | 0.006 | 0.003 | 0.009 | 0.001 | 0.006 | 0.005 | 0.003 | 0.004 | 0.003 | 0.014 | 0.003 |
| 2-methyl-2-butene | 0.006 | 0.004 | 0.005 | 0.002 | 0.005 | 0.005 | 0.005 | 0.002 | 0.003 | 0.010 | 0.005 |
| 1-pentene | 0.012 | 0.015 | 0.008 | 0.004 | 0.020 | 0.006 | 0.008 | 0.005 | 0.005 | 0.016 | 0.011 |
| 2-methyl-1-butene | 0.010 | 0.007 | 0.014 | 0.005 | 0.010 | 0.008 | 0.005 | 0.009 | 0.008 | 0.019 | 0.007 |
| c-2-pentene | 0.006 | 0.003 | 0.007 | 0.002 | 0.005 | 0.003 | 0.003 | 0.004 | 0.002 | 0.011 | 0.005 |
| 2,2-dimethylbutane | 0.009 | 0.004 | 0.015 | 0.004 | 0.007 | 0.005 | 0.004 | 0.003 | 0.003 | 0.010 | 0.015 |
| methylcyclopentane | 0.014 | 0.004 | 0.026 | 0.005 | 0.013 | 0.024 | 0.017 | 0.010 | 0.005 | 0.021 | 0.020 |
| cyclohexane | 0.006 | 0.001 | 0.010 | 0.004 | 0.004 | 0.005 | 0.012 | 0.002 | 0.001 | 0.007 | 0.010 |
| 2,3-dimethylbutane | 0.014 | 0.006 | 0.026 | 0.007 | 0.012 | 0.011 | 0.009 | 0.010 | 0.007 | 0.017 | 0.022 |

| Date | 20/06/07 | 20/06/07 | 21/06/07 | 21/06/07 | 21/06/07 | 22/06/07 | 22/06/07 | 23/06/07 | 23/06/07 | 23/06/07 | 24/06/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-methylpentane | 0.041 | 0.015 | 0.088 | 0.019 | 0.033 | 0.060 | 0.051 | 0.035 | 0.018 | 0.061 | 0.074 |
| 3-methylpentane | 0.025 | 0.008 | 0.057 | 0.013 | 0.019 | 0.050 | 0.041 | 0.020 | 0.010 | 0.039 | 0.045 |
| n-hexane | 0.035 | 0.011 | 0.062 | 0.016 | 0.025 | 0.082 | 0.063 | 0.024 | 0.010 | 0.060 | 0.057 |
| isoprene | 0.333 | 0.191 | 0.326 | 0.022 | 0.252 | 0.189 | 0.026 | 0.163 | 0.023 | 0.062 | 0.021 |
| t-2-hexene | 0.006 | 0.010 | 0.006 | 0.005 | 0.017 | 0.008 | 0.013 | 0.010 | 0.006 | 0.016 | 0.004 |
| 1-hexene | 0.012 | 0.006 | 0.008 | 0.004 | 0.014 | 0.006 | 0.005 | 0.007 | 0.008 | 0.010 | 0.007 |
| c-2-hexene | 0.003 | 0.003 | 0.006 | 0.003 | 0.002 | 0.006 | 0.001 | 0.004 | 0.003 | 0.006 | 0.002 |
| methylcyclohexane | 0.004 | 0.001 | 0.010 | 0.002 | 0.003 | 0.008 | 0.004 | 0.003 | 0.001 | 0.008 | 0.012 |
| heptane | 0.014 | 0.010 | 0.022 | 0.005 | 0.013 | 0.018 | 0.014 | 0.015 | 0.007 | 0.021 | 0.024 |
| benzene | 0.102 | 0.088 | 0.126 | 0.084 | 0.077 | 0.125 | 0.102 | 0.078 | 0.056 | 0.077 | 0.148 |
| octane | 0.009 | 0.010 | 0.008 | 0.004 | 0.003 | 0.010 | 0.007 | 0.008 | 0.005 | 0.014 | 0.010 |
| toluene | 0.106 | 0.042 | 0.180 | 0.057 | 0.095 | 0.112 | 0.075 | 0.103 | 0.044 | 0.185 | 0.138 |
| nonane | 0.011 | 0.011 | 0.015 | 0.004 | 0.004 | 0.003 | 0.003 | 0.003 | 0.005 | 0.025 | 0.009 |
| ethylbenzene | 0.015 | 0.007 | 0.022 | 0.005 | 0.004 | 0.016 | 0.007 | 0.009 | 0.004 | 0.023 | 0.019 |
| p,m-xylene | 0.030 | N/A | 0.061 | 0.017 | N/A | N/A | 0.017 | 0.040 | 0.017 | 0.131 | 0.032 |
| o-xylene | 0.011 | 0.005 | 0.022 | 0.004 | 0.004 | 0.014 | 0.007 | 0.008 | 0.003 | 0.028 | 0.013 |

| Date | 24/06/07 | 24/06/07 | 25/06/07 | 25/06/07 | 25/06/07 | 26/06/07 | 26/06/07 | 26/06/07 | 27/06/07 | 27/06/07 | 27/06/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | 13:45 | 19:34 | 9:00 | 13:36 | 17:55 | 8:52 | 14:17 | 21:08 | 8:48 | 14:43 | 17:39 |
| propane | 1.287 | 1.206 | 1.997 | 1.453 | 0.986 | 2.282 | 0.779 | 0.711 | 1.925 | 0.968 | 0.446 |
| i-butane | 0.196 | 0.178 | 0.392 | 0.238 | 0.131 | 0.634 | 0.149 | 0.092 | 0.724 | 0.336 | 0.111 |
| acetylene | 0.267 | 0.286 | 0.442 | 0.213 | 0.185 | 0.394 | 0.179 | 0.119 | 0.203 | 0.160 | 0.107 |
| butane | 0.387 | 0.340 | 0.882 | 0.423 | 0.234 | 0.972 | 0.258 | 0.228 | 1.151 | 0.398 | 0.326 |
| t-2-butene | 0.004 | 0.004 | 0.012 | LDL | 0.006 | 0.003 | 0.001 | 0.007 | 0.015 | 0.006 | 0.005 |
| 1-butene | 0.004 | N/A | 0.020 | 0.017 | 0.022 | 0.047 | N/A | 0.025 | 0.051 | 0.021 | 0.006 |
| 2-methylpropene | 0.025 | 0.025 | 0.043 | 0.041 | 0.047 | 0.050 | 0.028 | 0.053 | 0.067 | 0.043 | 0.031 |
| 2,2-dimethylpropane | 0.005 | 0.005 | 0.008 | 0.004 | 0.006 | 0.007 | 0.002 | 0.002 | 0.006 | 0.003 | 0.005 |
| c-2-butene | 0.002 | 0.004 | 0.011 | 0.004 | 0.006 | 0.008 | 0.004 | 0.007 | 0.020 | 0.008 | 0.006 |
| cyclopentane | 0.055 | 0.058 | 0.050 | 0.055 | 0.105 | 0.046 | 0.041 | 0.050 | 0.050 | 0.045 | N/A |
| i-pentane | 0.286 | 0.241 | 1.024 | 0.309 | 0.157 | 1.135 | 0.179 | 0.209 | 1.219 | 0.333 | 0.512 |
| pentane | 0.148 | 0.121 | 0.512 | 0.137 | 0.089 | 0.516 | 0.092 | 0.120 | 0.528 | 0.147 | 0.256 |
| propyne | 0.007 | 0.008 | 0.019 | 0.005 | 0.005 | 0.016 | 0.006 | 0.004 | 0.012 | 0.004 | 0.005 |
| 1,3-butadiene | 0.003 | 0.005 | 0.018 | 0.007 | 0.002 | 0.007 | 0.002 | 0.002 | 0.014 | 0.003 | 0.002 |
| t-2-pentene | 0.004 | 0.006 | 0.015 | 0.003 | 0.004 | 0.008 | 0.006 | 0.004 | 0.018 | 0.006 | 0.008 |
| 2-methyl-2-butene | 0.006 | 0.006 | 0.013 | 0.007 | 0.024 | 0.006 | 0.003 | 0.024 | 0.005 | 0.006 | 0.007 |
| 1-pentene | 0.005 | 0.005 | 0.022 | 0.014 | 0.006 | 0.029 | 0.016 | 0.005 | 0.025 | 0.019 | 0.011 |
| 2-methyl-1-butene | 0.008 | 0.010 | 0.018 | 0.011 | 0.012 | 0.021 | 0.011 | 0.012 | 0.022 | 0.009 | 0.015 |
| c-2-pentene | 0.003 | 0.006 | 0.010 | 0.006 | 0.007 | 0.009 | 0.005 | 0.007 | 0.011 | 0.006 | 0.006 |
| 2,2-dimethylbutane | 0.012 | 0.011 | 0.035 | 0.012 | 0.009 | 0.035 | 0.009 | 0.008 | 0.031 | 0.009 | 0.015 |
| methylcyclopentane | 0.017 | 0.011 | 0.073 | 0.008 | 0.007 | 0.100 | 0.008 | 0.009 | 0.114 | 0.016 | 0.021 |
| cyclohexane | 0.007 | 0.003 | 0.027 | 0.002 | 0.001 | 0.037 | 0.003 | 0.003 | 0.056 | 0.011 | 0.005 |
| 2,3-dimethylbutane | 0.016 | 0.012 | 0.051 | 0.012 | 0.009 | 0.060 | 0.010 | 0.012 | 0.073 | 0.018 | 0.024 |
| 2-methylpentane | 0.056 | 0.041 | 0.215 | 0.048 | 0.028 | 0.241 | 0.029 | 0.038 | 0.240 | 0.051 | 0.098 |
| 3-methylpentane | 0.035 | 0.023 | 0.130 | 0.029 | 0.015 | 0.153 | 0.016 | 0.022 | 0.151 | 0.029 | 0.054 |
| n-hexane | 0.068 | 0.032 | 0.148 | 0.034 | 0.027 | 0.192 | 0.030 | 0.028 | 0.181 | 0.040 | 0.051 |
| isoprene | 0.040 | 0.089 | 0.173 | 0.138 | 0.074 | 0.305 | 0.313 | 0.042 | 0.414 | 0.294 | 0.756 |
| t-2-hexene | 0.004 | 0.005 | 0.014 | 0.004 | 0.005 | 0.008 | 0.007 | 0.011 | 0.014 | 0.011 | 0.008 |

| Date | 24/06/07 | 24/06/07 | 25/06/07 | 25/06/07 | 25/06/07 | 26/06/07 | 26/06/07 | 26/06/07 | 27/06/07 | 27/06/07 | 27/06/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-hexene | 0.007 | 0.008 | 0.014 | 0.007 | 0.012 | 0.012 | 0.010 | 0.012 | 0.019 | 0.011 | 0.007 |
| c-2-hexene | 0.002 | 0.003 | 0.006 | 0.003 | 0.004 | 0.001 | 0.007 | 0.005 | 0.025 | 0.006 | 0.003 |
| methylcyclohexane | 0.005 | 0.002 | 0.025 | 0.003 | 0.002 | 0.055 | 0.002 | 0.003 | LDL | 0.013 | 0.006 |
| heptane | 0.018 | 0.012 | 0.066 | 0.009 | 0.011 | 0.076 | 0.012 | 0.012 | 0.093 | 0.025 | 0.019 |
| benzene | 0.153 | 0.138 | 0.223 | 0.122 | 0.093 | 0.200 | 0.098 | 0.093 | 0.203 | 0.107 | 0.074 |
| octane | 0.011 | 0.005 | 0.031 | 0.007 | 0.007 | 0.035 | 0.008 | 0.008 | 0.051 | 0.016 | 0.012 |
| toluene | 0.102 | 0.084 | 0.489 | 0.089 | 0.126 | 0.276 | 0.090 | 0.164 | 0.424 | 0.395 | 0.441 |
| nonane | 0.008 | 0.003 | 0.032 | 0.009 | 0.011 | 0.028 | 0.005 | 0.012 | 0.021 | 0.014 | 0.008 |
| ethylbenzene | 0.012 | 0.009 | 0.081 | 0.011 | 0.010 | 0.039 | 0.012 | 0.013 | 0.025 | 0.011 | 0.028 |
| p,m-xylene | 0.021 | 0.113 | 0.213 | 0.019 | 0.065 | 0.154 | 0.030 | 0.045 | 0.138 | 0.013 | 0.073 |
| o-xylene | 0.008 | 0.005 | 0.065 | 0.010 | 0.007 | 0.052 | 0.013 | 0.013 | 0.049 | 0.014 | 0.016 |

| Date | 28/06/07 | 28/06/07 | 28/06/07 | 3/07/07 | 3/07/07 | 3/07/07 | 4/07/07 | 4/07/07 | 4/07/07 | 5/07/07 | 5/07/07 | 5/07/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | 9:10 | 14:30 | 18:30 | 8:44 | 14:07 | 18:51 | 9:08 | 13:50 | 17:30 | 8:48 | 13:43 | 18:58 |
| propane | 0.569 | 0.449 | 1.420 | 1.529 | N/A | 0.443 | 1.105 | 0.690 | 0.561 | 1.569 | 0.660 | 0.266 |
| i-butane | 0.250 | 0.097 | 0.488 | 0.267 | 0.060 | 0.062 | 0.166 | 0.093 | 0.079 | 0.325 | 0.110 | 0.051 |
| acetylene | 0.132 | 0.204 | 0.116 | 0.277 | 0.151 | 0.135 | 0.254 | 0.148 | 0.232 | 0.243 | 0.375 | 0.090 |
| butane | 0.340 | 0.184 | 1.114 | 0.705 | 0.147 | 0.146 | 0.321 | 0.231 | 0.180 | 0.607 | 0.261 | 0.143 |
| t-2-butene | 0.007 | 0.011 | 0.003 | 0.008 | 0.002 | 0.005 | 0.005 | 0.005 | 0.007 | 0.005 | 0.009 | 0.010 |
| 1-butene | 0.021 | 0.043 | 0.082 | 0.021 | 0.005 | 0.021 | 0.017 | 0.021 | 0.025 | 0.031 | 0.021 | 0.036 |
| 2-methylpropene | 0.038 | 0.054 | 0.084 | 0.034 | 0.031 | 0.036 | 0.032 | 0.041 | 0.038 | 0.046 | 0.042 | 0.070 |
| 2,2-dimethylpropane | 0.002 | 0.002 | 0.003 | 0.002 | 0.001 | 0.002 | 0.003 | 0.001 | 0.005 | 0.003 | 0.004 | 0.002 |
| c-2-butene | 0.007 | 0.009 | 0.010 | 0.006 | 0.003 | 0.007 | 0.007 | 0.008 | 0.007 | 0.007 | 0.006 | 0.010 |
| cyclopentane | N/A | 0.050 | 0.041 | 0.049 | 0.073 | 0.050 | 0.110 | 0.054 | 0.101 | 0.047 | 0.117 | 0.053 |
| i-pentane | 0.245 | 0.188 | 0.852 | 0.430 | 0.125 | 0.134 | 0.321 | 0.191 | 0.182 | 0.838 | 0.346 | 0.199 |
| pentane | 0.154 | 0.085 | 0.486 | 0.325 | 0.054 | 0.055 | 0.163 | 0.092 | 0.101 | 0.395 | 0.183 | 0.092 |
| propyne | 0.006 | 0.015 | 0.009 | 0.007 | 0.003 | 0.002 | 0.010 | 0.004 | 0.007 | 0.012 | 0.010 | 0.006 |
| 1,3-butadiene | 0.022 | 0.028 | LDL | 0.005 | LDL | 0.003 | 0.002 | 0.005 | 0.003 | 0.012 | 0.003 | 0.003 |
| t-2-pentene | 0.010 | 0.009 | 0.006 | 0.008 | 0.003 | 0.006 | 0.010 | 0.007 | 0.005 | 0.005 | 0.005 | 0.005 |
| 2-methyl-2-butene | 0.020 | 0.015 | 0.005 | 0.008 | 0.003 | 0.012 | 0.001 | 0.017 | 0.013 | 0.006 | 0.019 | 0.005 |
| 1-pentene | 0.007 | LDL | 0.018 | 0.017 | 0.007 | LDL | 0.019 | 0.002 | 0.011 | 0.022 | 0.006 | 0.025 |
| 2-methyl-1-butene | 0.014 | 0.013 | 0.006 | 0.008 | 0.008 | 0.010 | 0.012 | 0.011 | 0.009 | 0.014 | 0.012 | 0.014 |
| c-2-pentene | 0.008 | 0.006 | 0.007 | 0.004 | 0.003 | 0.006 | 0.011 | 0.007 | 0.005 | 0.008 | 0.005 | 0.006 |
| 2,2-dimethylbutane | 0.006 | 0.006 | 0.020 | 0.009 | 0.005 | 0.005 | 0.017 | 0.006 | 0.009 | 0.029 | 0.015 | 0.008 |
| methylcyclopentane | 0.022 | 0.009 | 0.073 | 0.037 | 0.005 | 0.005 | 0.023 | 0.008 | 0.012 | 0.061 | 0.016 | 0.015 |
| cyclohexane | 0.034 | 0.003 | 0.000 | 0.014 | 0.002 | 0.001 | 0.006 | 0.001 | 0.004 | 0.021 | 0.005 | 0.013 |
| 2,3-dimethylbutane | 0.016 | 0.010 | 0.044 | 0.020 | 0.008 | 0.007 | 0.020 | 0.009 | 0.013 | 0.049 | 0.020 | 0.005 |
| 2-methylpentane | 0.061 | 0.034 | 0.215 | 0.114 | 0.022 | 0.018 | 0.079 | 0.030 | 0.037 | 0.168 | 0.066 | 0.043 |
| 3-methylpentane | 0.034 | 0.019 | 0.147 | 0.060 | 0.012 | 0.010 | 0.042 | 0.017 | 0.020 | 0.108 | 0.038 | 0.026 |
| n-hexane | 0.054 | 0.024 | 0.255 | 0.105 | 0.015 | 0.014 | 0.054 | 0.023 | 0.027 | 0.115 | 0.044 | 0.032 |
| isoprene | 0.382 | 0.211 | 0.175 | 0.302 | 0.028 | 0.066 | 0.043 | 0.197 | 0.122 | 0.327 | 0.698 | 0.268 |
| t-2-hexene | 0.011 | LDL | 0.006 | 0.005 | 0.005 | 0.014 | 0.015 | 0.014 | 0.010 | 0.007 | 0.008 | 0.006 |

| Date | 28/06/07 | 28/06/07 | 28/06/07 | 3/07/07 | 3/07/07 | 3/07/07 | 4/07/07 | 4/07/07 | 4/07/07 | 5/07/07 | 5/07/07 | 5/07/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-hexene | 0.011 | 0.019 | 0.011 | 0.005 | 0.006 | 0.014 | 0.016 | 0.016 | 0.012 | 0.011 | 0.013 | 0.016 |
| c-2-hexene | 0.006 | 0.005 | 0.001 | 0.003 | 0.004 | 0.006 | 0.011 | 0.007 | 0.004 | 0.004 | 0.006 | 0.003 |
| methylcyclohexane | 0.030 | 0.002 | 0.023 | 0.016 | 0.001 | 0.001 | 0.007 | 0.003 | 0.003 | 0.020 | 0.006 | 0.007 |
| heptane | 0.039 | 0.010 | 0.040 | 0.038 | 0.008 | 0.011 | 0.019 | 0.007 | 0.013 | 0.044 | 0.021 | 0.016 |
| benzene | 0.078 | 0.111 | 0.125 | 0.100 | 0.070 | 0.059 | 0.109 | 0.074 | 0.084 | 0.210 | 0.123 | 0.075 |
| octane | 0.018 | 0.005 | 0.018 | 0.014 | 0.004 | 0.006 | 0.008 | 0.008 | 0.007 | 0.015 | 0.009 | 0.010 |
| toluene | 0.392 | 0.346 | 0.336 | 0.298 | 0.150 | 0.126 | 0.250 | 0.141 | 0.174 | 0.574 | 0.344 | 0.394 |
| nonane | 0.008 | 0.012 | 0.013 | 0.016 | 0.005 | 0.005 | 0.011 | 0.006 | 0.010 | 0.007 | 0.011 | 0.015 |
| ethylbenzene | 0.026 | 0.015 | 0.021 | 0.024 | 0.034 | 0.002 | 0.016 | 0.005 | 0.008 | 0.037 | 0.019 | 0.020 |
| p,m-xylene | 0.098 | 0.040 | 0.042 | 0.093 | 0.045 | 0.016 | 0.054 | 0.006 | 0.020 | 0.117 | 0.038 | 0.069 |
| o-xylene | 0.022 | 0.013 | 0.012 | 0.021 | 0.009 | 0.006 | 0.023 | 0.002 | 0.004 | 0.038 | 0.007 | 0.024 |

N/A- no results available, LDL- lower than detection limit

## A1.2: Concentrations (ppbv) of VOC in Harrow Samples (cartridges)

| Start Date | End Date | Crtdg | Start Time | End Time | Flow mL/min | TotVolume mL | pentane | hexane | benzene | heptane | toluene | p-xylene | nonane | decane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6/20/07 | 6/21/07 | 51 | 9:10 | 9:40 | 37.38 | 54989 | 0.32 | 0.01 | 0.07 | N/A | 0.23 | N/A | 0.06 | 0.01 |
| 6/21/07 | 6/22/07 | 26 | 9:48 | 9:36 | 37-38 | 53458 | LDL | LDL | 0.44 | LDL | 0.13 | N/A | LDL | LDL |
| 7/4/07 | 7/5/07 | 62 | 9:05 | 9:03 | 38 | 53863 | 2.74 | 0.07 | N/A | 0.07 | 1.05 | 0.14 | 0.02 | 0.01 |
| 7/6/07 | 7/7/07 | 53 | 9:05 | 9:03 | 38 | 53873 | LDL | LDL | 0.00 | N/A | 0.01 | 0.00 | 0.00 | LDL |
| 7/9/07 | 7/10/07 | 34 | 9:15 | 9:06 | 38 | 53553 | LDL | LDL | 0.02 | 0.04 | 0.02 | LDL | LDL | LDL |

N/A- no results available, LDL- lower than detection limit

## A2.1: Concentrations (ppbv) of VOC in Ridgetown Samples (canisters)

| Date | 18/06/07 | 19/06/07 | 19/06/07 | 19/06/07 | 19/06/07 | 19/06/07 | 20/06/07 | 20/06/07 | 20/06/07 | 20/06/07 | 21/06/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | 20:05 | 9:25 | 14:15 | 18:05 | 21:09 | 23:45 | 8:45 | 11:21 | 13:52 | 21:21 | 8:20 |
| propane | 0.867 | 0.843 | 0.411 | 0.393 | N/A | N/A | 1.868 | 0.360 | 0.570 | 0.248 | N/A |
| i-butane | 0.145 | 0.195 | 0.071 | 0.069 | 0.074 | 0.079 | 0.584 | 0.116 | 0.203 | 0.073 | 0.261 |
| acetylene | 0.186 | 0.077 | 0.092 | 0.156 | 0.116 | 0.090 | 0.184 | 0.114 | 0.116 | N/A | 0.344 |
| butane | 0.319 | 0.353 | 0.134 | 0.147 | 0.170 | 0.123 | 0.932 | 0.275 | 0.415 | 0.237 | 0.477 |
| t-2-butene | 0.003 | 0.008 | 0.006 | 0.004 | 0.008 | 0.003 | LDL | 0.002 | 0.004 | 0.028 | 0.005 |
| 1-butene | 0.029 | 0.029 | 0.007 | 0.008 | 0.013 | 0.009 | LDL | 0.007 | 0.005 | 0.016 | 0.008 |
| 2-methylpropene | 0.046 | 0.044 | 0.029 | 0.032 | 0.027 | 0.026 | 0.216 | 0.012 | 0.028 | 0.038 | 0.025 |
| 2,2-dimethylpropane | 0.002 | 0.002 | 0.002 | 0.001 | 0.002 | 0.002 | 0.006 | 0.004 | 0.004 | 0.002 | 0.004 |
| c-2-butene | 0.002 | 0.008 | 0.004 | 0.004 | 0.009 | 0.002 | 0.012 | 0.003 | 0.004 | 0.026 | 0.008 |
| cyclopentane | 0.056 | 0.036 | 0.058 | 0.059 | 0.054 | 0.051 | 0.075 | 0.087 | 0.073 | 0.049 | 0.048 |
| i-pentane | 0.293 | 0.415 | 0.117 | 0.199 | 0.199 | 0.116 | 0.562 | 0.113 | 0.260 | 0.360 | 0.700 |
| pentane | 0.146 | 0.201 | 0.068 | 0.098 | 0.108 | 0.068 | 0.307 | 0.085 | 0.170 | 0.219 | 0.349 |
| propyne | 0.006 | 0.015 | LDL | 0.005 | 0.003 | 0.002 | 0.012 | 0.005 | 0.005 | 0.006 | 0.013 |
| 1,3-butadiene | 0.003 | 0.004 | 0.001 | 0.002 | 0.003 | 0.002 | 0.019 | LDL | LDL | 0.006 | 0.005 |
| t-2-pentene | 0.004 | 0.008 | 0.008 | 0.009 | 0.012 | 0.005 | 0.003 | 0.003 | 0.007 | LDL | 0.008 |
| 2-methyl-2-butene | 0.003 | 0.004 | 0.011 | 0.006 | 0.011 | 0.003 | 0.001 | 0.003 | 0.015 | 0.058 | 0.004 |
| 1-pentene | 0.030 | 0.025 | 0.006 | 0.013 | 0.014 | 0.009 | 0.002 | 0.006 | 0.005 | 0.032 | 0.015 |
| 2-methyl-1-butene | 0.008 | 0.012 | 0.011 | 0.010 | 0.014 | 0.006 | 0.009 | 0.007 | 0.010 | 0.030 | 0.019 |
| c-2-pentene | 0.003 | 0.005 | 0.007 | 0.006 | 0.008 | 0.004 | 0.001 | 0.001 | 0.008 | 0.036 | 0.008 |
| 2,2-dimethylbutane | 0.012 | 0.015 | 0.005 | 0.013 | 0.011 | 0.004 | 0.016 | 0.004 | 0.007 | 0.023 | 0.019 |
| methylcyclopentane | 0.014 | 0.028 | 0.009 | 0.016 | 0.017 | 0.007 | 0.074 | 0.011 | 0.017 | 0.035 | 0.057 |
| cyclohexane | 0.004 | 0.008 | 0.003 | 0.005 | 0.007 | 0.003 | LDL | 0.035 | 0.027 | 0.012 | 0.011 |
| 2,3-dimethylbutane | 0.015 | 0.019 | 0.009 | 0.015 | 0.016 | 0.008 | 0.037 | 0.008 | 0.013 | 0.027 | 0.032 |
| 2-methylpentane | 0.050 | 0.082 | 0.029 | 0.052 | 0.058 | 0.029 | 0.186 | 0.023 | 0.052 | 0.117 | 0.125 |
| 3-methylpentane | 0.027 | 0.048 | 0.017 | 0.030 | 0.033 | 0.016 | 0.167 | 0.014 | 0.032 | 0.063 | 0.085 |
| n-hexane | 0.039 | 0.068 | 0.022 | 0.029 | 0.037 | 0.021 | 0.305 | 0.026 | 0.051 | 0.054 | 0.124 |

| Date | 18/06/07 | 19/06/07 | 19/06/07 | 19/06/07 | 19/06/07 | 19/06/07 | 20/06/07 | 20/06/07 | 20/06/07 | 20/06/07 | 21/06/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| isoprene | 0.109 | 0.055 | 0.123 | 0.229 | 0.279 | 0.025 | 0.069 | 0.028 | 0.047 | 0.775 | 0.058 |
| t-2-hexene | 0.004 | 0.008 | 0.006 | 0.006 | 0.009 | 0.004 | 0.003 | 0.009 | 0.004 | 0.026 | 0.017 |
| 1-hexene | 0.018 | 0.017 | 0.006 | 0.007 | 0.009 | 0.006 | 0.006 | 0.003 | 0.011 | 0.018 | 0.009 |
| c-2-hexene | 0.007 | 0.004 | 0.002 | 0.005 | 0.007 | 0.005 | 0.006 | 0.003 | 0.008 | 0.010 | 0.004 |
| methylcyclohexane | 0.008 | 0.011 | 0.002 | 0.003 | 0.005 | 0.003 | LDL | 0.010 | 0.009 | 0.005 | 0.013 |
| heptane | 0.021 | 0.027 | 0.009 | 0.013 | 0.014 | 0.008 | 0.071 | 0.019 | 0.017 | 0.032 | 0.032 |
| benzene | 0.124 | 0.110 | 0.061 | 0.202 | 0.070 | 0.064 | 0.239 | 0.053 | 0.073 | 0.132 | 0.183 |
| octane | 0.010 | 0.023 | 0.004 | 0.005 | 0.005 | 0.004 | 0.029 | 0.010 | 0.007 | 0.014 | 0.011 |
| toluene | 0.092 | 0.170 | 0.078 | 0.144 | 0.175 | 0.125 | 0.601 | 0.371 | 0.143 | 0.571 | 0.336 |
| nonane | 0.006 | 0.030 | 0.003 | 0.003 | 0.004 | 0.005 | 0.010 | 0.005 | 0.004 | 0.012 | 0.007 |
| ethylbenzene | 0.010 | 0.018 | 0.007 | 0.011 | 0.016 | 0.008 | 0.035 | 0.008 | 0.008 | 0.050 | 0.027 |
| p,m-xylene | 0.018 | 0.049 | 0.019 | 0.026 | 0.043 | 0.028 | 0.058 | 0.015 | 0.016 | N/A | 0.154 |
| o-xylene | 0.008 | 0.017 | 0.007 | 0.007 | 0.014 | 0.007 | 0.021 | 0.005 | 0.003 | LDL | 0.022 |

| Date | 21/06/07 | 21/06/07 | 21/06/07 | 22/06/07 | 22/06/07 | 22/06/07 | 22/06/07 | 23/06/07 | 23/06/07 | 23/06/07 | 23/06/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | 11:52 | 14:37 | 20:50 | 8:20 | 10:45 | 13:35 | 16:00 | 8:16 | 11:09 | 13:52 | 16:15 |
| propane | 0.479 | 0.726 | 0.179 | 0.506 | 0.408 | 0.144 | 0.111 | 0.143 | 0.139 | 0.159 | 0.109 |
| i-butane | 0.082 | 0.243 | 0.028 | 0.104 | 0.022 | 0.009 | 0.018 | 0.024 | 0.020 | 0.027 | 0.023 |
| acetylene | 0.124 | 0.188 | N/A | 0.097 | 0.090 | 0.082 | 0.088 | 0.075 | 0.076 | 0.072 | 0.080 |
| butane | 0.199 | 0.484 | 0.078 | 0.178 | 0.089 | 0.031 | N/A | 0.059 | 0.041 | 0.078 | 0.052 |
| t-2-butene | 0.003 | 0.019 | 0.002 | 0.006 | 0.007 | 0.004 | 0.003 | 0.006 | 0.007 | 0.003 | 0.003 |
| 1-butene |  | 0.022 | 0.010 | 0.015 | 0.024 | 0.008 | 0.003 | 0.009 | 0.015 | 0.009 | 0.009 |
| 2-methylpropene | 0.016 | 0.062 | 0.033 | 0.041 | 0.046 | 0.021 | 0.017 | 0.027 | 0.060 | 0.030 | 0.025 |
| 2,2-dimethylpropane | 0.002 | 0.002 | 0.004 | 0.004 | 0.003 | LDL | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 |
| c-2-butene | 0.004 | 0.020 | 0.003 | 0.007 | 0.008 | 0.003 | 0.003 | 0.003 | 0.004 | 0.004 | 0.003 |
| cyclopentane | 0.047 | N/A | N/A | N/A | 0.056 | 0.079 | 0.064 | 0.085 | 0.084 | 0.054 | 0.055 |
| i-pentane | 0.249 | 0.561 | 0.090 | 0.267 | 0.059 | 0.031 | 0.057 | 0.074 | 0.048 | 0.094 | 0.085 |
| pentane | 0.109 | 0.270 | 0.030 | 0.090 | 0.026 | 0.024 | N/A | 0.046 | 0.031 | 0.039 | 0.033 |
| propyne | 0.005 | 0.010 | 0.003 | 0.006 | LDL | 0.002 | 0.003 | 0.002 | 0.002 | 0.001 | 0.003 |
| 1,3-butadiene | LDL | 0.008 | 0.002 | 0.010 | 0.003 | 0.002 | LDL | 0.002 | 0.002 | 0.001 | 0.002 |
| t-2-pentene | 0.006 | 0.016 | 0.004 | 0.006 | 0.004 | 0.003 | 0.003 | 0.002 | 0.004 | 0.003 | 0.004 |
| 2-methyl-2-butene | 0.006 | 0.014 | 0.002 | 0.004 | 0.004 | 0.003 | 0.008 | 0.015 | 0.019 | 0.002 | 0.003 |
| 1-pentene | 0.008 | 0.022 | 0.010 | 0.014 | 0.013 | 0.007 | LDL | 0.001 | 0.004 | 0.008 | 0.007 |
| 2-methyl-1-butene | 0.011 | 0.015 | 0.005 | 0.012 | 0.010 | 0.007 | 0.009 | 0.011 | 0.013 | 0.008 | 0.006 |
| c-2-pentene | 0.007 | 0.010 | 0.002 | 0.006 | 0.005 | 0.004 | 0.003 | 0.006 | 0.007 | 0.003 | 0.002 |
| 2,2-dimethylbutane | 0.008 | 0.015 | LDL | LDL | 0.003 | 0.002 | 0.002 | 0.002 | 0.001 | 0.002 | 0.002 |
| methylcyclopentane | 0.013 | 0.034 | 0.005 | 0.054 | 0.006 | 0.002 | 0.002 | 0.005 | 0.005 | 0.004 | 0.003 |
| cyclohexane | 0.002 | 0.009 | 0.015 | 0.011 | 0.002 | LDL | LDL | 0.002 | 0.025 | 0.001 | 0.001 |
| 2,3-dimethylbutane | 0.012 | 0.023 | 0.008 | LDL | 0.008 | 0.009 | 0.005 | 0.008 | 0.007 | 0.006 | 0.008 |
| 2-methylpentane | 0.039 | 0.100 | 0.016 | 0.042 | 0.007 | 0.010 | 0.014 | 0.018 | 0.015 | 0.016 | 0.014 |
| 3-methylpentane | 0.023 | 0.064 | 0.013 | 0.035 | 0.005 | 0.005 | 0.007 | 0.010 | 0.009 | 0.010 | 0.009 |
| n-hexane | 0.026 | 0.120 | 0.017 | N/A | 0.010 | 0.010 | N/A | 0.010 | 0.011 | 0.012 | 0.011 |
| isoprene | 0.070 | 0.091 | 0.113 | 0.160 | 0.078 | 0.049 | 0.058 | 0.071 | 0.085 | 0.021 | 0.045 |
| t-2-hexene | 0.012 | 0.007 | 0.003 | 0.010 | 0.010 | 0.005 | 0.005 | 0.006 | 0.006 | 0.004 | 0.003 |

| Date | 21/06/07 | 21/06/07 | 21/06/07 | 22/06/07 | 22/06/07 | 22/06/07 | 22/06/07 | 23/06/07 | 23/06/07 | 23/06/07 | 23/06/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-hexene | 0.009 | 0.009 | 0.007 | 0.012 | 0.010 | 0.006 | 0.004 | 0.012 | 0.014 | 0.006 | 0.005 |
| c-2-hexene | 0.006 | 0.004 | 0.007 | 0.001 | 0.004 | 0.004 | 0.004 | 0.006 | 0.007 | 0.002 | 0.001 |
| methylcyclohexane | 0.004 | 0.012 | 0.004 | 0.014 | 0.001 | 0.001 | 0.001 | 0.002 | 0.001 | 0.001 | 0.001 |
| heptane | 0.011 | 0.042 | 0.009 | 0.030 | 0.008 | 0.006 | 0.003 | 0.010 | 0.014 | 0.005 | 0.006 |
| benzene | 0.111 | 0.118 | 0.057 | 0.091 | 0.060 | 0.034 | N/A | 0.045 | 0.096 | 0.036 | 0.033 |
| octane | 0.006 | 0.014 | 0.004 | 0.020 | 0.005 | 0.006 | 0.003 | 0.004 | 0.027 | 0.004 | 0.003 |
| toluene | 0.172 | 0.335 | 0.100 | 0.405 | 0.140 | 0.113 | 0.129 | 0.265 | 0.210 | 0.174 | 0.193 |
| nonane | 0.008 | 0.006 | 0.002 | 0.009 | 0.006 | 0.007 | 0.007 | 0.007 | 0.071 | 0.004 | 0.001 |
| ethylbenzene | 0.012 | 0.039 | 0.001 | 0.037 | 0.004 | 0.007 | 0.003 | 0.005 | 0.029 | 0.004 | 0.004 |
| p,m-xylene | 0.206 | 0.119 | 0.090 | 0.150 | 0.055 | N/A | 0.009 | 0.019 | N/A | 0.011 | LDL |
| o-xylene | 0.009 | 0.033 | 0.002 | 0.029 | 0.005 | 0.004 | 0.004 | LDL | LDL | 0.005 | 0.001 |

| Date | 24/06/07 | 24/06/07 | 24/06/07 | 24/06/07 | 25/06/07 | 25/06/07 | 25/06/07 | 25/06/07 | 25/06/07 | 26/06/07 | 26/06/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | 8:09 | 13:10 | 16:04 | 21:39 | 8:16 | 11:02 | 14:18 | 17:02 | 21:07 | 8:39 | 11:10 |
| propane | 0.566 | 0.426 | 0.856 | 1.022 | 2.547 | 1.488 | 1.596 | 1.095 | 1.511 | 2.119 | 0.926 |
| i-butane | 0.096 | 0.089 | 0.150 | 0.180 | 0.400 | 0.203 | 0.195 | 0.143 | 0.184 | 0.408 | 0.152 |
| acetylene | 0.208 | 0.144 | 0.149 | 0.157 | 0.376 | 0.172 | N/A | 0.172 | 0.150 | 0.349 | 0.229 |
| butane | 0.212 | 0.180 | 0.362 | 0.391 | 0.886 | 0.444 | 0.458 | 0.276 | 0.389 | 0.907 | 0.292 |
| t-2-butene | 0.006 | 0.005 | 0.005 | 0.005 | 0.014 | 0.002 | 0.009 | 0.006 | 0.006 | 0.003 | 0.002 |
| 1-butene | 0.020 | 0.013 | 0.022 | 0.012 | 0.027 | 0.014 | 0.030 | 0.009 | 0.014 | 0.016 | 0.014 |
| 2-methylpropene | 0.034 | 0.040 | 0.036 | 0.033 | 0.057 | 0.030 | 0.046 | 0.037 | 0.036 | 0.041 | 0.043 |
| 2,2-dimethylpropane | 0.002 | 0.002 | 0.004 | 0.005 | 0.011 | 0.002 | 0.006 | 0.004 | 0.004 | 0.008 | 0.003 |
| c-2-butene | 0.004 | 0.005 | 0.006 | 0.004 | 0.014 | 0.002 | 0.014 | 0.007 | 0.006 | 0.006 | 0.003 |
| cyclopentane | 0.056 | 0.073 | 0.050 | 0.045 | 0.045 | 0.046 | 0.049 | 0.059 | 0.047 | 0.047 | N/A |
| i-pentane | 0.207 | 0.166 | 0.317 | 0.317 | 0.786 | 0.299 | 0.229 | 0.239 | 0.236 | 0.988 | 0.299 |
| pentane | 0.121 | 0.080 | 0.141 | 0.155 | 0.404 | 0.145 | 0.114 | 0.109 | 0.127 | 0.449 | 0.119 |
| propyne | 0.009 | 0.004 | 0.007 | 0.007 | 0.014 | 0.006 | 0.008 | 0.009 | 0.006 | 0.016 | 0.004 |
| 1,3-butadiene | 0.002 | 0.002 | 0.001 | 0.006 | 0.016 | LDL | 0.005 | 0.004 | 0.004 | 0.003 | LDL |
| t-2-pentene | 0.005 | 0.007 | 0.006 | 0.006 | 0.019 | 0.004 | 0.009 | 0.014 | 0.007 | 0.005 | 0.006 |
| 2-methyl-2-butene | 0.004 | 0.010 | 0.009 | 0.005 | 0.011 | 0.008 | 0.011 | 0.007 | 0.005 | 0.005 | 0.003 |
| 1-pentene | 0.011 | 0.011 | 0.015 | 0.008 | 0.016 | 0.002 | 0.028 | 0.014 | 0.014 | 0.012 | 0.012 |
| 2-methyl-1-butene | 0.010 | 0.012 | 0.010 | 0.010 | 0.025 | 0.007 | 0.014 | 0.017 | 0.016 | 0.010 | 0.010 |
| c-2-pentene | 0.005 | 0.006 | 0.007 | 0.006 | 0.016 | 0.004 | 0.010 | 0.010 | 0.006 | 0.004 | 0.006 |
| 2,2-dimethylbutane | 0.010 | 0.008 | 0.015 | 0.012 | 0.029 | 0.012 | 0.013 | 0.014 | 0.009 | 0.041 | 0.014 |
| methylcyclopentane | 0.019 | 0.009 | 0.014 | 0.016 | 0.058 | 0.043 | 0.010 | 0.012 | 0.013 | 0.089 | 0.019 |
| cyclohexane | 0.008 | 0.003 | 0.004 | 0.004 | 0.021 | 0.012 | 0.002 | 0.005 | 0.006 | 0.027 | 0.002 |
| 2,3-dimethylbutane | 0.019 | 0.011 | 0.013 | 0.014 | 0.038 | 0.008 | 0.010 | 0.014 | 0.013 | 0.056 | 0.015 |
| 2-methylpentane | 0.055 | 0.033 | 0.053 | 0.056 | 0.181 | N/A | 0.035 | 0.043 | 0.043 | 0.217 | 0.051 |
| 3-methylpentane | 0.032 | 0.019 | 0.027 | 0.035 | 0.118 | 0.045 | 0.023 | 0.025 | 0.025 | 0.150 | 0.032 |
| n-hexane | 0.037 | 0.022 | 0.037 | 0.036 | 0.142 | N/A | 0.038 | 0.031 | 0.032 | 0.233 | 0.055 |
| isoprene | 0.048 | 0.022 | 0.053 | 0.122 | 0.110 | 0.061 | 0.058 | 0.161 | 0.260 | 0.156 | 0.117 |
| t-2-hexene | 0.005 | 0.007 | 0.006 | 0.003 | 0.009 | LDL | 0.011 | 0.006 | 0.009 | 0.004 | 0.002 |

| Date | 24/06/07 | 24/06/07 | 24/06/07 | 24/06/07 | 25/06/07 | 25/06/07 | 25/06/07 | 25/06/07 | 25/06/07 | 26/06/07 | 26/06/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-hexene | 0.010 | 0.009 | 0.007 | 0.007 | 0.016 | 0.005 | 0.016 | 0.011 | 0.012 | 0.009 | 0.009 |
| c-2-hexene | 0.003 | 0.005 | 0.002 | 0.005 | 0.003 | 0.007 | 0.011 | 0.011 | 0.005 | 0.006 | 0.002 |
| methylcyclohexane | 0.008 | 0.003 | 0.004 | 0.006 | 0.023 | 0.005 | 0.004 | 0.004 | 0.002 | 0.037 | 0.002 |
| heptane | 0.024 | 0.009 | 0.039 | 0.013 | 0.052 | 0.029 | 0.015 | 0.013 | 0.011 | 0.081 | 0.016 |
| benzene | 0.084 | 0.070 | 0.153 | 0.114 | 0.199 | 0.188 | 0.090 | 0.087 | 0.107 | 0.237 | 0.128 |
| octane | 0.012 | 0.006 | 0.006 | 0.005 | 0.019 | 0.011 | 0.018 | 0.004 | 0.004 | 0.024 | 0.009 |
| toluene | 0.410 | 0.161 | 0.205 | 0.229 | 0.569 | 0.227 | 0.156 | 0.161 | 0.148 | 0.552 | 0.186 |
| nonane | 0.010 | 0.005 | 0.009 | 0.002 | 0.008 | 0.011 | 0.010 | 0.009 | 0.003 | 0.018 | 0.008 |
| ethylbenzene | 0.016 | 0.006 | 0.013 | 0.010 | 0.051 | 0.010 | 0.044 | 0.010 | 0.011 | 0.051 | 0.070 |
| p,m-xylene | 0.038 | 0.014 | 0.023 | N/A | 0.152 | 0.015 | 0.130 | 0.024 | 0.028 | N/A | N/A |
| o-xylene | 0.017 | 0.003 | 0.012 | 0.008 | 0.046 | 0.012 | 0.036 | 0.012 | 0.010 | 0.040 | 0.004 |

| Date | 26/06/07 | 27/06/07 | 27/06/07 | 27/06/07 | 28/06/07 | 28/06/07 | 28/06/07 | 29/06/07 | 29/06/07 | 29/06/07 | 29/06/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | 15:10 | 8:26 | 10:55 | 16:00 | 8:13 | 12:54 | 16:36 | 8:00 | 11:40 | 16:08 | 21:11 |
| propane | 0.508 | 1.194 | 0.705 | 0.502 | 0.306 | 0.249 | 0.461 | 0.174 | 0.148 | 0.145 | 0.138 |
| i-butane | 0.075 | 0.236 | 0.140 | 0.083 | 0.057 | 0.044 | 0.044 | 0.047 | 0.043 | 0.035 | 0.024 |
| acetylene | 0.139 | 0.297 | N/A | 0.124 | 0.089 | 0.079 | 0.114 | 0.066 | 0.075 | 0.077 | 0.065 |
| butane | 0.146 | 0.439 | 0.235 | 0.155 | 0.140 | 0.092 | 0.178 | 0.055 | 0.057 | 0.053 | 0.060 |
| t-2-butene | 0.005 | 0.006 | 0.005 | 0.002 | 0.005 | 0.004 | 0.012 | 0.006 | 0.002 | 0.005 | 0.007 |
| 1-butene | 0.015 | 0.018 | 0.011 | 0.012 | 0.013 | 0.008 | 0.045 | 0.040 | 0.018 | 0.020 | 0.034 |
| 2-methylpropene | 0.036 | 0.039 | 0.029 | 0.032 | 0.039 | 0.027 | 0.056 | 0.054 | 0.039 | 0.038 | 0.065 |
| 2,2-dimethylpropane | 0.003 | 0.003 | 0.003 | 0.002 | 0.002 | 0.001 | 0.001 | 0.002 | 0.001 | 0.002 | 0.001 |
| c-2-butene | 0.007 | 0.006 | 0.002 | 0.005 | 0.005 | 0.004 | 0.017 | 0.011 | 0.003 | 0.005 | 0.007 |
| cyclopentane | 0.056 | N/A | N/A | 0.058 | 0.054 | 0.055 | 0.049 | 0.057 | 0.057 | 0.089 | 0.030 |
| i-pentane | 0.173 | 0.400 | 0.226 | 0.183 | 0.232 | 0.090 | 0.095 | 0.086 | 0.082 | 0.064 | 0.068 |
| pentane | 0.065 | 0.229 | 0.104 | 0.077 | 0.160 | 0.036 | 0.070 | 0.034 | 0.033 | 0.049 | 0.056 |
| propyne | 0.001 | 0.008 | 0.003 | 0.006 | 0.003 | 0.004 | 0.005 | 0.004 | 0.003 | 0.002 | 0.002 |
| 1,3-butadiene | 0.001 | 0.002 | 0.001 | 0.006 | 0.003 | 0.002 | 0.022 | 0.003 | LDL | 0.003 | 0.005 |
| t-2-pentene | 0.005 | 0.011 | 0.005 | 0.006 | 0.006 | 0.007 | 0.009 | 0.004 | 0.004 | 0.006 | 0.007 |
| 2-methyl-2-butene | 0.006 | 0.012 | 0.005 | 0.005 | 0.005 | 0.003 | 0.008 | 0.003 | 0.003 | 0.005 | 0.004 |
| 1-pentene | 0.010 | 0.006 | 0.008 | 0.011 | 0.013 | 0.009 | 0.022 | 0.018 | 0.014 | 0.016 | 0.024 |
| 2-methyl-1-butene | 0.009 | 0.013 | 0.009 | 0.013 | 0.014 | 0.012 | 0.023 | 0.011 | 0.011 | 0.011 | 0.013 |
| c-2-pentene | 0.004 | 0.008 | 0.003 | 0.009 | 0.007 | 0.006 | 0.013 | 0.004 | 0.005 | 0.005 | 0.006 |
| 2,2-dimethylbutane | 0.008 | 0.016 | 0.009 | 0.009 | 0.007 | 0.003 | 0.002 | 0.002 | 0.001 | 0.003 | 0.003 |
| methylcyclopentane | 0.007 | 0.036 | 0.014 | 0.014 | 0.013 | 0.004 | 0.003 | 0.004 | 0.004 | 0.004 | 0.006 |
| cyclohexane | 0.002 | 0.015 | 0.005 | 0.005 | 0.005 | 0.001 | 0.014 | 0.002 | 0.001 | LDL | LDL |
| 2,3-dimethylbutane | 0.012 | 0.026 | 0.012 | 0.012 | 0.015 | 0.006 | 0.006 | 0.008 | 0.006 | 0.007 | 0.007 |
| 2-methylpentane | 0.029 | 0.093 | 0.038 | 0.034 | 0.062 | 0.012 | 0.018 | 0.013 | 0.013 | 0.017 | 0.015 |
| 3-methylpentane | 0.018 | 0.054 | 0.025 | 0.021 | 0.035 | 0.007 | 0.008 | 0.008 | 0.008 | 0.009 | 0.007 |
| n-hexane | 0.019 | 0.069 | 0.035 | 0.027 | 0.033 | 0.010 | N/A | 0.014 | 0.012 | 0.015 | 0.016 |
| isoprene | 0.075 | 0.231 | 0.339 | 0.136 | 0.098 | 0.064 | N/A | 0.080 | 0.029 | 0.042 | 0.168 |
| t-2-hexene | 0.003 | 0.008 | 0.003 | 0.008 | 0.016 | 0.007 | 0.007 | 0.006 | 0.006 | 0.005 | 0.008 |

| Date | 26/06/07 | 27/06/07 | 27/06/07 | 27/06/07 | 28/06/07 | 28/06/07 | 28/06/07 | 29/06/07 | 29/06/07 | 29/06/07 | 29/06/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-hexene | 0.006 | 0.010 | 0.005 | 0.011 | 0.013 | 0.010 | 0.014 | 0.012 | 0.011 | 0.011 | 0.018 |
| c-2-hexene | 0.002 | 0.006 | 0.004 | 0.005 | 0.007 | 0.008 | 0.006 | 0.003 | 0.006 | 0.005 | 0.007 |
| methylcyclohexane | LDL | 0.015 | 0.003 | 0.005 | 0.005 | LDL | 0.002 | 0.002 | 0.002 | 0.001 | 0.001 |
| heptane | 0.009 | 0.030 | 0.013 | 0.014 | 0.027 | 0.005 | N/A | 0.007 | 0.005 | 0.009 | 0.010 |
| benzene | 0.095 | 0.135 | 0.079 | 0.081 | 0.083 | 0.050 | 0.088 | 0.051 | 0.041 | 0.054 | 0.053 |
| octane | 0.005 | 0.012 | 0.007 | 0.006 | 0.011 | 0.003 | 0.018 | 0.004 | 0.004 | 0.005 | 0.013 |
| toluene | 0.167 | 0.346 | 0.182 | 0.211 | 0.366 | 0.170 | 0.125 | 0.269 | 0.224 | 0.226 | 0.251 |
| nonane | 0.004 | 0.003 | 0.009 | 0.005 | 0.010 | 0.007 | 0.007 | 0.006 | 0.007 | 0.006 | 0.005 |
| ethylbenzene | 0.009 | 0.018 | 0.014 | 0.007 | 0.025 | 0.031 | 0.007 | 0.005 | 0.007 | 0.008 | 0.005 |
| p,m-xylene | 0.051 | 0.091 | 0.068 | 0.082 | 0.742 | 0.027 | 0.102 | 0.128 | 0.046 | N/A | LDL |
| o-xylene | 0.007 | 0.014 | 0.011 | 0.007 | 0.028 | 0.002 | 0.007 | 0.005 | 0.005 | 0.008 | 0.004 |

| Date | 30/06/07 | 30/06/07 | 30/06/07 | 30/06/07 | 1/07/07 | 1/07/07 | 1/07/07 | 2/07/07 | 2/07/07 | 2/07/07 | 2/07/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | 8:10 | 17:40 | 19:35 | 22:00 | 8:14 | 16:30 | 21:10 | 8:07 | 11:30 | 14:56 | 17:05 |
| propane | 0.467 | 0.131 | 0.076 | 0.144 | 0.138 | N/A | N/A | 0.265 | 0.084 | 0.065 | 0.081 |
| i-butane | 0.085 | 0.008 | 0.010 | 0.024 | 0.018 | 0.008 | 0.007 | 0.080 | 0.016 | 0.009 | 0.011 |
| acetylene | 0.089 | 0.008 | N/A | 0.165 | 0.071 | 0.029 | 0.036 | 0.077 | 0.047 | 0.040 | 0.039 |
| butane | 0.166 | 0.068 | 0.034 | 0.078 | 0.031 | 0.018 | 0.014 | 0.108 | 0.034 | 0.027 | 0.027 |
| t-2-butene | 0.004 | LDL | 0.002 | 0.010 | 0.002 | 0.003 | 0.004 | 0.003 | 0.002 | LDL | LDL |
| 1-butene | 0.008 | LDL | 0.006 | 0.024 | 0.004 | 0.005 | 0.011 | 0.009 | 0.007 | 0.012 | 0.008 |
| 2-methylpropene | 0.026 | 0.053 | 0.024 | 0.038 | 0.020 | 0.018 | 0.017 | 0.024 | 0.025 | 0.018 | 0.019 |
| 2,2-dimethylpropane | 0.005 | 0.001 | 0.001 | 0.001 | LDL | LDL | 0.001 | 0.003 | 0.001 | LDL | LDL |
| c-2-butene | 0.003 | LDL | 0.003 | 0.005 | 0.003 | 0.002 | 0.004 | 0.004 | 0.002 | LDL | LDL |
| cyclopentane | 0.031 | 0.047 | 0.050 | 0.039 | 0.082 | 0.042 | 0.030 | 0.085 | 0.043 | 0.042 | 0.043 |
| i-pentane | 0.168 | 0.061 | 0.036 | 0.116 | 0.038 | 0.019 | 0.020 | 0.099 | 0.030 | 0.019 | 0.022 |
| pentane | 0.108 | 0.010 | 0.012 | 0.076 | 0.023 | 0.013 | 0.009 | 0.053 | 0.023 | 0.019 | 0.016 |
| propyne | 0.004 | 0.004 | 0.002 | 0.008 | 0.004 | 0.001 | 0.002 | 0.004 | 0.002 | 0.002 | 0.001 |
| 1,3-butadiene | 0.004 | LDL | 0.002 | 0.010 | LDL | 0.001 | 0.001 | 0.006 | 0.001 | LDL | LDL |
| t-2-pentene | 0.004 | 0.001 | 0.004 | 0.008 | 0.005 | 0.003 | 0.007 | 0.006 | 0.001 | LDL | LDL |
| 2-methyl-2-butene | 0.011 | 0.003 | 0.002 | 0.006 | LDL | 0.002 | 0.002 | LDL | 0.002 | 0.002 | 0.003 |
| 1-pentene | 0.001 | LDL | 0.008 | 0.021 | 0.010 | 0.007 | 0.011 | 0.016 | 0.008 | 0.005 | 0.005 |
| 2-methyl-1-butene | 0.011 | 0.006 | 0.005 | 0.014 | 0.007 | 0.007 | 0.007 | 0.008 | 0.004 | 0.003 | 0.003 |
| c-2-pentene | 0.004 | 0.001 | 0.008 | 0.006 | 0.004 | 0.003 | 0.005 | 0.006 | 0.001 | LDL | 0.001 |
| 2,2-dimethylbutane | 0.005 | 0.001 | 0.001 | 0.003 | LDL | LDL | LDL | 0.002 | 0.001 | LDL | LDL |
| methylcyclopentane | 0.021 | 0.002 | 0.001 | 0.012 | 0.003 | LDL | LDL | 0.008 | 0.002 | LDL | LDL |
| cyclohexane | 0.007 | 0.001 | 0.001 | LDL | LDL | 0.001 | 0.016 | 0.001 | 0.001 | LDL | LDL |
| 2,3-dimethylbutane | 0.011 | 0.005 | 0.004 | 0.005 | 0.006 | 0.004 | 0.003 | 0.009 | 0.004 | 0.001 | 0.001 |
| 2-methylpentane | 0.043 | 0.006 | 0.005 | LDL | 0.010 | 0.003 | 0.002 | 0.023 | 0.007 | 0.003 | 0.003 |
| 3-methylpentane | 0.027 | 0.005 | 0.003 | 0.026 | 0.004 | 0.002 | 0.002 | 0.013 | 0.004 | 0.001 | 0.002 |
| n-hexane | 0.051 | 0.002 | 0.004 | 0.021 | 0.006 | 0.004 | 0.004 | 0.019 | 0.007 | 0.008 | 0.004 |
| isoprene | 0.094 | 0.085 | 0.199 | 0.139 | 0.104 | 0.044 | 0.039 | 0.072 | 0.044 | 0.003 | 0.018 |
| t-2-hexene | 0.007 | 0.002 | 0.004 | 0.004 | 0.004 | 0.004 | LDL | LDL | 0.002 | 0.004 | 0.003 |

| Date | 30/06/07 | 30/06/07 | 30/06/07 | 30/06/07 | 1/07/07 | 1/07/07 | 1/07/07 | 2/07/07 | 2/07/07 | 2/07/07 | 2/07/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-hexene | 0.007 | 0.003 | 0.006 | 0.008 | 0.007 | 0.006 | 0.009 | 0.013 | 0.005 | 0.005 | 0.003 |
| c-2-hexene | 0.002 | 0.002 | 0.006 | 0.005 | 0.002 | 0.004 | 0.007 | 0.003 | 0.007 | 0.001 | 0.002 |
| methylcyclohexane | 0.005 | 0.001 | 0.001 | 0.003 | LDL | LDL | 0.001 | 0.002 | 0.002 | 0.000 | 0.001 |
| heptane | 0.013 | 0.003 | 0.002 | 0.010 | 0.002 | 0.001 | 0.003 | 0.006 | 0.003 | 0.002 | 0.002 |
| benzene | 0.053 | 0.037 | 0.032 | 0.061 | 0.039 | 0.026 | 0.033 | 0.054 | 0.025 | 0.021 | N/A |
| octane | 0.008 | 0.004 | 0.001 | 0.007 | 0.001 | 0.002 | 0.001 | LDL | 0.003 | 0.001 | 0.002 |
| toluene | 0.219 | 0.203 | 0.162 | 0.303 | 0.229 | 0.151 | N/A | 0.254 | 0.258 | N/A | 0.075 |
| nonane | 0.005 | 0.005 | 0.003 | 0.007 | 0.002 | 0.005 | 0.004 | 0.001 | 0.003 | LDL | LDL |
| ethylbenzene | 0.013 | 0.002 | 0.001 | 0.012 | LDL | 0.002 | 0.001 | LDL | 0.002 | LDL | LDL |
| p,m-xylene | 0.033 | 0.296 | LDL | 0.047 | LDL | LDL | LDL | LDL | 0.012 | LDL | LDL |
| o-xylene | 0.010 | 0.002 | 0.003 | 0.012 | LDL | 0.003 | 0.001 | LDL | 0.003 | 0.001 | 0.004 |

| Date | 3/07/07 | 3/07/07 | 3/07/07 | 3/07/07 | 3/07/07 | 4/07/07 | 4/07/07 | 4/07/07 | 5/07/07 | 5/07/07 | 5/07/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | 8:14 | 10:55 | 15:15 | 17:49 | 21:15 | 8:25 | 11:04 | 16:15 | 7:58 | 12:00 | 15:40 |
| propane | 0.159 | 0.178 | 0.235 | 0.385 | 0.350 | 1.111 | 0.802 | 0.804 | 1.018 | 1.061 | 0.381 |
| i-butane | 0.027 | 0.027 | 0.034 | 0.055 | 0.094 | 0.241 | 0.210 | 0.143 | 0.259 | 0.240 | 0.099 |
| acetylene | 0.066 | 0.062 | 0.066 | N/A | 0.099 | 0.210 | 0.179 | 0.197 | 0.240 | 0.258 | 0.103 |
| butane | 0.069 | 0.106 | 0.074 | 0.147 | 0.184 | 0.431 | 0.317 | 0.298 | 0.477 | 0.381 | 0.165 |
| t-2-butene | LDL | LDL | LDL | 0.001 | 0.006 | 0.001 | 0.002 | 0.003 | 0.007 | 0.006 | 0.001 |
| 1-butene | 0.009 |  | 0.011 | 0.026 | 0.023 | 0.013 | 0.009 | 0.002 | 0.014 | 0.019 | 0.007 |
| 2-methylpropene | 0.019 | 0.015 | 0.020 | 0.034 | 0.028 | 0.021 | 0.018 | 0.013 | 0.039 | 0.031 | 0.026 |
| 2,2-dimethylpropane | LDL | 0.001 | LDL | 0.001 | 0.001 | 0.003 | 0.002 | 0.003 | 0.004 | 0.005 | 0.001 |
| c-2-butene | LDL | LDL | 0.001 | LDL | 0.006 | 0.001 | 0.003 | 0.003 | 0.008 | 0.008 | 0.004 |
| cyclopentane | 0.042 | 0.045 | 0.044 | 0.038 | 0.052 | 0.052 | 0.051 | 0.050 | N/A | N/A | 0.056 |
| i-pentane | 0.042 | 0.103 | 0.050 | 0.095 | 0.191 | 0.449 | 0.352 | 0.361 | 0.454 | N/A | 0.175 |
| pentane | 0.025 | 0.027 | 0.027 | 0.041 | 0.102 | 0.229 | 0.162 | 0.159 | 0.240 | N/A | 0.075 |
| propyne | 0.003 | 0.003 | 0.001 | 0.004 | 0.003 | 0.005 | 0.005 | 0.008 | 0.012 | 0.009 | 0.003 |
| 1,3-butadiene | LDL | LDL | LDL | LDL | LDL | 0.001 | 0.001 | 0.002 | 0.005 | LDL | 0.001 |
| t-2-pentene | LDL | LDL | 0.003 | 0.002 | 0.006 | 0.001 | 0.004 | 0.005 | 0.011 | 0.009 | 0.001 |
| 2-methyl-2-butene | 0.001 | 0.002 | 0.005 | LDL | 0.003 | 0.003 | 0.005 | 0.006 | 0.010 | 0.005 | 0.002 |
| 1-pentene | 0.005 | LDl | 0.011 | 0.016 | 0.019 | 0.007 | 0.003 | 0.004 | 0.025 | 0.023 | 0.019 |
| 2-methyl-1-butene | 0.002 | 0.005 | 0.005 | 0.004 | 0.009 | 0.004 | 0.007 | 0.010 | 0.011 | 0.008 | 0.008 |
| c-2-pentene | LDL | LDL | 0.002 | 0.001 | 0.003 | 0.003 | 0.002 | 0.004 | 0.012 | 0.007 | 0.003 |
| 2,2-dimethylbutane | LDL | 0.004 | 0.002 | 0.004 | 0.004 | 0.016 | 0.011 | 0.014 | 0.016 | 0.016 | 0.007 |
| methylcyclopentane | 0.002 | 0.004 | 0.002 | 0.004 | 0.012 | 0.034 | 0.022 | 0.020 | 0.035 | 0.027 | 0.009 |
| cyclohexane | 0.001 | 0.001 | 0.014 | LDL | 0.003 | 0.011 | 0.006 | 0.007 | 0.029 | 0.013 | 0.012 |
| 2,3-dimethylbutane | 0.004 | 0.007 | 0.004 | 0.005 | 0.011 | 0.024 | 0.017 | 0.018 | 0.026 | 0.021 | 0.010 |
| 2-methylpentane | 0.005 | 0.012 | 0.010 | 0.013 | 0.035 | 0.092 | 0.064 | 0.061 | 0.096 | 0.088 | 0.027 |
| 3-methylpentane | 0.003 | 0.007 | 0.006 | 0.007 | 0.020 | 0.049 | 0.030 | 0.034 | 0.062 | 0.054 | 0.016 |
| n-hexane | 0.007 | 0.006 | 0.010 | 0.005 | 0.030 | 0.078 | 0.045 | 0.047 | 0.092 | 0.068 | 0.025 |
| isoprene | 0.006 | 0.009 | 0.023 | 0.040 | 0.009 | 0.409 | 0.063 | 0.180 | 0.233 | 0.294 | 0.672 |
| t-2-hexene | 0.005 | 0.002 | 0.004 | 0.004 | 0.002 | 0.001 | 0.001 | 0.004 | 0.007 | 0.006 | 0.006 |

| Date | 3/07/07 | 3/07/07 | 3/07/07 | 3/07/07 | 3/07/07 | 4/07/07 | 4/07/07 | 4/07/07 | 5/07/07 | 5/07/07 | 5/07/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-hexene | 0.003 | 0.004 | 0.007 | 0.009 | 0.007 | 0.005 | 0.004 | 0.006 | 0.017 | 0.014 | 0.005 |
| c-2-hexene | 0.003 | 0.001 | 0.004 | 0.003 | 0.002 | 0.001 | 0.001 | 0.006 | 0.006 | 0.007 | 0.002 |
| methylcyclohexane | 0.001 | 0.001 | 0.002 | 0.002 | 0.005 | 0.011 | 0.006 | 0.007 | 0.012 | 0.008 | 0.002 |
| heptane | 0.004 | 0.002 | 0.003 | 0.007 | 0.011 | 0.023 | 0.021 | 0.014 | 0.027 | 0.024 | 0.007 |
| benzene | N/A | 0.055 | N/A | 0.047 | 0.029 | 0.083 | 0.071 | 0.123 | 0.134 | 0.131 | 0.054 |
| octane | 0.003 | 0.003 | 0.002 | 0.008 | 0.004 | 0.008 | 0.004 | 0.006 | 0.018 | 0.012 | 0.006 |
| toluene | 0.143 | 0.268 | 0.130 | 0.234 | 0.170 | 0.443 | 0.305 | 0.278 | 0.431 | 0.355 | 0.197 |
| nonane | LDL | 0.002 | LDL | LDL | LDL | 0.006 | 0.005 | 0.009 | 0.030 | 0.010 | 0.004 |
| ethylbenzene | LDL | 0.002 | LDL | LDL | 0.001 | 0.014 | 0.010 | 0.012 | 0.021 | 0.020 | 0.005 |
| p,m-xylene | LDL | 0.049 | 0.060 | N/A | 0.043 | 0.087 | 0.101 | N/A | 0.032 | 0.106 | 0.119 |
| o-xylene | 0.002 | 0.003 | 0.015 | N/A | 0.012 | 0.011 | 0.008 | 0.004 | 0.017 | 0.017 | 0.006 |

| Date | 5/07/07 | 6/07/07 | 6/07/07 | 6/07/07 | 6/07/07 | 7/07/07 | 7/07/07 | 7/07/07 | 7/07/07 | 7/07/07 | 8/07/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | 18:05 | 8:15 | 12:25 | 15:49 | 19:05 | 7:55 | 11:25 | 15:34 | 18:05 | 21:00 | 8:14 |
| propane | 0.447 | 2.703 | 0.325 | 0.507 | 0.223 | 0.934 | 0.789 | 0.326 | 0.298 | 0.356 | 0.715 |
| i-butane | 0.171 | 0.959 | 0.084 | 0.197 | 0.032 | 0.257 | 0.269 | 0.078 | 0.043 | 0.055 | 0.117 |
| acetylene | 0.152 | 0.245 | 0.130 | 0.156 | 0.155 | 0.185 | 0.163 | 0.193 | 0.144 | 0.149 | 0.182 |
| butane | 0.401 | 1.122 | 0.166 | 0.256 | 0.066 | 0.410 | 0.322 | 0.118 | 0.111 | 0.132 | 0.236 |
| t-2-butene | 0.014 | 0.039 | 0.001 | 0.003 | 0.011 | 0.020 | 0.005 | 0.003 | 0.005 | 0.010 | 0.005 |
| 1-butene | 0.013 |  | 0.002 | 0.004 | 0.042 | N/A | 0.011 | 0.012 | 0.010 | 0.054 | 0.012 |
| 2-methylpropene | 0.030 | 0.084 | 0.018 | 0.030 | 0.074 | 0.021 | 0.037 | 0.050 | 0.038 | 0.050 | 0.030 |
| 2,2-dimethylpropane | 0.003 | 0.008 | 0.002 | 0.004 | 0.002 | 0.003 | 0.005 | 0.001 | 0.001 | 0.001 | 0.002 |
| c-2-butene | 0.012 | 0.007 | 0.003 | 0.004 | 0.010 | 0.003 | 0.004 | 0.004 | 0.006 | 0.010 | 0.006 |
| cyclopentane | 0.102 | 0.039 | 0.047 | 0.084 | N/A | 0.022 | 0.060 | 0.048 | 0.057 | 0.056 | 0.059 |
| i-pentane | 0.393 | 1.087 | 0.165 | 0.156 | 0.064 | 0.417 | 0.289 | 0.133 | 0.137 | 0.194 | 0.267 |
| pentane | 0.224 | 0.524 | 0.085 | 0.096 | 0.031 | 0.252 | 0.139 | 0.067 | 0.064 | 0.100 | 0.124 |
| propyne | 0.003 | 0.010 | 0.006 | 0.006 | 0.009 | 0.006 | 0.009 | 0.005 | 0.007 | 0.004 | 0.006 |
| 1,3-butadiene | 0.004 |  | 0.004 | 0.005 | 0.003 | 0.004 | 0.002 | 0.002 | 0.002 | 0.003 | LDL |
| t-2-pentene | 0.018 | 0.006 | 0.003 | 0.004 | 0.007 | 0.003 | 0.005 | 0.004 | 0.008 | 0.009 | 0.010 |
| 2-methyl-2-butene | 0.010 | 0.005 | 0.004 | LDL | 0.007 | 0.004 | 0.005 | 0.006 | 0.010 | 0.007 | 0.003 |
| 1-pentene | 0.019 | 0.015 | 0.003 | 0.010 | 0.036 | 0.011 | 0.010 | 0.012 | 0.010 | 0.050 | 0.018 |
| 2-methyl-1-butene | 0.014 | 0.009 | 0.004 | 0.004 | 0.015 | 0.007 | 0.009 | 0.011 | 0.009 | 0.013 | 0.008 |
| c-2-pentene | 0.011 | 0.006 | 0.002 | 0.003 | 0.006 | 0.002 | 0.005 | 0.004 | 0.003 | 0.007 | 0.007 |
| 2,2-dimethylbutane | 0.010 | 0.029 | 0.004 | 0.005 | 0.002 | 0.012 | 0.010 | 0.006 | 0.005 | 0.006 | 0.007 |
| methylcyclopentane | 0.019 | 0.099 | 0.011 | 0.014 | 0.003 | 0.032 | 0.011 | 0.008 | 0.013 | 0.030 | 0.016 |
| cyclohexane | 0.011 | N/A | 0.004 | 0.020 | 0.002 | 0.037 | 0.005 | 0.001 | 0.002 | 0.004 | 0.005 |
| 2,3-dimethylbutane | 0.016 | 0.059 | 0.008 | 0.005 | 0.006 | 0.023 | 0.014 | 0.010 | 0.011 | 0.013 | 0.016 |
| 2-methylpentane | 0.075 | 0.267 | 0.030 | 0.036 | 0.009 | 0.092 | 0.054 | 0.023 | 0.029 | 0.048 | 0.050 |
| 3-methylpentane | 0.042 | 0.213 | 0.019 | 0.026 | 0.006 | 0.054 | 0.031 | 0.014 | 0.017 | 0.039 | 0.029 |
| n-hexane | 0.043 | 0.354 | 0.028 | 0.047 | 0.010 | 0.077 | 0.039 | 0.023 | 0.034 | 0.097 | 0.037 |
| isoprene | 0.228 | 0.089 | 0.064 | 0.103 | 0.272 | 0.092 | 0.260 | 0.656 | 0.349 | 0.280 | 0.203 |
| t-2-hexene | 0.007 | 0.004 | 0.004 | 0.009 | 0.005 | LDL | 0.006 | 0.004 | 0.005 | 0.004 | 0.007 |

| Date | 5/07/07 | 6/07/07 | 6/07/07 | 6/07/07 | 6/07/07 | 7/07/07 | 7/07/07 | 7/07/07 | 7/07/07 | 7/07/07 | 8/07/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-hexene | 0.008 | LDL | 0.002 | 0.005 | 0.025 | 0.008 | 0.008 | 0.008 | 0.005 | 0.027 | 0.009 |
| c-2-hexene | 0.006 | 0.005 | 0.002 | 0.004 | 0.005 | 0.012 | 0.004 | 0.003 | 0.002 | 0.002 | 0.003 |
| methylcyclohexane | 0.004 | 0.057 | 0.004 | 0.004 | 0.002 | 0.012 | 0.004 | 0.001 | 0.001 | 0.003 | 0.006 |
| heptane | 0.016 | 0.079 | 0.012 | 0.016 | 0.004 | 0.028 | 0.014 | N/A | N/A | 0.012 | 0.013 |
| benzene | 0.115 | 0.213 | 0.075 | 0.092 | 0.081 | 0.091 | 0.090 | N/A | 0.158 | 0.101 | 0.082 |
| octane | 0.007 | 0.032 | 0.005 | 0.006 | 0.021 | 0.009 | 0.008 | LDL | LDL | 0.009 | 0.007 |
| toluene | 0.258 | 0.512 | 0.250 | 0.294 | 0.202 | 0.324 | 0.272 | N/A | 0.629 | 0.320 | 0.364 |
| nonane | 0.001 | 0.009 | 0.003 | 0.007 | LDL | 0.006 | 0.003 | LDL | 0.003 | 0.011 | 0.005 |
| ethylbenzene | 0.014 | 0.035 | 0.006 | 0.008 | 0.002 | 0.022 | LDL | 0.008 | 0.010 | 0.009 | 0.012 |
| p,m-xylene | N/A | 0.102 | N/A | 0.094 | N/A | N/A | 0.117 | LDL | 0.326 | 0.093 | 0.103 |
| o-xylene | 0.016 | 0.027 | 0.005 | 0.009 | 0.002 | 0.020 | LDL | LDL | N/A | N/A | 0.011 |

| Date | 8/07/07 | 8/07/07 | 8/07/07 | 8/07/07 | 8/07/07 | 9/07/07 | 9/07/07 | 9/07/07 | 9/07/07 | 10/07/07 | 10/07/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | 12:45 | 15:30 | 18:05 | 21:15 | 23:30 | 8:05 | 10:30 | 16:03 | 23:50 | 8:07 | 11:10 |
| propane | 0.688 | 0.576 | 0.357 | 0.238 | 0.362 | 0.938 | 0.472 | 0.614 | 0.593 | 1.436 | 0.858 |
| i-butane | 0.148 | 0.153 | 0.075 | 0.043 | 0.072 | 0.135 | 0.077 | 0.086 | 0.114 | 0.510 | 0.153 |
| acetylene | 0.268 | 0.173 | 0.134 | 0.099 | 0.100 | 0.168 | 0.179 | 0.145 | 0.112 | 0.209 | 0.247 |
| butane | 0.282 | 0.241 | 0.142 | 0.117 | 0.153 | 0.327 | 0.166 | 0.203 | 0.246 | 0.580 | 0.417 |
| t-2-butene | 0.017 | 0.008 | 0.009 | 0.004 | 0.003 | 0.006 | 0.002 | 0.008 | 0.009 | 0.011 | 0.011 |
| 1-butene | N/A | 0.020 | 0.009 | 0.016 | 0.014 | N/A | 0.006 | 0.020 | 0.007 | 0.027 | 0.040 |
| 2-methylpropene | 0.029 | 0.066 | 0.039 | 0.015 | 0.017 | 0.029 | 0.018 | 0.043 | 0.039 | 0.060 | 0.084 |
| 2,2-dimethylpropane | 0.003 | 0.002 | 0.001 | 0.001 | 0.002 | 0.002 | 0.001 | 0.002 | 0.001 | 0.003 | 0.002 |
| c-2-butene | 0.007 | 0.011 | 0.009 | 0.007 | 0.006 | 0.007 | 0.004 | 0.008 | 0.004 | 0.009 | 0.011 |
| cyclopentane | 0.114 | 0.053 | 0.099 | 0.017 | 0.011 | 0.045 | 0.033 | 0.055 | 0.046 | 0.064 | 0.050 |
| i-pentane | 0.350 | 0.336 | 0.226 | 0.182 | 0.208 | 0.324 | 0.231 | 0.280 | 0.272 | 0.698 | 0.375 |
| pentane | 0.172 | 0.141 | 0.113 | 0.094 | 0.111 | 0.172 | 0.113 | 0.119 | 0.149 | 0.355 | 0.180 |
| propyne | 0.007 | 0.005 | 0.004 | 0.007 | 0.003 | 0.009 | 0.004 | 0.005 | 0.007 | 0.013 | 0.015 |
| 1,3-butadiene | LDL | 0.001 | LDL | LDL | LDL | 0.002 | LDL | 0.002 | 0.001 | 0.002 | 0.009 |
| t-2-pentene | 0.012 | 0.013 | 0.016 | 0.006 | 0.004 | 0.008 | 0.003 | 0.012 | 0.003 | 0.013 | 0.012 |
| 2-methyl-2-butene | 0.005 | 0.010 | 0.006 | 0.010 | 0.006 | 0.009 | 0.005 | 0.014 | 0.004 | 0.013 | 0.009 |
| 1-pentene | 0.022 | 0.029 | 0.020 | 0.014 | 0.012 | 0.013 | 0.006 | 0.016 | 0.014 | 0.019 | 0.021 |
| 2-methyl-1-butene | 0.011 | 0.012 | 0.014 | 0.010 | 0.008 | 0.011 | 0.005 | 0.013 | 0.006 | 0.017 | 0.015 |
| c-2-pentene | 0.011 | 0.010 | 0.011 | 0.007 | 0.006 | 0.007 | 0.002 | 0.009 | 0.004 | 0.008 | 0.007 |
| 2,2-dimethylbutane | 0.015 | 0.013 | 0.013 | 0.009 | 0.009 | 0.013 | 0.009 | 0.013 | 0.009 | 0.021 | 0.010 |
| methylcyclopentane | 0.019 | 0.012 | 0.013 | 0.012 | 0.015 | 0.024 | 0.014 | 0.012 | 0.011 | 0.058 | 0.020 |
| cyclohexane | 0.004 | 0.003 | 0.004 | 0.002 | 0.004 | 0.008 | 0.004 | 0.003 | 0.003 | 0.016 | 0.006 |
| 2,3-dimethylbutane | 0.017 | 0.016 | 0.016 | 0.012 | 0.010 | 0.018 | 0.012 | 0.015 | 0.012 | 0.035 | 0.016 |
| 2-methylpentane | 0.069 | 0.053 | 0.052 | 0.045 | 0.045 | 0.064 | 0.044 | 0.049 | 0.043 | 0.137 | 0.065 |
| 3-methylpentane | 0.040 | 0.029 | 0.029 | 0.025 | 0.026 | 0.039 | 0.026 | 0.026 | 0.024 | 0.083 | 0.039 |
| n-hexane | 0.049 | 0.034 | 0.027 | 0.021 | 0.027 | 0.058 | 0.031 | 0.032 | 0.035 | 0.109 | 0.047 |
| isoprene | 0.618 | 0.206 | 0.298 | 0.058 | 0.029 | 0.157 | 0.298 | 0.127 | 0.412 | 0.187 | 0.108 |
| t-2-hexene | 0.012 | 0.008 | 0.011 | 0.002 | 0.002 | 0.004 | 0.000 | 0.005 | 0.002 | 0.033 | 0.006 |

| Date | 8/07/07 | 8/07/07 | 8/07/07 | 8/07/07 | 8/07/07 | 9/07/07 | 9/07/07 | 9/07/07 | 9/07/07 | 10/07/07 | 10/07/07 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-hexene | 0.016 | 0.013 | 0.013 | 0.006 | 0.005 | 0.009 | 0.003 | 0.009 | 0.006 | 0.008 | 0.014 |
| c-2-hexene | 0.011 | 0.005 | 0.008 | 0.003 | 0.003 | 0.007 | 0.004 | 0.003 | 0.003 | 0.003 | 0.004 |
| methylcyclohexane | 0.004 | 0.000 | 0.002 | 0.002 | 0.005 | 0.008 | 0.005 | 0.002 | 0.002 | 0.020 | 0.005 |
| heptane | 0.016 | 0.010 | 0.010 | 0.010 | 0.011 | 0.017 | 0.010 | 0.012 | 0.013 | 0.040 | 0.017 |
| benzene | 0.107 | 0.088 | 0.061 | 0.027 | 0.030 | 0.076 | 0.060 | 0.067 | 0.073 | 0.128 | 0.110 |
| octane | 0.007 | 0.006 | 0.004 | 0.008 | 0.005 | 0.008 | 0.005 | 0.008 | N/A | 0.017 | 0.013 |
| toluene | 0.319 | 0.240 | 0.259 | 0.187 | 0.158 | 0.270 | 0.228 | 0.303 | 0.320 | 0.346 | 0.286 |
| nonane | 0.009 | 0.006 | 0.004 | 0.011 | 0.005 | 0.005 | 0.003 | 0.006 | 0.006 | 0.011 | 0.004 |
| ethylbenzene | 0.018 | 0.013 | 0.011 | 0.006 | 0.006 | 0.011 | 0.027 | 0.013 | 0.013 | 0.045 | 0.019 |
| p,m-xylene | 0.112 | N/A | 0.166 | 0.048 | 0.027 | N/A | 0.092 | 0.040 | 0.243 | 0.397 | N/A |
| o-xylene | 0.013 | 0.011 | 0.012 | 0.012 | 0.011 | 0.011 | 0.024 | N/A | 0.013 | 0.049 | 0.017 |

N/A- no results available, LDL- lower than detection limit

## A2.2: Concentrations (ppbv) of VOC in Ridgetown Samples (cartridges)

| Start Date | End Date | Crtdg | Start Time | End Time | Flow rate mL/min | TotVolume mL | pentane | hexane | benzene | heptane | toluene | p-xylene | nonane | decane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6/24/07 | 6/25/07 | 57 | 13:34 | 14:26 | 37 | 54168 | N/A | N/A | 0.03 | LDL | N/A | N/A | N/A | N/A |
| 6/26/07 | 6/27/07 | 59 | 15:26 | 16:10 | 37 | 53833 | N/A | 0.01 | 0.01 | 0.04 | 0.01 | LDL | LDL | LDL |
| 6/29/07 | 6/30/07 | 52 | 16:20 | 15:30 | 37 | 54847 | N/A | N/A | 0.15 | LDL | 0.20 | N/A | LDL | 0.01 |
| 7/1/07 | 7/2/07 | 48 | 16:24 | 15:37 | 37 | 50628 | N/A | 0.01 | 0.01 | N/A | 0.28 | 0.04 | 0.05 | LDL |

N/A- no results available, LDL- lower than detection limit

## A3: Concentrations (ppbv) of VOC in Egbert samples

| Start Date | End Date | Crtd | Start Time | End Time | Flow (mL/min) | TotVolume (mL) | hexane | benzene | heptane | toluene | octane | ethyl-benzene | p,m-xylene | o-xylene | nonane | decane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10/19/2009 | 10/20/2009 | **49** | 8:30 | 8:50 | 24 | 35208 | 1.96 | 0.05 | 0.47 | 0.08 | N/A | 0.01 | 0.02 | 0.01 | LDL | LDL |
| 10/21/2009 | 10/22/2009 | **144** | 8:49 | 8:45 | 24 | 34586 | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | LDL |
| 10/22/2009 | 10/23/2009 | **128** | 8:52 | 8:28 | 24 | 34137 | 2.04 | 0.04 | 0.40 | 0.06 | LDL | 0.01 | 0.01 | 0.01 | 0.004 | LDL |
| 10/23/2009 | 10/24/2009 | **132** | 8:34 | 16:07 | 24 | 10867 | 5.30 | 0.88 | 1.11 | 0.21 | LDL | 0.01 | 0.01 | 0.01 | 0.004 | LDL |
| 10/24/2009 | 10/26/2009 | **108** | 16:11 | 8:52 | 24 | 93478 | 0.59 | 0.05 | 0.13 | 0.07 | 0.003 | 0.01 | 0.01 | 0.001 | 0.0003 | LDL |
| 10/26/2009 | 10/26/2009 | **106** | 9:01 | 9:43 | 24 | 35733 | 1.84 | 0.05 | 0.35 | 0.15 | 0.01 | 0.02 | 0.04 | 0.02 | 0.003 | 0.003 |
| 10/27/2009 | 10/28/2009 | **141** | 9:49 | 8:51 | 24 | 33306 | N/A | 0.26 | 0.12 | LDL | LDL | LDL | LDL | LDL | LDL | LDL |
| 10/28/2009 | 10/29/2009 | **65** | 8:55 | 8:23 | 24 | 33802 | N/A | N/A | N/A | LDL | LDL | LDL | LDL | LDL | LDL | LDL |
| 10/29/2009 | 10/30/2009 | **41** | 8:26 | 8:25 | 24 | 34458 | N/A | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL |
| 10/30/2009 | 10/30/2009 | **54** | 8:30 | 16:03 | 24 | 10923 | LDL | N/A | 0.19 | LDL | LDL | 0.04 | 0.11 | 0.02 | 0.03 | LDL |
| 10/30/2009 | 11/2/2009 | **52** | 15:07 | 8:52 | 24 | 95117 | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL |
| 11/2/2009 | 11/3/2009 | **103** | 8:57 | 9:47 | 24 | 35895 | 1.56 | 0.08 | 0.31 | 0.13 | LDL | N/A | N/A | LDL | LDL | LDL |
| 11/3/2009 | 11/4/2009 | **80** | 9:49 | 9:38 | 24 | 34479 | N/A | 0.18 | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL |
| 11/4/2009 | 11/5/2009 | **16** | 9:42 | 8:42 | 24 | 33302 | 1.95 | 0.05 | 0.41 | 0.23 | 0.01 | 0.06 | 0.08 | 0.03 | 0.000 | 0.004 |
| 11/5/2009 | 11/6/2009 | **11** | 8:45 | 9:57 | 24 | 36466 | 1.03 | 0.03 | 0.20 | 0.04 | N/A | 0.01 | 0.01 | 0.004 | LDL | LDL |
| 11/6/2009 | 11/6/2009 | **116** | 10:01 | 15:53 | 24 | 8532 | 5.12 | 0.07 | 0.00 | 0.07 | 0.01 | 0.02 | 0.03 | 0.004 | 0.01 | LDL |
| 11/6/2009 | 11/7/2009 | **133** | 15:58 | 10:23 | 24 | 26530 | 1.18 | 0.12 | 0.27 | 0.17 | N/A | 0.02 | 0.04 | 0.02 | 0.004 | N/A |
| 11/7/2009 | 11/8/2009 | **123** | 10:30 | 9:23 | 24 | 33044 | 1.42 | 0.08 | 0.32 | 0.14 | N/A | 0.02 | 0.03 | 0.01 | LDL | LDL |
| 11/8/2009 | 11/9/2009 | **131** | 9:31 | 8:46 | 24 | 33737 | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| 11/9/2009 | 11/10/2009 | **22** | 8:51 | 11:16 | 24 | 38204 | 1.00 | 0.06 | 0.20 | 0.08 | LDL | LDL | LDL | 0.02 | LDL | LDL |
| 11/10/2009 | 11/12/2009 | **36** | 11:19 | 8:31 | 24 | 65411 | 0.63 | 0.06 | 0.14 | 0.11 | N/A | 0.01 | 0.03 | 0.01 | 0.001 | 0.002 |
| 11/12/2009 | 11/13/2009 | **40** | 8:36 | 8:05 | 24 | 33997 | 1.55 | 0.07 | 0.36 | 0.23 | 0.01 | 0.03 | 0.07 | 0.02 | 0.004 | 0.004 |
| 11/13/2009 | 11/13/2009 | **123** | 8:07 | 16:16 | 24 | 11662 | 4.02 | 0.24 | 0.90 | 0.39 | N/A | 0.05 | 0.08 | 0.03 | LDL | LDL |
| 11/13/2009 | 11/16/2009 | **27** | 16:11 | 8:38 | 24 | 93209 | 0.67 | 0.05 | 0.16 | 0.13 | 0.005 | 0.01 | 0.03 | 0.01 | 0.002 | 0.002 |

| Start Date | End Date | Crtd | Start Time | End Time | Flow (mL/min) | TotVolume (mL) | hexane | benzene | heptane | toluene | octane | ethyl-benzene | p,m-xylene | o-xylene | nonane | decane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 11/16/2009 | 11/17/2009 | **115** | 8:41 | 8:43 | 24 | 34769 | 1.85 | 0.10 | 0.43 | 0.06 | N/A | 0.01 | 0.01 | 0.003 | LDL | LDL |
| 11/17/2009 | 11/18/2009 | **109** | 8:47 | 8:16 | 24 | 34024 | N/A | 0.16 | 1.51 | 0.36 | 0.02 | 0.06 | 0.15 | 0.05 | 0.01 | 0.01 |
| 11/18/2009 | 11/19/2009 | **113** | 8:18 | 8:34 | 24 | 35111 | LDL | 0.18 | N/A | 0.13 | 0.01 | 0.02 | 0.04 | 0.03 | 0.01 | LDL |
| 11/19/2009 | 11/20/2009 | **47** | 8:37 | 8:25 | 24 | 34420 | 0.66 | 0.06 | 0.19 | 0.20 | N/A | 0.02 | 0.05 | 0.02 | 0.003 | 0.003 |
| 11/20/2009 | 11/21/2009 | **122** | 8:28 | N/A | 24 | 48576 | N/A | 0.09 | 0.24 | 0.10 | LDL | 0.01 | 0.01 | 0.01 | LDL | LDL |
| 11/23/2009 | 11/25/2009 | **33** | 10:47 | 8:27 | 24 | 66030 | N/A | 0.09 | 0.92 | 0.14 | N/A | 0.01 | 0.02 | 0.01 | LDL | 0.002 |
| 11/26/2009 | 11/27/2009 | **60** | 10:51 | 8:07 | 24 | 30823 | N/A | 0.14 | 1.61 | 0.15 | 0.01 | 0.03 | 0.06 | 0.02 | 0.002 | 0.003 |
| 11/27/2009 | 11/27/2009 | **133** | 8:10 | 15:27 | 24 | 10610 | N/A | 0.53 | 4.83 | 1.15 | 0.05 | 0.19 | 0.47 | 0.14 | 0.03 | 0.03 |
| 11/30/2009 | 12/1/2009 | **51** | 8:35 | 9:37 | 24 | 36212 | N/A | 0.15 | 1.32 | 0.07 | 0.01 | 0.06 | 0.14 | 0.04 | 0.01 | 0.01 |
| 12/1/2009 | 12/2/2009 | **20** | 9:40 | 9:11 | 24 | 34027 | N/A | 0.13 | 1.76 | 0.17 | 0.01 | 0.02 | 0.05 | 0.01 | 0.002 | 0.002 |
| 12/2/2009 | 12/3/2009 | **12** | 9:13 | 9:53 | 24 | 35702 | N/A | 0.10 | 0.81 | 0.25 | 0.01 | 0.03 | 0.07 | 0.03 | 0.01 | 0.003 |
| 12/3/2009 | 12/4/2009 | **104** | 9:57 | 8:32 | 24 | 32675 | N/A | 0.14 | 1.80 | 0.09 | LDL | 0.01 | 0.02 | 0.01 | LDL | LDL |
| 12/4/2009 | 12/7/2009 | **119** | 8:35 | 16:49 | 24 | 11942 | N/A | 0.18 | 4.86 | 0.20 | 0.01 | 0.02 | 0.04 | 0.02 | 0.01 | LDL |
| 12/7/2009 | 12/8/2009 | **137** | 16:52 | 10:36 | 24 | 141749 | N/A | 0.10 | 0.11 | 0.07 | 0.004 | 0.01 | 0.03 | 0.01 | LDL | 0.003 |
| 12/8/2009 | 12/9/2009 | **153** | 10:39 | 9:51 | 24 | 33581 | 0.18 | 0.14 | 0.40 | LDL | LDL | LDL | LDL | LDL | LDL | LDL |
| 12/9/2009 | 12/10/2009 | **154** | 9:53 | 8:33 | 24 | 32806 | N/A | 0.15 | 0.99 | 0.11 | 0.003 | 0.02 | 0.04 | 0.02 | LDL | LDL |
| 12/10/2009 | 12/11/2009 | **111** | 8:37 | 9:46 | 24 | 36419 | 5.24 | 0.07 | 0.91 | 0.07 | LDL | 0.01 | 0.01 | 0.01 | 0.01 | 0.006 |
| 12/11/2009 | 12/11/2009 | **146** | 9:48 | 16:03 | 24 | 9091 | 15.88 | 0.13 | 3.06 | 0.11 | 0.01 | 0.01 | 0.02 | 0.01 | LDL | LDL |
| 12/11/2009 | 11/14/2009 | **136** | 16:06 | 9:37 | 24 | 94776 | 0.98 | 0.08 | 0.16 | 0.05 | N/A | LDL | LDL | LDL | LDL | LDL |
| 12/14/2009 | 12/15/2009 | **149** | 9:40 | 8:54 | 24 | 33634 | N/A | 0.16 | 0.31 | 0.36 | 0.02 | 0.06 | 0.15 | 0.05 | 0.01 | 0.01 |
| 12/15/2009 | 12/16/2009 | **79** | 8:57 | 10:54 | 24 | 37570 | 1.52 | 0.08 | 0.26 | 0.06 | 0.003 | 0.01 | 0.01 | 0.004 | LDL | LDL |
| 12/16/2009 | 12/17/2009 | **100** | 10:56 | 9:50 | 24 | 33128 | N/A | 0.14 | 1.50 | 0.15 | 0.01 | 0.03 | 0.05 | 0.02 | 0.002 | 0.003 |
| 12/17/2009 | 12/21/2009 | **142** | 9:54 | 8:44 | 24 | 137363 | 0.44 | 0.24 | 0.10 | 0.14 | 0.01 | 0.02 | 0.04 | 0.02 | 0.003 | 0.003 |
| 1/18/2010 | 1/19/2010 | **158** | 9:13 | 10:20 | 24 | 36385 | N/A | 0.19 | 2.92 | 0.16 | 0.01 | 0.03 | 0.04 | 0.02 | 0.01 | N/A |
| 1/19/2010 | 1/20/2010 | **113** | 10:23 | 11:13 | 24 | 35976 | 0.87 | 0.09 | 0.20 | 0.12 | N/A | 0.01 | 0.03 | 0.01 | 0.003 | N/A |

| Start Date | End Date | Crtd | Start Time | End Time | Flow (mL/min) | TotVolume (mL) | hexane | benzene | heptane | toluene | octane | ethyl-benzene | p,m-xylene | o-xylene | nonane | decane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1/20/2010 | 1/21/2010 | **163** | 11:15 | 10:13 | 24 | 33284 | LDL | LDL | N/A | 0.16 | LDL | N/A | N/A | N/A | N/A | LDL |
| 1/21/2010 | 1/22/2010 | **165** | 10:16 | 9:10 | 24 | 33200 | LDL | 0.37 | N/A | 0.16 | N/A | 0.02 | 0.02 | 0.01 | 0.02 | LDL |
| 1/22/2010 | 1/25/2010 | **118** | 9:14 | 11:34 | 24 | 107696 | N/A | 0.07 | N/A | 0.18 | N/A | 0.02 | 0.03 | 0.01 | 0.005 | LDL |
| 1/25/2010 | 1/26/2010 | **115** | 11:40 | 11:13 | 24 | 34145 | 1.89 | 0.11 | 0.44 | 0.06 | N/A | 0.01 | 0.01 | 0.00 | LDL | LDL |
|  |  | **106** |  |  |  | travelblank | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL |
|  |  | **115** |  |  |  | travelblank | N/A | N/A | N/A | LDL | LDL | LDL | LDL | LDL | LDL | LDL |

## A4: Concentrations (ppbv) of VOC in Toronto samples

| Start Date | End Date | Crtd | Start Time | End Time | Flow (mL/min) | TotVolume (mL) | hexane | benzene | heptane | toluene | octane | ethyl-benzene | p,m-xylene | o-xylene | nonane | decane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10/13/2009 | 10/14/2009 | 117 | 9:53 | 8:42 | 24 | 32912 | 0.27 | 0.05 | LDL | 0.40 | 0.03 | 0.05 | 0.09 | 0.03 | LDL | 0.01 |
| 10/19/2009 | 10/20/2009 | 100 | 8:28 | 8:57 | 24 | 34691 | 1.09 | 0.15 | 0.23 | 0.98 | 0.06 | 0.08 | 0.22 | 0.07 | 0.01 | 0.01 |
| 10/20/2009 | 10/21/2009 | 29 | 9:08 | 8:41 | 24 | 33462 | 0.98 | 0.18 | N/A | 1.57 | 0.22 | 0.15 | 0.35 | 0.10 | 0.09 | 0.02 |
| 10/21/2009 | 10/22/2009 | 84 | 8:56 | 8:06 | 24 | 32877 | 0.88 | 0.12 | 0.28 | 1.27 | 0.07 | 0.08 | 0.23 | 0.08 | 0.02 | 0.02 |
| 10/22/2009 | 10/23/2009 | 25 | 8:20 | 8:24 | 24 | 34143 | 0.34 | N/A | N/A | 6.24 | 0.05 | 0.05 | 0.14 | 0.04 | 0.01 | 0.01 |
| 10/23/2009 | 10/23/2009 | 125 | 8:34 | 14:34 | 24 | 8497 | N/A | 0.12 | LDL | 0.37 | 0.02 | 0.03 | 0.03 | LDL | LDL | LDL |
| 10/23/2009 | 10/26/2009 | 105 | 14:38 | 8:44 | 24 | 93522 | 0.06 | LDL | LDL | 0.14 | 0.03 | 0.04 | 0.10 | 0.03 | LDL | 0.01 |
| 10/26/2009 | 10/27/2009 | 127 | 8:54 | 8:51 | 24 | 33903 | 0.66 | 0.07 | LDL | 0.37 | 0.03 | 0.06 | 0.19 | 0.06 | 0.02 | 0.01 |
| 10/27/2009 | 10/28/2009 | 129 | 8:58 | 8:42 | 24 | 33680 | LDL | 0.05 | N/A | 0.99 | 0.19 | 0.16 | 0.42 | 0.13 | 0.02 | 0.02 |
| 10/28/2009 | 10/29/2009 | 118 | 8:51 | 8:50 | 24 | 33989 | N/A | 0.03 | LDL | 0.26 | 0.02 | 0.03 | 0.09 | N/A | LDL | LDL |
| 10/29/2009 | 10/30/2009 | 110 | 8:57 | 8:37 | 24 | 33562 | N/A | 0.04 | LDL | 0.63 | 2.37 | 0.06 | 0.17 | 0.06 | LDL | 0.01 |
| 10/30/2009 | 10/30/2009 | 103 | 8:42 | 14:35 | 24 | 8355 | 1.13 | 0.20 | LDL | 0.11 | LDL | 0.08 | 0.18 | N/A | LDL | 0.04 |
| 10/30/2009 | 11/2/2009 | 101 | 14:39 | 8:22 | 24 | 94500 | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| 11/2/2009 | 11/3/2009 | 48 | 8:29 | 8:25 | 24 | 33923 | N/A | 0.12 | 0.18 | 0.73 | 0.07 | 0.09 | 0.24 | 0.08 | 0.02 | 0.01 |
| 11/3/2009 | 11/4/2009 | 23 | 8:35 | 7:31 | 24 | 32475 | N/A | 0.11 | N/A | 0.86 | 0.12 | 0.01 | 0.01 | 0.05 | 0.01 | 0.01 |
| 11/4/2009 | 11/5/2009 | 120 | 7:37 | 8:32 | 24 | 35297 | N/A | 0.09 | 0.17 | 0.54 | N/A | 0.05 | 0.14 | 0.05 | 0.01 | 0.003 |
| 11/5/2009 | 11/6/2009 | 21 | 8:41 | 8:19 | 24 | 33480 | 0.44 | N/A | LDL | 0.77 | 0.002 | 0.05 | 0.14 | 0.04 | 0.01 | 0.01 |
| 11/6/2009 | 11/6/2009 | 114 | 8:25 | 2:34 | 24 | 8709 | N/A | 0.33 | LDL | 0.74 | 0.09 | 0.04 | 0.10 | 0.04 | LDL | 0.01 |
| 11/6/2009 | 11/7/2009 | 121 | 14:36 | 8:32 | 24 | 25432 | N/A | 0.13 | LDL | 0.60 | LDL | 0.05 | 0.14 | N/A | LDL | LDL |
| 11/7/2009 | 11/8/2009 | 18 | 8:40 | 8:43 | 24 | 34079 | N/A | 0.16 | 0.25 | 0.85 | N/A | 0.06 | 0.15 | 0.05 | 0.01 | N/A |
| 11/8/2009 | 11/9/2009 | 130 | 8:49 | 8:45 | 24 | 33837 | LDL | 0.10 | LDL | 0.68 | 0.09 | 0.07 | 0.20 | 0.08 | 0.02 | 0.02 |
| 11/9/2009 | 11/10/2009 | 107 | 8:51 | 8:52 | 24 | 34039 | 1.00 | 0.14 | 0.19 | 0.56 | 0.06 | 0.03 | 0.06 | 0.02 | LDL | LDL |
| 11/10/2009 | 11/11/2009 | 13 | 8:58 | 8:51 | 24 | 33850 | 1.31 | 0.15 | 0.08 | 0.60 | LDL | 0.02 | 0.05 | 0.02 | LDL | N/A |
| 11/11/2009 | 11/12/2009 | 10 | 8:57 | 8:17 | 24 | 33060 | 1.29 | 0.08 | 0.12 | 0.61 | 0.03 | 0.04 | 0.10 | 0.03 | LDL | N/A |
| 11/12/2009 | 11/13/2009 | 18 | 8:22 | 10:57 | 24 | 37630 | N/A | 0.15 | 0.23 | 0.77 | N/A | 0.06 | 0.13 | 0.05 | 0.01 | N/A |
| 11/13/2009 | 11/16/2009 | 14 | 11:05 | 8:33 | 24 | 98364 | 0.62 | 0.07 | 0.11 | 0.38 | 0.01 | 0.03 | 0.07 | 0.02 | LDL | N/A |
| 11/16/2009 | 11/17/2009 | 55 | 8:39 | 8:33 | 24 | 33833 | 1.66 | 0.08 | 0.17 | 0.70 | 0.02 | 0.05 | 0.10 | 0.03 | LDL | N/A |
| 11/17/2009 | 11/18/2009 | 126 | 8:39 | 8:56 | 24 | 34414 | 1.03 | 0.16 | 0.08 | 0.53 | 0.04 | 0.05 | 0.12 | 0.04 | LDL | N/A |
| 11/19/2009 | 11/20/2009 | 134 | 8:52 | 8:50 | 24 | 33940 | LDL | 0.17 | N/A | 1.46 | 0.05 | 0.11 | 0.30 | 0.04 | LDL | N/A |
| 11/23/2009 | 11/24/2009 | 69 | 7:51 | 9:10 | 24 | 35839 | N/A | N/A | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL |
| 11/24/2009 | 11/26/2009 | 15 | 9:14 | 8:48 | 24 | 67284 | N/A | 0.07 | 0.29 | 0.44 | 0.01 | 0.03 | 0.07 | 0.02 | LDL | N/A |

| Start Date | End Date | Crtd | Start Time | End Time | Flow (mL/min) | TotVolume (mL) | hexane | benzene | heptane | toluene | octane | ethyl-benzene | p,m-xylene | o-xylene | nonane | decane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 11/26/2009 | 11/27/2009 | 81 | 8:52 | 8:26 | 24 | 33380 | 1.34 | 0.16 | 0.64 | 1.50 | 0.31 | 0.18 | 0.48 | 0.13 | 0.01 | 0.02 |
| 11/27/2009 | 11/30/2009 | 44 | 8:30 | 8:52 | 24 | 102397 | LDL | 0.08 | LDL | 0.61 | N/A | 0.05 | 0.12 | 0.04 | 0.003 | 0.01 |
| 11/30/2009 | 31/11/2009 | 124 | 8:56 | 9:03 | 24 | 34111 | 0.91 | 0.25 | N/A | 1.41 | 0.15 | 0.13 | 0.37 | 0.10 | 0.01 | 0.02 |
| 12/1/2009 | 12/2/2009 | 102 | 9:07 | 9:45 | 24 | 34902 | 0.83 | N/A | N/A | 0.88 | 0.13 | 0.08 | 0.22 | 0.06 | LDL | N/A |
| 12/2/2009 | 12/3/2009 | 39 | 9:50 | 7:54 | 24 | 31220 | N/A | 0.13 | 0.07 | 0.39 | 0.02 | 0.03 | 0.07 | 0.02 | LDL | N/A |
| 12/3/2009 | 12/4/2009 | 30 | 7:58 | 7:33 | 24 | 33408 | 0.46 | 0.07 | 0.15 | 0.58 | 0.06 | 0.05 | 0.12 | 0.03 | LDL | N/A |
| 12/4/2009 | 12/7/2009 | 8 | 7:39 | 8:06 | 24 | 102585 | 0.49 | 0.06 | 0.10 | 0.48 | 0.02 | 0.04 | 0.10 | 0.03 | 0.004 | N/A |
| 12/7/2009 | 12/8/2009 | 46 | 8:11 | 8:01 | 24 | 33753 | 0.70 | N/A | N/A | 1.06 | 0.17 | 0.08 | 0.20 | 0.06 | 0.001 | 0.01 |
| 12/8/2009 | 12/9/2009 | 59 | 8:07 | 9:28 | 24 | 35910 | LDL | 0.25 | 0.02 | 0.32 | 0.03 | 0.05 | 0.12 | 0.04 | 0.01 | 0.01 |
| 12/9/2009 | 12/10/2009 | 112 | 9:32 | 9:39 | 24 | 34194 | 0.51 | 0.20 | N/A | 0.62 | 0.11 | 0.08 | 0.23 | 0.06 | 0.01 | 0.01 |
| 12/10/2009 | 12/11/2009 | 148 | 9:45 | 9:48 | 24 | 34060 | N/A | 0.74 | N/A | 0.56 | 0.04 | 0.05 | 0.17 | 0.04 | 0.01 | 0.01 |
| 12/11/2009 | 12/14/2009 | 140 | 9:53 | 9:32 | 24 | 101432 | N/A | 0.05 | N/A | 0.44 | 0.01 | 0.04 | 0.11 | 0.03 | 0.01 | N/A |
| 12/14/2009 | 12/15/2009 | 24 | 9:37 | 10:16 | 24 | 34949 | N/A | 0.28 | 0.29 | 0.54 | 0.06 | 0.07 | 0.18 | 0.06 | 0.01 | 0.01 |
| 12/15/2009 | 12/16/2009 | 138 | 10:16 | 9:11 | 24 | 32343 | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| 12/16/2009 | 12/17/2009 | 155 | 9:17 | 9:46 | 24 | 34710 | N/A | 0.28 | 0.29 | 0.55 | 0.06 | 0.07 | 0.18 | 0.06 | 0.01 | 0.01 |
| 12/17/2009 | 12/18/2009 | 145 | 9:52 | 8:52 | 24 | 32612 | 0.31 | 0.12 | 1.96 | 0.59 | 0.04 | 0.05 | 0.13 | 0.04 | 0.001 | N/A |
| 1/18/2010 | 1/19/2010 | 166 | 9:10 | 9:44 | 24 | 34821 | 1.50 | 0.12 | 0.04 | 0.86 | LDL | 0.08 | 0.20 | 0.05 | LDL | N/A |
| 1/19/2010 | 1/20/2010 | 139 | 9:49 | 10:05 | 24 | 34404 | 0.55 | 0.12 | 0.04 | 0.81 | 0.13 | 0.09 | 0.25 | 0.06 | LDL | N/A |
| 1/20/2010 | 1/21/2010 | 110 | 10:09 | 9:30 | 24 | 33091 | 0.07 | 0.09 | 0.07 | 0.40 | 0.02 | 0.03 | 0.07 | 0.02 | LDL | LDL |
| 1/21/2010 | 1/25/2010 | 32 | 9:35 | 10:18 | 24 | 33946 | N/A | 0.09 | LDL | 0.22 | LDL | 0.02 | 0.03 | 0.01 | LDL | LDL |
| 1/22/2010 | 1/25/2010 | 85 | 10:22 | 11:30 | 24 | 301564 | 0.09 | 0.02 | 0.02 | 0.12 | 0.01 | 0.01 | 0.03 | 0.01 | 0.002 | N/A |
| 1/25/2010 | 1/26/2010 | 105 | 11:35 | 10:59 | 24 | 33146 | 0.16 | LDL | LDL | 0.40 | 0.08 | 0.10 | 0.29 | 0.10 | LDL | 0.02 |
| 1/26/2010 | 1/27/2010 | 109 | 11:02 | 10:33 | 24 | 33342 | 0.79 | 0.07 | 0.18 | 0.66 | 0.01 | 0.07 | 0.16 | 0.03 | LDL | N/A |
| 06-Mar-10 | 07-Mar-10 | 103 | 9:02 | 9:05 | 24 | 34270 | N/A | 0.08 | N/A | 1.04 | 0.07 | 0.20 | 0.56 | 0.13 | 0.003 | N/A |
| 07-Mar-10 | 08-Mar-10 | 104 | 9:07 | 8:40 | 24 | 32440 | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| 12-Mar-10 | 13-Mar-10 | 114 | 8:25 | 8:55 | 24 | 34817 | 1.61 | 0.09 | LDL | 0.42 | N/A | 0.02 | 0.06 | 0.02 | 0.01 | N/A |
| 13-Mar-10 | 14-Mar-10 | 101 | 8:58 | 8:30 | 24 | 33338 | 0.44 | 0.28 | N/A | 1.54 | 0.08 | 0.02 | 0.19 | 0.09 | LDL | N/A |
| 14-Mar-10 | 15-Mar-10 | 113 | 8:30 | 9:05 | 24 | 34821 | N/A | 0.18 | LDL | 0.15 | LDL | LDL | N/A | 0.01 | LDL | N/A |
| 15-Mar-10 | 16-Mar-10 | 42 | 9:08 | 9:03 | 24 | 33888 | N/A | 0.12 | LDL | 1.16 | 0.05 | 0.16 | 0.41 | 0.09 | 0.01 | N/A |
| 19-Mar-10 | 20-Mar-10 | 152 | 8:58 | 9:08 | 24 | 34263 | 0.14 | 0.10 | LDL | 0.33 | LDL | 0.03 | 0.08 | 0.02 | LDL | N/A |
| 20-Mar-10 | 21-Mar-10 | 112 | 9:09 | 9:00 | 24 | 33753 | 0.27 | 0.12 | N/A | 1.39 | 0.10 | 0.11 | 0.24 | 0.07 | 0.05 | N/A |
| 21-Mar-10 | 22-Mar-10 | 168 | 9:00 | 9:00 | 24 | 33963 | 0.18 | 0.03 | LDL | 0.28 | 0.01 | 0.03 | 0.08 | 0.01 | LDL | N/A |
| 22-Mar-10 | 23-Mar-10 | 159 | 9:03 | 9:05 | 24 | 34049 | 0.44 | 0.04 | 0.05 | 0.32 | 0.02 | LDL | 0.04 | 0.02 | 0.001 | N/A |

| Start Date | End Date | Crtd | Start Time | End Time | Flow (mL/min) | TotVolume (mL) | hexane | benzene | heptane | toluene | octane | ethyl-benzene | p,m-xylene | o-xylene | nonane | decane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 30-Aug-10 | 31-Aug-10 | 111 | 9:16 | 9:10 | 24 | 33796 | 0.95 | 0.30 | 0.16 | 1.48 | N/A | 0.09 | 0.21 | LDL | LDL | N/A |
| 31-Aug-10 | 01-Sep-10 | 68 | 9:13 | 8:47 | 24 | 33361 | N/A | N/A | N/A | 2.11 | 0.15 | 0.15 | 0.39 | N/A | N/A | N/A |
| 07-Sep-10 | 08-Sep-10 | 113 | 9:20 | 8:46 | 18 | 23839 | N/A | 0.27 | LDL | 0.22 | LDL | LDL | N/A | 0.01 | LDL | N/A |
| 08-Sep-10 | 09-Sep-10 | 103 | 8:40 | 8:42 | 19 | 25994 | N/A | 0.11 | N/A | 1.37 | 0.09 | 0.26 | 0.74 | 0.17 | 0.004 | N/A |
| 09-Sep-10 | 10-Sep-10 | 109 | 8:45 | 8:45 | 18 | 24781 | LDL | LDL | LDL | 0.20 | LDL | 0.03 | 0.04 | 0.01 | LDL | N/A |
| 09-Sep-10 | 10-Sep-10 | 123 | 8:45 | 8:45 | 18 | 26467 | LDL | LDL | LDL | 0.28 | LDL | 0.02 | 0.04 | 0.01 | LDL | N/A |
| 10-Sep-10 | 13-Sep-10 | 115 | 8:49 | 9:20 | 19 | 77950 | N/A | 0.09 | 0.01 | 0.50 | 0.02 | 0.05 | N/A | 0.03 | LDL | N/A |
| 10-Sep-10 | 13-Sep-10 | 41 | 8:49 | 9:20 | 19 | 83179 | N/A | N/A | N/A | 0.16 | N/A | N/A | N/A | N/A | N/A | N/A |
| 13-Sep-10 | 14-Sep-10 | 11 | 10:10 | 8:47 | 40 | 28181 | N/A | 0.02 | 0.02 | 0.38 | LDL | 0.03 | 0.08 | 0.02 | LDL | N/A |
| 13-Sep-10 | 14-Sep-10 | 131 | 10:10 | 8:47 | 40 | 29044 | 0.10 | 0.04 | 0.02 | 0.15 | 0.003 | 0.01 | 0.04 | 0.01 | LDL | N/A |
| 14-Sep-10 | 15-Sep-10 | 36 | 8:50 | 8:44 | 40 | 30767 | 0.11 | 0.03 | 0.09 | 0.37 | 0.04 | 0.07 | 0.18 | 0.06 | 0.01 | N/A |
| 14-Sep-10 | 15-Sep-10 | 77 | 8:50 | 8:44 | 40 | 29129 | 0.16 | 0.02 | 0.04 | 0.09 | 0.01 | LDL | LDL | LDL | LDL | N/A |
| 16-Sep-10 | 17-Sep-10 | 22 | 8:53 | 14:25 | 40 | 42973 | 0.02 | 0.03 | LDL | 0.16 | LDL | 0.01 | N/A | 0.01 | LDL | N/A |
| 16-Sep-10 | 17-Sep-10 | 54 | 8:53 | 14:25 | 40 | 29760 | 0.04 | 0.03 | 0.01 | 0.05 | N/A | LDL | LDL | LDL | LDL | N/A |
| 17-Sep-10 | 20-Sep-10 | 144 | 14:25 | 9:10 | 40 | 45102 | 0.17 | 0.47 | N/A | N/A | N/A | 0.03 | 0.09 | 0.02 | LDL | N/A |

N/A- no results available, LDL- lower than detection limit

# APPENDIX B: Meteorological Information

## B1: Details for Egbert samples

| Parameter | | Meteorological conditions | | | | | | | | | Back Trajectories (start coordinates) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Start Date | End Date | Max Temp | Min Temp | Mean Temp | Total Rain | Total Snow | Total Precip | Snow on Grnd | Dir of Max Gust | Spd of Max Gust | 100 m | | 500 m | | 1000 m | |
| 10/19/2009 | 10/20/2009 | 15 | -1.3 | 6.9 | M | M | 0.3 | | 200 | 43 | 41.0 | -84.0 | 44.0 | -84.0 | 44.5 | -91.0 |
| 10/21/2009 | 10/22/2009 | 11.7 | 8.5 | 10.1 | M | M | M | | | <31 | 41.0 | -100.0 | 42.0 | -100.0 | 50.0 | -130.0 |
| 10/22/2009 | 10/23/2009 | 13.8 | 1.5 | 7.7 | M | M | 0.7 | | 330 | 44 | 61.0 | -82.0 | 60.0 | -90.0 | 48.0 | -95.0 |
| 10/23/2009 | 10/24/2009 | 10.7 | 0.8 | 5.8 | M | M | 5.5 | | 110 | 44 | 35.0 | -93.0 | 55.0 | -80.0 | 55.0 | -80.0 |
| 10/23/2009 | 10/26/2009 | 11.2 | 2.7 | 7 | M | M | 2.75 | | 165 | 44 | 60.0 | -105.0 | 61.0 | -115.0 | 50.0 | -130.0 |
| 10/26/2009 | 10/26/2009 | 11.8 | 3 | 7.4 | M | M | M | | 130 | 33 | 45.0 | -105.0 | 53.0 | -110.0 | 55.0 | -135.0 |
| 10/27/2009 | 10/28/2009 | 14.4 | 7.2 | 10.8 | M | M | 10.5 | | | <31 | 58.0 | -70.0 | 58.0 | -70.0 | 60.0 | -76.0 |
| 10/28/2009 | 10/29/2009 | 11.8 | 4.8 | 8.3 | M | M | 1.6 | | | <31 | 46.0 | -77.0 | 45.0 | -77.0 | 32.0 | -93.0 |
| 10/29/2009 | 10/30/2009 | 10.2 | 1.7 | 6 | M | M | 0 | | | <31 | 45.0 | -70.0 | 40.0 | -70.0 | 30.0 | -90.0 |
| 10/30/2009 | 10/30/2009 | 15.3 | 8.6 | 12 | M | M | 10.4 | | | 54 | 40.0 | -75.0 | 38.0 | -85.0 | 30.0 | -85.0 |
| 10/30/2009 | 11/2/2009 | 13.2 | 5.5 | 9.4 | M | M | 3.7 | | | 58.5 | 60.0 | -90.0 | 55.0 | -100.0 | 60.0 | -140.0 |
| 11/2/2009 | 11/3/2009 | 9.8 | -0.5 | 4.7 | M | M | 1.1 | | 160 | 32 | 58.0 | -135.0 | 58.0 | -110.0 | 58.0 | -115.0 |
| 11/3/2009 | 11/4/2009 | 7.2 | 0.4 | 3.8 | M | M | 0.8 | | 320 | 43 | 56.0 | -95.0 | 52.0 | -98.0 | 58.0 | -118.0 |
| 11/4/2009 | 11/5/2009 | 4.9 | -1.7 | 1.6 | M | M | M | | | <31 | 45.0 | -90.0 | 60.0 | -115.0 | 60.0 | -115.0 |
| 11/5/2009 | 11/6/2009 | 5.6 | -1.2 | 2.2 | M | M | 2.8 | | 330 | 57 | 55.0 | -95.0 | 55.0 | -110.0 | 58.0 | -137.0 |
| 11/6/2009 | 11/6/2009 | 3.9 | -2.4 | 0.8 | M | M | 0.3 | | | <31 | 51.0 | -85.0 | 53.0 | -90.0 | 54.0 | -94.0 |
| 11/6/2009 | 11/7/2009 | 3.9 | -2.4 | 0.8 | M | M | 0.3 | | | <31 | 50.0 | -110.0 | 55.0 | -115.0 | 60.0 | -117.0 |
| 11/7/2009 | 11/8/2009 | 15.9 | 2.5 | 9.2 | M | M | 0 | | 180 | 39 | 30.0 | -100.0 | 60.0 | -180.0 | 60.0 | -180.0 |
| 11/8/2009 | 11/9/2009 | 17.2 | 2.7 | 10 | M | M | 1 | | | <31 | 37.0 | -87.0 | 28.0 | -95.0 | 29.0 | -89.0 |
| 11/9/2009 | 11/10/2009 | 18.7 | 3.3 | 11 | M | M | 0 | | | <31 | 48.0 | -110.0 | 48.0 | -110.0 | 49.0 | -150.0 |

| Parameter | | Meteorological conditions | | | | | | | | | Back Trajectories (start coordinates) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Start Date | End Date | Max Temp | Min Temp | Mean Temp | Total Rain | Total Snow | Total Precip | Snow on Grnd | Dir of Max Gust | Spd of Max Gust | 100 m | | 500 m | | 1000 m | |
| 11/10/2009 | 11/12/2009 | 10.9 | -0.5 | 5.2 | M | M | 0 | | 310 | 33 | 55.0 | -90.0 | 48.0 | -90.0 | 55.0 | 90.0 |
| 11/12/2009 | 11/13/2009 | 9.7 | -5.8 | 2 | M | M | 1 | | | <31 | 55.0 | -97.0 | 58.0 | -115.0 | 57.0 | -109.0 |
| 11/13/2009 | 11/13/2009 | 11.3 | -3.9 | 3.7 | M | M | 0.6 | | | <31 | 45.0 | -74.0 | 45.0 | -63.0 | 45.0 | -64.0 |
| 11/13/2009 | 11/16/2009 | 12.7 | 0.7 | 6.7 | M | M | 0.2 | | 350 | 35 | 48.0 | -135.0 | 48.0 | -135.0 | 60.0 | -140.0 |
| 11/16/2009 | 11/17/2009 | 7.4 | -3.5 | 2 | M | M | 0 | | 340 | 33 | 46.0 | -110.0 | 52.0 | -110.0 | 46.0 | -120.0 |
| 11/17/2009 | 11/18/2009 | 7.2 | -5.5 | 0.9 | M | M | 0 | | | <31 | 51.0 | -91.0 | 52.0 | -105.0 | 52.0 | -98.0 |
| 11/18/2009 | 11/19/2009 | 10.9 | -2.9 | 4 | M | M | 0 | | 130 | 32 | 50.0 | -93.0 | 55.0 | -78.0 | 53.0 | -71.0 |
| 11/19/2009 | 11/20/2009 | 9.3 | 0.7 | 5 | M | M | 9 | | | <31 | 37.0 | -95.0 | 45.0 | -84.0 | 44.0 | -80.0 |
| 11/20/2009 | 11/21/2009 | 8.8 | 3.3 | 6.1 | M | M | 1.5 | | 280 | 41 | 47.0 | -90.0 | 47.0 | -85.0 | 43.0 | 87.0 |
| 11/23/2009 | 11/25/2009 | 7 | 1.65 | 4.35 | M | M | 0 | | | <31 | 57.0 | -83.0 | 58.0 | -83.0 | 37.0 | -85.0 |
| 11/26/2009 | 11/27/2009 | 8.5 | 0.4 | 4.5 | M | M | 0 | | 230 | 35 | 45.0 | -105.0 | 50.0 | -110.0 | 50.0 | -135.0 |
| 11/27/2009 | 11/27/2009 | 5.4 | -0.7 | 2.4 | M | M | 0.4 | | 330 | 44 | 41.0 | -92.0 | 44.0 | -91.0 | 41.0 | -94.0 |
| 11/30/2009 | 31/11/2009 | 3.7 | -1.5 | 1.1 | M | M | 0.3 | | 340 | 39 | 43.0 | -50.0 | 55.0 | -80.0 | 60.0 | -20.0 |
| 12/1/2009 | 12/2/2009 | 5.4 | -0.9 | 2.3 | M | M | 0.6 | | 260 | 32 | 40.0 | -63.0 | 50.0 | -47.0 | 50.0 | -85.0 |
| 12/2/2009 | 12/3/2009 | 9 | 0.7 | 4.9 | M | M | 9.4 | | | <31 | 32.0 | -60.0 | 32.0 | -60.0 | 50.0 | -43.0 |
| 12/3/2009 | 12/4/2009 | 5.8 | -0.9 | 2.5 | M | M | 3.1 | | 320 | 33 | 38.0 | -60.0 | 39.0 | -35.0 | 60.0 | -40.0 |
| 12/4/2009 | 12/7/2009 | 1.1 | -4.8 | -1.9 | M | M | 0.2 | | 233 | 43 | 55.0 | -50.0 | 48.0 | -40.0 | 48.0 | -40.0 |
| 12/7/2009 | 12/8/2009 | 0.7 | -3.5 | -1.4 | M | M | 0 | | | <31 | 51.0 | -91.0 | 53.0 | -87.0 | 54.0 | -87.0 |
| 12/8/2009 | 12/9/2009 | -1.6 | -6.1 | -3.9 | M | M | 0.6 | | 100 | 48 | 41.0 | -85.0 | 41.0 | -85.0 | 42.0 | -87.0 |
| 12/9/2009 | 12/10/2009 | 4.1 | -3.1 | 0.5 | M | M | 7.2 | | 120 | 67 | 50.0 | -100.0 | 60.0 | -100.0 | 61.0 | -100.0 |
| 12/10/2009 | 12/11/2009 | -0.8 | -9 | -4.9 | M | M | 0.6 | | 260 | 57 | 51.0 | -105.0 | 52.0 | -120.0 | 55.0 | -115.0 |
| 12/11/2009 | 12/11/2009 | -7 | -9.9 | -8.5 | M | M | 0 | | 270 | 46 | 45.0 | -102.0 | 48.0 | -105.0 | 48.0 | -105.0 |

| Parameter | | Meteorological conditions | | | | | | | | | Back Trajectories (start coordinates) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Start Date | End Date | Max Temp | Min Temp | Mean Temp | Total Rain | Total Snow | Total Precip | Snow on Grnd | Dir of Max Gust | Spd of Max Gust | 100 m | | 500 m | | 1000 m | |
| 12/11/2009 | 11/14/2009 | -1.7 | -7.7 | -4.7 | M | M | 0.4 | | 223 | 39 | 68.0 | -120.0 | 65.0 | -138.0 | 50.0 | -120.0 |
| 12/14/2009 | 12/15/2009 | 1.3 | -1.2 | 0.1 | M | M | | | | <31 | 62.0 | -75.0 | 70.0 | -130.0 | 55.0 | -115.0 |
| 12/15/2009 | 12/16/2009 | 0.2 | -8.3 | -4.1 | M | M | | | 340 | 54 | 60.0 | -120.0 | 75.0 | -115.0 | 78.0 | -90.0 |
| 12/16/2009 | 12/17/2009 | -4.3 | -9.3 | -6.8 | M | 2 | 0 | 1 | 290 | 43 | 70.0 | -120.0 | 73.0 | -60.0 | 70.0 | -120.0 |
| 12/17/2009 | 12/21/2009 | -4.7 | -12.42 | -8.56 | M | 3 | 0 | 1.8 | | <31 | 60.0 | -110.0 | 64.0 | -110.0 | 67.0 | -130.0 |
| 1/18/2010 | 1/19/2010 | 2 | -3.5 | -0.8 | M | M | 0 | 13 | | <31 | 50.0 | -122.0 | 55.0 | -122.0 | 55.0 | -120.0 |
| 1/19/2010 | 1/20/2010 | 0.7 | -4.6 | -2 | 0 | 5 | 1.6 | 12 | | <31 | 70.0 | -115.0 | 60.0 | -95.0 | 60.0 | -95.0 |
| 1/20/2010 | 1/21/2010 | -4.3 | -10.7 | -7.5 | M | M | 0.4 | 18 | | <31 | 55.0 | -90.0 | 55.0 | -85.0 | 53.0 | -97.0 |
| 1/21/2010 | 1/22/2010 | -2.1 | -15.5 | -8.8 | M | M | 0 | 16 | | <31 | 43.0 | -79.0 | 41.0 | -79.0 | 38.0 | -95.0 |
| 1/22/2010 | 1/25/2010 | 0.7 | -10.6 | -5.0 | M | M | 0.5 | 15 | 140 | 37 | 63.0 | -65.0 | 59.0 | -23.0 | 63.0 | -25.0 |
| 1/25/2010 | 1/26/2010 | 2.8 | -1.3 | 0.8 | M | M | 2.9 | 3 | | 57 | 52.0 | -51.0 | 55.0 | -55.0 | 45.0 | -55.0 |

M- missing, Temperature in °C, Wind direction in degrees, Wind speed in km/h, Back trajectory coordinates in degrees, empty cells- data is not available

## B2: Details for Toronto samples

| Parameter | | Meteorological conditions | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Start Date** | **End Date** | **Max Temp** | **Min Temp** | **Mean Temp** | **Total Rain** | **Total Snow** | **Total Precip** | **Snow on Grnd** | **Direction of Max Gust** | **Speed of Max Gust** |
| 10/13/2009 | 10/14/2009 | 10.7 | 2.4 | 6.6 | 0.2 | 0 | 0.2 | 0 | 340 | 52 |
| 10/19/2009 | 10/20/2009 | 15.2 | 0.3 | 7.8 | 0.0 | 0 | 0.0 | 0 | 220 | 41 |
| 10/20/2009 | 10/21/2009 | 16.4 | 10.9 | 13.7 | 0.0 | 0 | 0.0 | 0 | | M |
| 10/21/2009 | 10/22/2009 | 14.4 | 9.5 | 12.0 | 2.8 | 0 | 2.8 | 0 | | <31 |
| 10/22/2009 | 10/23/2009 | 16.5 | 3.8 | 10.2 | 0.6 | 0 | 0.6 | 0 | 280 | 46 |
| 10/23/2009 | 10/23/2009 | 11.0 | 2.9 | 7.0 | 14.8 | 0 | 14.8 | 0 | 90 | 57 |
| 10/23/2009 | 10/26/2009 | 12.4 | 4.7 | 8.6 | 4.9 | 0 | 4.9 | 0 | 178 | 46.75 |
| 10/26/2009 | 10/27/2009 | 11.8 | 5.8 | 8.8 | 0.0 | 0 | 0.0 | 0 | 90 | 39 |
| 10/27/2009 | 10/28/2009 | 16.3 | 8.2 | 12.3 | 1.2 | 0 | 1.2 | 0 | | <31 |
| 10/28/2009 | 10/29/2009 | 13.0 | 9.6 | 11.3 | 2.2 | 0 | 2.2 | 0 | | <31 |
| 10/29/2009 | 10/30/2009 | 11.0 | 9.2 | 10.1 | 0.0 | 0 | 0.0 | 0 | | <31 |
| 10/30/2009 | 10/30/2009 | 15.0 | 9.7 | 12.4 | 2.6 | 0 | 2.6 | 0 | | <31 |
| 10/30/2009 | 11/2/2009 | 13.2 | 5.5 | 9.4 | 1.9 | 0 | 1.9 | 0 | 260 | 56 |
| 11/2/2009 | 11/3/2009 | 10.4 | 1.1 | 5.8 | 1.6 | 0 | 1.6 | 0 | | <31 |
| 11/3/2009 | 11/4/2009 | 8.9 | 0.9 | 4.9 | T | 0 | T | 0 | 330 | 50 |
| 11/4/2009 | 11/5/2009 | 6.2 | -1.2 | 2.5 | 1.8 | 0 | 1.8 | 0 | | <31 |
| 11/5/2009 | 11/6/2009 | 7.5 | 1.3 | 4.4 | 1.6 | 0 | 1.6 | 0 | 320 | 69 |
| 11/6/2009 | 11/6/2009 | 4.9 | -1.1 | 1.9 | 0.0 | 0 | 0.0 | 0 | | <31 |
| 11/6/2009 | 11/7/2009 | 4.9 | -1.1 | 1.9 | 0.0 | 0 | 0.0 | 0 | | <31 |
| 11/7/2009 | 11/8/2009 | 16.1 | 4.5 | 10.3 | 0.0 | 0 | 0.0 | 0 | 210 | 41 |
| 11/8/2009 | 11/9/2009 | 18.1 | 4.7 | 11.4 | 0.0 | 0 | 0.0 | 0 | | <31 |
| 11/9/2009 | 11/10/2009 | 19.1 | 3.9 | 11.5 | 0.0 | 0 | 0.0 | 0 | | <31 |
| 11/10/2009 | 11/11/2009 | 13.5 | 3.3 | 8.4 | 0.0 | 0 | 0.0 | 0 | | M |

| Parameter | | Meteorological conditions | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Start Date | End Date | Max Temp | Min Temp | Mean Temp | Total Rain | Total Snow | Total Precip | Snow on Grnd | Direction of Max Gust | Speed of Max Gust |
| 11/11/2009 | 11/12/2009 | 9.0 | -0.5 | 4.3 | 0.0 | 0 | 0.0 | 0 | | <31 |
| 11/12/2009 | 11/13/2009 | 9.6 | -1.8 | 3.9 | 0.0 | 0 | 0.0 | 0 | | <31 |
| 11/13/2009 | 11/16/2009 | 12.3 | 1.0 | 6.7 | 0.0 | 0 | 0.0 | 0 | 310 | 37 |
| 11/16/2009 | 11/17/2009 | 8.8 | -0.2 | 4.3 | 0.0 | 0 | 0.0 | 0 | | <31 |
| 11/17/2009 | 11/18/2009 | 7.5 | -2.3 | 2.6 | 0.0 | 0 | 0.0 | 0 | | <31 |
| 11/19/2009 | 11/20/2009 | 10.2 | 2.0 | 6.1 | 12.6 | 0 | 12.6 | 0 | 250 | 37 |
| 11/20/2009 | 11/23/2009 | 10.6 | 2.8 | 6.7 | 2.8 | 0 | 2.8 | 0 | 260 | 43.5 |
| 11/23/2009 | 11/24/2009 | 9.8 | 2.4 | 6.1 | 0.0 | 0 | 0.0 | 0 | | <31 |
| 11/24/2009 | 11/26/2009 | 9.3 | 5.0 | 7.2 | 2.6 | 0 | 2.6 | 0 | 230 | 35 |
| 11/26/2009 | 11/27/2009 | 9.5 | 1.3 | 5.4 | 0.4 | 0 | 0.4 | 0 | 230 | 35 |
| 11/27/2009 | 11/30/2009 | 6.5 | -0.5 | 3.0 | 1.4 | 0 | 1.4 | 0 | 313 | 41.33333 |
| 11/30/2009 | 12/1/2009 | 5.5 | -0.7 | 2.4 | 0.6 | 0 | 0.6 | 0 | 320 | 35 |
| 12/1/2009 | 12/2/2009 | 7.0 | 0.3 | 3.7 | 0.0 | 0.2 | 0.2 | T | 240 | 44 |
| 12/2/2009 | 12/3/2009 | 10.2 | 0.2 | 5.2 | 15.6 | 0 | 15.6 | 0 | 90 | 46 |
| 12/3/2009 | 12/4/2009 | 7.6 | -0.6 | 3.5 | 5.0 | 0 | 5.0 | 0 | 300 | 54 |
| 12/4/2009 | 12/7/2009 | 2.1 | -4.0 | -1.0 | 0.0 | 0 | 0.0 | 0 | 235 | 45.5 |
| 12/7/2009 | 12/8/2009 | 1.6 | -2.7 | -0.6 | 0.0 | T | T | 0 | | <31 |
| 12/8/2009 | 12/9/2009 | 2.1 | -4.5 | -1.2 | 0.0 | T | T | 0 | 110 | 61 |
| 12/9/2009 | 12/10/2009 | 6.1 | -0.9 | 2.6 | 10.2 | 9.6 | 26.2 | 5 | 230 | 76 |
| 12/10/2009 | 12/11/2009 | -0.8 | -9.5 | -5.2 | 0.0 | 1.4 | 1.0 | 2 | 240 | 74 |
| 12/11/2009 | 12/14/2009 | 0.5 | -4.7 | -2.1 | 0.9 | 0 | 1.7 | 1.25 | 240 | 45.66667 |
| 12/14/2009 | 12/15/2009 | 3.8 | 0.4 | 2.1 | 2.6 | 0 | 2.6 | 1 | | <31 |
| 12/15/2009 | 12/16/2009 | 3.0 | -5.0 | -1.0 | 0.0 | 0.6 | 0.6 | T | 310 | 50 |
| 12/16/2009 | 12/17/2009 | -3.6 | -6.3 | -5.0 | 0.0 | 0.6 | 0.4 | T | 260 | 41 |

| Parameter | | Meteorological conditions | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Start Date | End Date | Max Temp | Min Temp | Mean Temp | Total Rain | Total Snow | Total Precip | Snow on Grnd | Direction of Max Gust | Speed of Max Gust |
| 12/17/2009 | 12/18/2009 | -4.7 | -11.7 | -8.2 | 0.0 | T | T | T | | <31 |
| 1/18/2010 | 1/19/2010 | 1.0 | -2.9 | -1.0 | 0.0 | 0 | 0.0 | 0 | | <31 |
| 1/19/2010 | 1/20/2010 | 2.0 | -3.8 | -0.9 | 0.0 | 0.2 | 0.2 | 0 | 350 | 32 |
| 1/20/2010 | 1/21/2010 | -1.8 | -7.7 | -4.8 | 0.0 | 0 | 0.0 | T | 340 | 35 |
| 1/21/2010 | 1/25/2010 | 0.9 | -8.9 | -4.0 | 0.0 | 0 | 0.0 | T | 100 | 37 |
| 1/22/2010 | 1/25/2010 | 4.3 | -2.6 | 0.9 | 4.3 | 0 | 4.3 | 0 | 157 | 37.33333 |
| 1/25/2010 | 1/26/2010 | 6.7 | 0.2 | 3.5 | 10.8 | 0 | 10.8 | 0 | 260 | 48 |
| 1/26/2010 | 1/27/2010 | 0.3 | -1.9 | -0.8 | 0.0 | 0.2 | 0.2 | 0 | 260 | 56 |
| 3/06/2010 | 3/07/2010 | 9.0 | -4.0 | 2.5 | 0.0 | 0 | 0.0 | T | | <31 |
| 3/07/2010 | 3/08/2010 | 11.3 | -2.7 | 4.3 | 0.0 | 0 | 0.0 | T | 270 | 41 |
| 3/12/2010 | 3/13/2010 | 7.5 | 5.1 | 6.3 | 21.6 | 0 | 21.6 | 0 | 90 | 54 |
| 3/13/2010 | 3/14/2010 | 6.7 | 4.0 | 5.4 | 20.6 | 0 | 20.6 | 0 | 70 | 78 |
| 3/14/2010 | 3/15/2010 | 5.8 | 3.3 | 4.6 | 4.0 | 0 | 4.0 | 0 | 80 | 70 |
| 3/15/2010 | 3/16/2010 | 13.2 | 3.0 | 8.1 | T | 0 | T | 0 | 40 | 33 |
| 3/19/2010 | 3/20/2010 | 19.1 | 3.1 | 11.1 | 0.0 | 0 | 0.0 | 0 | 240 | 50 |
| 3/20/2010 | 3/21/2010 | 5.3 | -1.2 | 2.1 | 0.0 | 0 | 0.0 | 0 | 350 | 32 |
| 3/21/2010 | 3/22/2010 | 5.3 | -1.6 | 1.9 | 0.0 | T | T | T | | <31 |
| 3/22/2010 | 3/23/2010 | 7.9 | -0.8 | 3.6 | 4.0 | 0 | 4.0 | 0 | 50 | 41 |
| 8/30/2010 | 8/31/2010 | 34.5 | 20.0 | 27.3 | 0.0 | 0 | 0.0 | 0 | 220 | 39 |
| 8/31/2010 | 9/01/2010 | 33.7 | 21.7 | 27.7 | 0.0 | 0 | 0.0 | 0 | 250 | 33 |
| 9/01/2010 | 9/02/2010 | 32.7 | 21.4 | 27.1 | 0.0 | 0 | 0.0 | 0 | 230 | 46 |
| 9/02/2010 | 9/03/2010 | 30.4 | 22.6 | 26.5 | 4.2 | 0 | 4.2 | 0 | 290 | 35 |
| 9/03/2010 | 9/04/2010 | 25.7 | 15.1 | 20.4 | 9.6 | 0 | 9.6 | 0 | 250 | 57 |
| 9/07/2010 | 9/08/2010 | 30.2 | 15.3 | 22.8 | 0.0 | 0 | 0.0 | 0 | 220 | 59 |

| Parameter | | Meteorological conditions | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Start Date | End Date | Max Temp | Min Temp | Mean Temp | Total Rain | Total Snow | Total Precip | Snow on Grnd | Direction of Max Gust | Speed of Max Gust |
| 9/07/2010 | 9/08/2010 | 30.2 | 15.3 | 22.8 | 0.0 | 0 | 0.0 | 0 | 220 | 60 |
| 9/08/2010 | 9/09/2010 | 19.3 | 14.2 | 16.8 | 0.2 | 0 | 0.2 | 0 | 290 | 61 |
| 9/08/2010 | 9/09/2010 | 19.3 | 14.2 | 16.8 | 0.2 | 0 | 0.2 | 0 | 290 | 62 |
| 9/09/2010 | 9/10/2010 | 16.8 | 12.4 | 14.6 | T | 0 | T | 0 | 320 | 41 |
| 9/09/2010 | 9/10/2010 | 16.8 | 12.4 | 14.6 | T | 1 | T | 0 | 320 | 42 |
| 9/10/2010 | 9/13/2010 | 20.7 | 11.8 | 16.3 | 0.0 | 0 | 0.0 | 0 | | <31 |
| 9/10/2010 | 9/13/2010 | 20.7 | 11.8 | 16.3 | 0.0 | 0 | 0.0 | 0 | | <32 |
| 9/13/2010 | 9/14/2010 | 24.3 | 12.6 | 18.5 | 1.8 | 0 | 1.8 | 0 | 290 | 48 |
| 9/13/2010 | 9/14/2010 | 24.3 | 12.6 | 18.5 | 1.8 | 0 | 1.8 | 0 | 290 | 49 |
| 9/14/2010 | 9/15/2010 | 20.5 | 9.7 | 15.1 | 0.0 | 0 | 0.0 | 0 | 270 | 46 |
| 9/14/2010 | 9/15/2010 | 20.5 | 9.7 | 15.1 | 0.0 | 0 | 0.0 | 0 | 270 | 47 |
| 9/15/2010 | 9/16/2010 | 17.9 | 8.2 | 13.1 | 0.0 | 0 | 0.0 | 0 | | <31 |
| 9/15/2010 | 9/16/2010 | 17.9 | 8.2 | 13.1 | 0.0 | 0 | 0.0 | 0 | | <32 |
| 9/16/2010 | 9/17/2010 | 14.5 | 11.4 | 13.0 | 27.2 | 0 | 27.2 | 0 | 40 | 33 |
| 9/16/2010 | 9/17/2010 | 14.5 | 11.4 | 13.0 | 27.2 | 0 | 27.2 | 0 | 40 | 34 |
| 9/17/2010 | 9/20/2010 | 16.8 | 8.6 | 12.7 | 0.0 | 0 | 0.0 | 0 | | <31 |
| 9/17/2010 | 9/20/2010 | 16.8 | 8.6 | 12.7 | 0.0 | 0 | 0.0 | 0 | | <32 |
| 9/20/2010 | 9/22/2010 | 22.7 | 9.8 | 16.3 | 3.0 | 0 | 3.0 | 0 | 255 | 77 |
| 9/20/2010 | 9/22/2010 | 22.7 | 9.8 | 16.3 | 3.0 | 0 | 3.0 | 0 | 255 | 77 |
| 9/22/2010 | 9/24/2010 | 24.6 | 12.2 | 18.4 | 3.0 | 0 | 3.0 | 0 | 265 | 91 |
| 9/22/2010 | 9/24/2010 | 24.6 | 12.2 | 18.4 | 3.0 | 0 | 3.0 | 0 | 265 | 91 |

M- missing, Temperature in °C, Wind direction in degrees, Wind speed in km/h, Back trajectory coordinates in degrees, empty cells: data is not available

# APPENDIX C: Stable Carbon Isotope Composition of Ambient VOC

## C1: Isotopic composition of VOC in Egbert Samples

| Start Date | End Date | Crt | Start Time | End Time | Flow (mL/min) | TotVol (mL) | hexane | benzene | heptane | toluene | octane | ethyl-benzene | p,m-xylene | o-xylene | nonane | decane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10/19/2009 | 10/20/2009 | **49** | 8:30 | 8:50 | 24 | 35208 | -25.12 | -21.39 | -22.49 | -23.65 | N/A | -23.22 | -24.85 | -24.03 | LDL | LDL |
| 10/21/2009 | 10/22/2009 | **144** | 8:49 | 8:45 | 24 | 34586 | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | LDL |
| 10/22/2009 | 10/23/2009 | **128** | 8:52 | 8:28 | 24 | 34137 | -27.10 | -22.16 | -23.85 | -22.73 | LDL | -26.58 | -25.93 | -26.67 | -28.29 | LDL |
| 10/23/2009 | 10/24/2009 | **132** | 8:34 | 16:07 | 24 | 10867 | -27.82 | -27.09 | -23.74 | -25.93 | LDL | -23.45 | -23.33 | -21.70 | LDL | LDL |
| 10/24/2009 | 10/26/2009 | **108** | 16:11 | 8:52 | 24 | 93478 | -28.11 | -25.85 | -26.52 | -24.70 | N/A | -25.82 | -17.80 | -24.19 | N/A | LDL |
| 10/26/2009 | 10/26/2009 | **106** | 9:01 | 9:43 | 24 | 35733 | -26.08 | -15.25 | -25.57 | -25.68 | N/A | -23.43 | -23.09 | -22.81 | LDL | LDL |
| 10/27/2009 | 10/28/2009 | **141** | 9:49 | 8:51 | 24 | 33306 | N/A | -22.24 | N/A | LDL | LDL | LDL | LDL | LDL | LDL | LDL |
| 10/28/2009 | 10/29/2009 | **65** | 8:55 | 8:23 | 24 | 33802 | N/A | N/A | N/A | LDL | LDL | LDL | LDL | N/A | N/A | LDL |
| 10/29/2009 | 10/30/2009 | **41** | 8:26 | 8:25 | 24 | 34458 | N/A | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL |
| 10/30/2009 | 10/30/2009 | **54** | 8:30 | 16:03 | 24 | 10923 | LDL | N/A | -29.69 | LDL | LDL | LDL | LDL | LDL | -27.54 | LDL |
| 10/30/2009 | 11/2/2009 | **52** | 15:07 | 8:52 | 24 | 95117 | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL |
| 11/2/2009 | 11/3/2009 | **103** | 8:57 | 9:47 | 24 | 35895 | -27.37 | -28.12 | -28.87 | -28.47 | LDL | N/A | N/A | LDL | LDL | LDL |
| 11/3/2009 | 11/4/2009 | **80** | 9:49 | 9:38 | 24 | 34479 | N/A | -27.34 | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL |
| 11/4/2009 | 11/5/2009 | **16** | 9:42 | 8:42 | 24 | 33302 | -27.05 | -21.31 | -24.86 | -26.92 | N/A | -10.15 | -17.79 | -23.35 | -24.78 | -23.04 |
| 11/5/2009 | 11/6/2009 | **11** | 8:45 | 9:57 | 24 | 36466 | -27.06 | -21.52 | -24.30 | -24.20 | N/A | -21.54 | -20.40 | -21.55 | LDL | LDL |
| 11/6/2009 | 11/6/2009 | **116** | 10:01 | 15:53 | 24 | 8532 | -27.31 | -28.57 | -24.66 | -27.50 | LDL | -17.52 | -20.00 | -20.85 | LDL | LDL |
| 11/6/2009 | 11/7/2009 | **133** | 15:58 | 10:23 | 24 | 26530 | -23.96 | -25.43 | -21.75 | -22.33 | N/A | -18.60 | -19.80 | -18.95 | -31.22 | N/A |
| 11/7/2009 | 11/8/2009 | **123** | 10:30 | 9:23 | 24 | 33044 | -27.10 | -26.22 | -24.25 | -25.03 | N/A | -21.57 | -23.65 | -21.19 | LDL | LDL |
| 11/8/2009 | 11/9/2009 | **131** | 9:31 | 8:46 | 24 | 33737 | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| 11/9/2009 | 11/10/2009 | **22** | 8:51 | 11:16 | 24 | 38204 | -27.33 | -26.93 | -26.11 | -25.44 | LDL | LDL | LDL | -16.09 | LDL | LDL |
| 11/10/2009 | 11/12/2009 | **36** | 11:19 | 8:31 | 24 | 65411 | -29.01 | -25.46 | -24.53 | -25.95 | N/A | -25.42 | -25.83 | -26.14 | LDL | -25.11 |

| **Start Date** | **End Date** | **Crt** | **Start Time** | **End Time** | **Flow (mL/min)** | **TotVol (mL)** | **hexane** | **benzene** | **heptane** | **toluene** | **octane** | **ethyl-benzene** | **p,m-xylene** | **o-xylene** | **nonane** | **decane** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 11/12/2009 | 11/13/2009 | **40** | 8:36 | 8:05 | 24 | 33997 | -28.22 | -25.22 | -24.57 | -25.97 | N/A | -27.63 | -28.26 | -23.90 | N/A | N/A |
| 11/13/2009 | 11/13/2009 | **123** | 8:07 | 16:16 | 24 | 11662 | -27.10 | -26.22 | -24.25 | -25.03 | N/A | -21.57 | -23.65 | -21.19 | LDL | LDL |
| 11/13/2009 | 11/16/2009 | **27** | 16:11 | 8:38 | 24 | 93209 | -26.27 | -27.49 | -23.48 | -25.11 | N/A | -26.76 | -27.89 | -24.47 | LDL | LDL |
| 11/16/2009 | 11/17/2009 | **115** | 8:41 | 8:43 | 24 | 34769 | -24.66 | -26.11 | -21.70 | -23.53 | N/A | -22.37 | -21.53 | -22.11 | LDL | LDL |
| 11/17/2009 | 11/18/2009 | **109** | 8:47 | 8:16 | 24 | 34024 | N/A | -24.02 | -21.31 | -20.84 | N/A | -26.11 | -29.50 | -21.33 | -23.62 | -24.39 |
| 11/18/2009 | 11/19/2009 | **113** | 8:18 | 8:34 | 24 | 35111 | LDL | -24.14 | N/A | -23.64 | N/A | -23.86 | -23.28 | -24.80 | -30.98 | LDL |
| 11/19/2009 | 11/20/2009 | **47** | 8:37 | 8:25 | 24 | 34420 | -27.01 | -24.05 | -17.71 | -24.90 | N/A | -27.76 | -23.37 | -24.81 | -17.25 | -26.83 |
| 11/20/2009 | 11/21/2009 | **122** | 8:28 | ? | 24 | 48576 | N/A | -23.92 | -24.57 | -23.14 | LDL | -24.61 | -23.60 | -25.22 | LDL | LDL |
| 11/23/2009 | 11/25/2009 | **33** | 10:47 | 8:27 | 24 | 66030 | N/A | -25.64 | -25.01 | -23.97 | N/A | -27.15 | -25.13 | -27.74 | LDL | N/A |
| 11/26/2009 | 11/27/2009 | **60** | 10:51 | 8:07 | 24 | 30823 | N/A | -28.91 | -24.74 | -25.80 | N/A | -27.70 | -27.70 | -28.41 | LDL | LDL |
| 11/27/2009 | 11/27/2009 | **133** | 8:10 | 15:27 | 24 | 10610 | N/A | -25.43 | -21.08 | -21.78 | N/A | -27.89 | -26.13 | -27.27 | -29.67 | -24.39 |
| 11/30/2009 | 12/1/2009 | **51** | 8:35 | 9:37 | 24 | 36212 | N/A | -26.37 | -22.71 | -23.98 | N/A | -26.55 | -25.72 | -24.45 | -29.95 | -27.17 |
| 12/1/2009 | 12/2/2009 | **20** | 9:40 | 9:11 | 24 | 34027 | N/A | -23.51 | -23.84 | -24.96 | N/A | -24.59 | -23.83 | -21.11 | LDL | LDL |
| 12/2/2009 | 12/3/2009 | **12** | 9:13 | 9:53 | 24 | 35702 | N/A | -26.34 | -24.96 | -25.32 | N/A | -24.48 | -24.70 | -23.54 | -25.01 | N/A |
| 12/3/2009 | 12/4/2009 | **104** | 9:57 | 8:32 | 24 | 32675 | N/A | -24.75 | -24.75 | -26.01 | LDL | -27.13 | -27.65 | -23.49 | LDL | LDL |
| 12/4/2009 | 12/7/2009 | **119** | 8:35 | 16:49 | 24 | 11942 | N/A | N/A | -22.48 | -26.02 | LDL | -26.28 | -24.58 | -25.52 | -30.31 | LDL |
| 12/7/2009 | 12/8/2009 | **137** | 16:52 | 10:36 | 24 | 141749 | N/A | -29.63 | -26.57 | -27.85 | N/A | -27.43 | -28.29 | -26.19 | LDL | LDL |
| 12/8/2009 | 12/9/2009 | **153** | 10:39 | 9:51 | 24 | 33581 | -20.21 | -26.48 | -26.03 | LDL | LDL | LDL | LDL | LDL | LDL | LDL |
| 12/9/2009 | 12/10/2009 | **154** | 9:53 | 8:33 | 24 | 32806 | N/A | -25.59 | -23.63 | -23.27 | N/A | -23.77 | -22.56 | -22.47 | LDL | LDL |
| 12/10/2009 | 12/11/2009 | **111** | 8:37 | 9:46 | 24 | 36419 | N/A | -27.06 | -23.59 | -24.76 | LDL | -22.32 | -22.12 | -24.40 | LDL | N/A |
| 12/11/2009 | 12/11/2009 | **146** | 9:48 | 16:03 | 24 | 9091 | N/A | -28.64 | -24.48 | -26.98 | LDL | LDL | LDL | LDL | LDL | LDL |
| 12/11/2009 | 11/14/2009 | **136** | 16:06 | 9:37 | 24 | 94776 | N/A | -27.41 | -23.36 | -26.29 | N/A | LDL | LDL | LDL | LDL | LDL |
| 12/14/2009 | 12/15/2009 | **149** | 9:40 | 8:54 | 24 | 33634 | N/A | -25.00 | -21.08 | -21.78 | N/A | -17.88 | -17.18 | -19.46 | -21.33 | LDL |
| 12/15/2009 | 12/16/2009 | **79** | 8:57 | 10:54 | 24 | 37570 | -24.82 | -24.52 | -22.43 | -25.30 | -31.37 | -24.81 | -25.40 | -24.98 | LDL | LDL |
| 12/16/2009 | 12/17/2009 | **100** | 10:56 | 9:50 | 24 | 33128 | N/A | -26.97 | -24.40 | -25.97 | N/A | -24.67 | -25.41 | -25.90 | LDL | LDL |

| Start Date | End Date | Crt | Start Time | End Time | Flow (mL/min) | TotVol (mL) | hexane | benzene | heptane | toluene | octane | ethyl-benzene | p,m-xylene | o-xylene | nonane | decane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12/17/2009 | 12/21/2009 | **142** | 9:54 | 8:44 | 24 | 137363 | -24.06 | -22.63 | -25.16 | -23.83 | N/A | -21.82 | -23.95 | -23.00 | LDL | -27.28 |
| 1/18/2010 | 1/19/2010 | **158** | 9:13 | 10:20 | 24 | 36385 | N/A | -22.24 | N/A | -24.55 | N/A | -22.02 | -23.37 | -22.71 | -29.29 | N/A |
| 1/19/2010 | 1/20/2010 | **113** | 10:23 | 11:13 | 24 | 35976 | -23.96 | -25.43 | -21.75 | -22.33 | N/A | -18.60 | -19.80 | -18.95 | -31.22 | N/A |
| 1/20/2010 | 1/21/2010 | **163** | 11:15 | 10:13 | 24 | 33284 | LDL | N/A | LDL | -24.22 | LDL | N/A | N/A | N/A | N/A | LDL |
| 1/21/2010 | 1/22/2010 | **165** | 10:16 | 9:10 | 24 | 33200 | LDL | -26.18 | N/A | -26.50 | N/A | -23.51 | -24.35 | -25.30 | -24.28 | LDL |
| 1/22/2010 | 1/25/2010 | **118** | 9:14 | 11:34 | 24 | 107696 | N/A | N/A | N/A | -24.04 | N/A | -23.76 | -24.33 | -22.20 | LDL | N/A |
| 1/25/2010 | 1/26/2010 | **115** | 11:40 | 11:13 | 24 | 34145 | -24.66 | -26.11 | -21.70 | -23.53 | N/A | -22.37 | -21.53 | -22.11 | LDL | LDL |
|  |  | **106** |  |  |  | travel blank | LDL | LDL | LDL | -22.72 | LDL | LDL | LDL | LDL | LDL | LDL |
|  |  | **115** |  |  |  | travel blank | LDL | LDL | LDL | -23.09 | LDL | LDL | LDL | LDL | LDL | LDL |
|  |  | **145** |  |  |  | travel blank | N/A | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL | LDL |

## C2: Isotopic composition of VOC in Toronto Samples

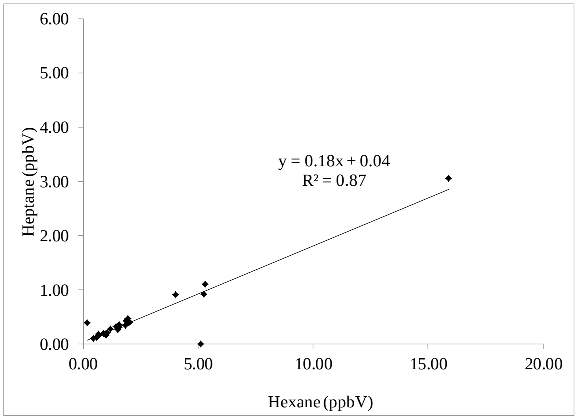
| Start Date | End Date | Crtdg | Start Time | End Time | Flow | TotVolume | hexane | benzene | heptane | toluene | octane | ethyl-benzene | p,m-xylene | o-xylene | nonane | decane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10/13/2009 | 10/14/2009 | 117 | 9:53 | 8:42 | 24 | 32912 | -21.64 | -26.01 | LDL | -20.64 | N/A | -17.92 | -18.56 | -18.27 | LDL | N/A |
| 10/19/2009 | 10/20/2009 | 100 | 8:28 | 8:57 | 24 | 34691 | -22.29 | -23.36 | N/A | -20.42 | -17.09 | -18.81 | -18.09 | -17.65 | -26.92 | N/A |
| 10/20/2009 | 10/21/2009 | 29 | 9:08 | 8:41 | 24 | 33462 | -24.24 | -25.99 | N/A | -23.33 | -14.02 | -20.50 | -20.69 | -21.78 | -21.93 | LDL |
| 10/21/2009 | 10/22/2009 | 84 | 8:56 | 8:06 | 24 | 32877 | -22.49 | -23.19 | -24.97 | -20.41 | -21.45 | -17.93 | -16.36 | -16.61 | N/A | -18.74 |
| 10/22/2009 | 10/23/2009 | 25 | 8:20 | 8:24 | 24 | 34143 | -25.20 | N/A | N/A | -21.69 | -11.26 | -17.55 | -18.08 | -16.50 | -19.76 | -28.06 |
| 10/23/2009 | 10/23/2009 | 125 | 8:34 | 14:34 | 24 | 8497 | N/A | -29.40 | LDL | -27.97 | LDL | LDL | LDL | LDL | LDL | LDL |
| 10/23/2009 | 10/26/2009 | 105 | 14:38 | 8:44 | 24 | 93522 | -24.89 | LDL | LDL | N/A | -22.08 | N/A | N/A | N/A | LDL | -26.38 |
| 10/26/2009 | 10/27/2009 | 127 | 8:54 | 8:51 | 24 | 33903 | -22.61 | -23.46 | LDL | -24.25 | -27.62 | -22.42 | -23.31 | -23.23 | LDL | -23.19 |
| 10/27/2009 | 10/28/2009 | 129 | 8:58 | 8:42 | 24 | 33680 | LDL | -24.72 | N/A | -21.07 | -24.38 | -17.68 | -18.36 | -18.19 | -17.05 | -29.85 |
| 10/28/2009 | 10/29/2009 | 118 | 8:51 | 8:50 | 24 | 33989 | N/A | -29.24 | LDL | -21.31 | -29.11 | -17.39 | -16.62 | N/A | LDL | LDL |
| 10/29/2009 | 10/30/2009 | 110 | 8:57 | 8:37 | 24 | 33562 | N/A | N/A | LDL | -23.45 | -31.88 | -18.86 | -19.39 | -18.68 | LDL | LDL |
| 10/30/2009 | 10/30/2009 | 103 | 8:42 | 14:35 | 24 | 8355 | -27.81 | -28.44 | LDL | -24.15 | LDL | -22.45 | -22.33 | N/A | LDL | N/A |
| 10/30/2009 | 11/2/2009 | 101 | 14:39 | 8:22 | 24 | 94500 | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| 11/2/2009 | 11/3/2009 | 48 | 8:29 | 8:25 | 24 | 33923 | N/A | -28.00 | -23.93 | -26.44 | -28.27 | -30.20 | -30.46 | -29.96 | N/A | -29.47 |
| 11/3/2009 | 11/4/2009 | 23 | 8:35 | 7:31 | 24 | 32475 | N/A | -27.24 | N/A | -26.08 | N/A | -31.69 | -31.58 | -29.16 | N/A | -24.48 |
| 11/4/2009 | 11/5/2009 | 120 | 7:37 | 8:32 | 24 | 35297 | N/A | -28.30 | N/A | -25.74 | N/A | -28.72 | -28.07 | -28.04 | N/A | N/A |
| 11/5/2009 | 11/6/2009 | 21 | 8:41 | 8:19 | 24 | 33480 | -28.99 | N/A | LDL | -24.23 | LDL | -25.07 | -25.23 | -25.26 | -21.86 | N/A |
| 11/6/2009 | 11/6/2009 | 114 | 8:25 | 2:34 | 24 | 8709 | N/A | -27.61 | LDL | -24.07 | -29.57 | -25.47 | -28.70 | LDL | LDL | LDL |
| 11/6/2009 | 11/7/2009 | 121 | 14:36 | 8:32 | 24 | 25432 | N/A | -28.39 | LDL | -25.63 | LDL | -32.62 | -33.04 | N/A | LDL | LDL |
| 11/7/2009 | 11/8/2009 | 18 | 8:40 | 8:43 | 24 | 34079 | N/A | -26.50 | -22.53 | -22.73 | N/A | -21.58 | -23.70 | -22.30 | -23.38 | N/A |
| 11/8/2009 | 11/9/2009 | 130 | 8:49 | 8:45 | 24 | 33837 | LDL | -22.77 | LDL | -20.41 | N/A | -22.43 | -22.55 | -21.51 | N/A | N/A |
| 11/9/2009 | 11/10/2009 | 107 | 8:51 | 8:52 | 24 | 34039 | -27.70 | -22.97 | N/A | -26.08 | N/A | -26.82 | -26.20 | LDL | LDL | LDL |
| 11/10/2009 | 11/11/2009 | 13 | 8:58 | 8:51 | 24 | 33850 | N/A | -22.46 | N/A | -26.86 | LDL | -25.06 | -25.37 | LDL | LDL | N/A |
| 11/11/2009 | 11/12/2009 | 10 | 8:57 | 8:17 | 24 | 33060 | N/A | N/A | N/A | -27.98 | N/A | -28.36 | -28.04 | LDL | LDL | N/A |
| 11/12/2009 | 11/13/2009 | 18 | 8:22 | 10:57 | 24 | 37630 | N/A | -26.50 | -22.53 | -22.73 | N/A | -21.58 | -23.70 | -22.30 | -23.38 | N/A |
| 11/13/2009 | 11/16/2009 | 14 | 11:05 | 8:33 | 24 | 98364 | -26.33 | -26.30 | -28.17 | -26.70 | LDL | -27.57 | -28.16 | N/A | LDL | N/A |
| 11/16/2009 | 11/17/2009 | 55 | 8:39 | 8:33 | 24 | 33833 | -27.84 | N/A | -24.87 | -27.80 | N/A | -28.15 | -27.86 | LDL | LDL | N/A |
| 11/17/2009 | 11/18/2009 | 126 | 8:39 | 8:56 | 24 | 34414 | N/A | -20.26 | -21.75 | -27.27 | LDL | -27.82 | N/A | LDL | LDL | N/A |
| 11/19/2009 | 11/20/2009 | 134 | 8:52 | 8:50 | 24 | 33940 | N/A | -23.27 | N/A | -27.92 | -22.06 | -21.78 | -21.81 | -21.69 | LDL | N/A |
| 11/23/2009 | 11/24/2009 | 69 | 9:14 | 8:48 | 24 | 67284 | N/A | N/A | LDL | -20.24 | LDL | -24.15 | -24.35 | -24.08 | LDL | -30.44 |
| 11/24/2009 | 11/26/2009 | 15 | 8:52 | 8:26 | 24 | 33380 | N/A | N/A | -21.52 | -24.35 | LDL | -21.66 | -21.18 | -21.05 | LDL | N/A |

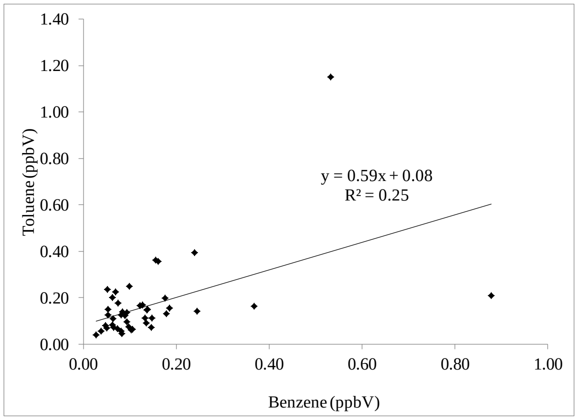
| Start Date | End Date | Crtdg | Start Time | End Time | Flow | TotVolume | hexane | benzene | heptane | toluene | octane | ethyl-benzene | p,m-xylene | o-xylene | nonane | decane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 11/26/2009 | 11/27/2009 | 81 | 8:30 | 8:52 | 24 | 102397 | -24.85 | N/A | N/A | -20.05 | -21.60 | -21.84 | -21.98 | -21.20 | -22.29 | -27.05 |
| 11/27/2009 | 11/30/2009 | 44 | 8:56 | 9:03 | 24 | 34111 | LDL | -23.66 | LDL | -24.52 | N/A | -19.51 | -19.73 | -19.68 | -21.60 | -33.84 |
| 11/30/2009 | 31/11/2009 | 124 | 9:07 | 9:45 | 24 | 34902 | -27.94 | -26.15 | N/A | -27.30 | N/A | -27.03 | -27.24 | -26.62 | -23.23 | -24.31 |
| 12/1/2009 | 12/2/2009 | 102 | 9:50 | 7:54 | 24 | 31220 | N/A | N/A | N/A | -25.68 | N/A | -28.02 | -28.42 | -22.32 | LDL | N/A |
| 12/2/2009 | 12/3/2009 | 39 | 7:58 | 7:33 | 24 | 33408 | N/A | N/A | LDL | -25.46 | N/A | -23.55 | -23.89 | -24.07 | LDL | N/A |
| 12/3/2009 | 12/4/2009 | 30 | 7:39 | 8:06 | 24 | 102585 | N/A | N/A | N/A | -25.84 | N/A | -22.39 | -22.71 | -26.86 | LDL | N/A |
| 12/4/2009 | 12/7/2009 | 8 | 8:11 | 8:01 | 24 | 33753 | N/A | -26.18 | N/A | -26.25 | N/A | -22.88 | -22.29 | -23.52 | N/A | N/A |
| 12/7/2009 | 12/8/2009 | 46 | 8:07 | 9:28 | 24 | 35910 | -25.10 | N/A | N/A | -26.17 | -31.58 | -28.41 | -28.42 | -29.08 | -24.59 | -23.45 |
| 12/8/2009 | 12/9/2009 | 59 | 9:32 | 9:39 | 24 | 34194 | LDL | N/A | -30.73 | -25.85 | LDL | N/A | N/A | -29.23 | LDL | LDL |
| 12/9/2009 | 12/10/2009 | 112 | 9:45 | 9:48 | 24 | 34060 | -25.17 | -24.98 | N/A | -18.67 | -16.55 | -20.27 | -19.15 | -20.63 | -29.16 | -19.11 |
| 12/10/2009 | 12/11/2009 | 148 | 9:53 | 9:32 | 24 | 101432 | N/A | -24.33 | N/A | -24.34 | N/A | -24.94 | -25.53 | -24.97 | LDL | -27.91 |
| 12/11/2009 | 12/14/2009 | 140 | 9:37 | 10:16 | 24 | 34949 | N/A | -25.97 | N/A | -24.47 | N/A | -24.61 | -24.97 | -24.10 | -26.08 | N/A |
| 12/14/2009 | 12/15/2009 | 24 | 10:16 | 9:11 | 24 | 32343 | N/A | N/A | N/A | -26.48 | N/A | -23.35 | -23.48 | -23.51 | N/A | N/A |
| 12/15/2009 | 12/16/2009 | 138 | 9:17 | 9:46 | 24 | 34710 | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| 12/16/2009 | 12/17/2009 | 155 | 9:52 | 8:52 | 24 | 32612 | N/A | -28.10 | N/A | -25.25 | N/A | -26.79 | -26.81 | -26.24 | N/A | -26.15 |
| 12/17/2009 | 12/18/2009 | 145 | 9:10 | 9:44 | 24 | 34821 | N/A | N/A | N/A | -26.66 | N/A | -20.62 | -19.70 | -18.65 | LDL | N/A |
| 1/18/2010 | 1/19/2010 | 166 | 9:49 | 10:05 | 24 | 34404 | -28.37 | N/A | LDL | -27.07 | LDL | -26.99 | -26.87 | -27.38 | LDL | N/A |
| 1/19/2010 | 1/20/2010 | 139 | 10:09 | 9:30 | 24 | 33091 | -23.79 | N/A | LDL | -26.81 | -20.89 | -23.26 | -23.32 | N/A | LDL | N/A |
| 1/20/2010 | 1/21/2010 | 110 | 9:35 | 10:18 | 24 | 33946 | N/A | -25.81 | N/A | -24.62 | N/A | -26.53 | -26.46 | LDL | LDL | LDL |
| 1/21/2010 | 1/25/2010 | 32 | 10:22 | 11:30 | 24 | 301564 | N/A | N/A | LDL | -27.40 | LDL | -24.06 | -24.63 | -25.06 | LDL | LDL |
| 1/22/2010 | 1/25/2010 | 85 | 11:35 | 10:59 | 24 | 33146 | -19.46 | -18.18 | -21.66 | -27.39 | N/A | -34.77 | -34.55 | N/A | LDL | N/A |
| 1/25/2010 | 1/26/2010 | 105 | 11:02 | 10:33 | 24 | 33342 | -24.89 | LDL | LDL | N/A | -22.08 | N/A | N/A | N/A | LDL | -26.38 |
| 1/26/2010 | 1/27/2010 | 109 | 9:02 | 9:05 | 24 | 34270 | -28.26 | -28.96 | -26.96 | -27.54 | N/A | -28.90 | -27.95 | -28.05 | LDL | N/A |
| 3/6/2010 | 3/7/2010 | 103 | 9:07 | 8:40 | 24 | 32440 | N/A | N/A | N/A | -27.16 | N/A | -23.36 | -23.83 | -26.09 | LDL | N/A |
| 3/7/2010 | 3/8/2010 | 104 | 8:25 | 8:55 | 24 | 34817 | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| 3/12/2010 | 3/13/2010 | 114 | 8:58 | 8:30 | 24 | 33338 | -27.30 | -22.33 | LDL | -28.52 | LDL | LDL | LDL | LDL | LDL | N/A |
| 3/13/2010 | 3/14/2010 | 101 | 8:30 | 9:05 | 24 | 34821 | -18.98 | -13.63 | N/A | -26.94 | -17.09 | -19.50 | -19.57 | -20.60 | LDL | N/A |
| 3/14/2010 | 3/15/2010 | 113 | 9:08 | 9:03 | 24 | 33888 | N/A | -26.85 | LDL | -24.74 | LDL | LDL | N/A | -23.28 | LDL | N/A |
| 3/15/2010 | 3/16/2010 | 42 | 8:58 | 9:08 | 24 | 34263 | N/A | -25.00 | LDL | -23.02 | N/A | -19.91 | -19.20 | -21.65 | LDL | N/A |
| 3/19/2010 | 3/20/2010 | 152 | 9:09 | 9:00 | 24 | 33753 | N/A | -26.79 | LDL | -27.04 | LDL | LDL | N/A | LDL | LDL | N/A |
| 3/20/2010 | 3/21/2010 | 112 | 9:00 | 9:00 | 24 | 33963 | -21.75 | N/A | N/A | -27.13 | -28.44 | -21.77 | -21.64 | -21.44 | -26.96 | N/A |
| 3/21/2010 | 3/22/2010 | 168 | 9:03 | 9:05 | 24 | 34049 | -27.02 | -16.64 | LDL | -24.37 | LDL | LDL | LDL | LDL | LDL | N/A |
| 3/22/2010 | 3/23/2010 | 159 | 9:16 | 9:10 | 24 | 33796 | N/A | N/A | N/A | -26.86 | LDL | LDL | LDL | LDL | LDL | N/A |

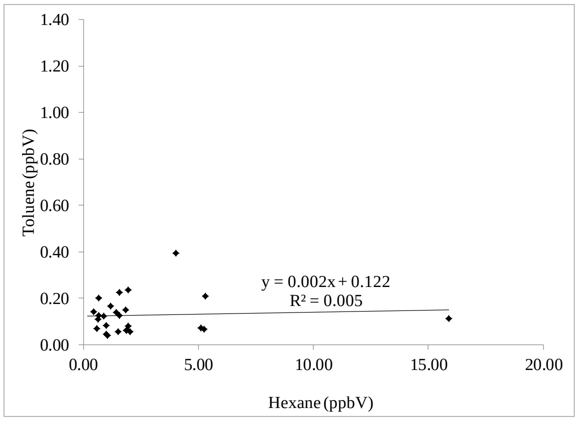
| Start Date | End Date | Crtdg | Start Time | End Time | Flow | TotVolume | hexane | benzene | heptane | toluene | octane | ethyl-benzene | p,m-xylene | o-xylene | nonane | decane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 8/30/2010 | 8/31/2010 | 111 | 9:13 | 8:47 | 24 | 33361 | N/A | -25.40 | -25.35 | -25.52 | N/A | -23.54 | -23.86 | LDL | LDL | N/A |
| 8/31/2010 | 9/1/2010 | 68 | 9:20 | 8:46 | 18 | 23839 | N/A | N/A | N/A | -23.69 | N/A | -21.25 | -20.90 | N/A | N/A | N/A |
| 9/7/2010 | 9/8/2010 | 113 | 8:49 | 9:20 | 19 | 83179 | N/A | -26.85 | LDL | -24.74 | LDL | LDL | N/A | -23.28 | LDL | N/A |
| 9/8/2010 | 9/9/2010 | 103 | 10:10 | 8:47 | 40 | 28181 | N/A | N/A | N/A | -27.16 | N/A | -23.36 | -23.83 | -26.09 | LDL | N/A |
| 9/9/2010 | 9/10/2010 | 109 | 8:50 | 8:44 | 40 | 30767 | N/A | LDL | LDL | -24.91 | LDL | LDL | LDL | LDL | LDL | N/A |
| 9/9/2010 | 9/10/2010 | 123 | 8:50 | 8:44 | 40 | 29129 | LDL | LDL | LDL | -26.31 | LDL | LDL | LDL | LDL | LDL | N/A |
| 9/10/2010 | 9/13/2010 | 115 | 8:53 | 14:25 | 40 | 42973 | N/A | -26.00 | N/A | -23.33 | N/A | -24.60 | N/A | -23.51 | LDL | N/A |
| 9/10/2010 | 9/13/2010 | 41 | 8:53 | 14:25 | 40 | 29760 | N/A | N/A | N/A | -27.31 | N/A | N/A | N/A | N/A | N/A | N/A |
| 9/13/2010 | 9/14/2010 | 11 | 10:10 | 8:47 | 40 | 28181 | N/A | LDL | LDL | -28.22 | LDL | -27.15 | -26.28 | LDL | LDL | N/A |
| 9/13/2010 | 9/14/2010 | 131 | 10:10 | 8:47 | 40 | 29044 | N/A | LDL | LDL | -27.32 | N/A | LDL | LDL | LDL | LDL | N/A |
| 9/14/2010 | 9/15/2010 | 36 | 8:50 | 8:44 | 40 | 30767 | N/A | -26.40 | -27.41 | -25.91 | N/A | LDL | N/A | LDL | LDL | N/A |
| 9/14/2010 | 9/15/2010 | 77 | 8:50 | 8:44 | 40 | 29129 | N/A | LDL | LDL | -7.73 | N/A | LDL | LDL | LDL | LDL | N/A |
| 9/16/2010 | 9/17/2010 | 22 | 8:53 | 14:25 | 40 | 42973 | N/A | N/A | LDL | -27.20 | LDL | LDL | N/A | LDL | LDL | N/A |
| 9/16/2010 | 9/17/2010 | 54 | 8:53 | 14:25 | 40 | 29760 | LDL | -18.90 | LDL | -16.81 | N/A | LDL | LDL | LDL | LDL | N/A |
| 9/17/2010 | 9/20/2010 | 144 | 14:25 | 9:10 | 40 | 45102 | N/A | -28.05 | N/A | N/A | N/A | -28.25 | -27.69 | LDL | LDL | N/A |

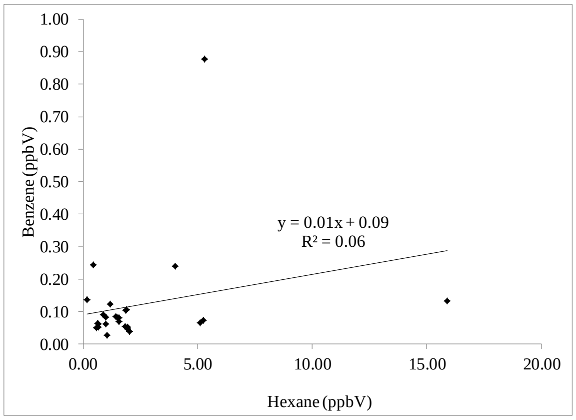
# APPENDIX D: Correlation of concentrations

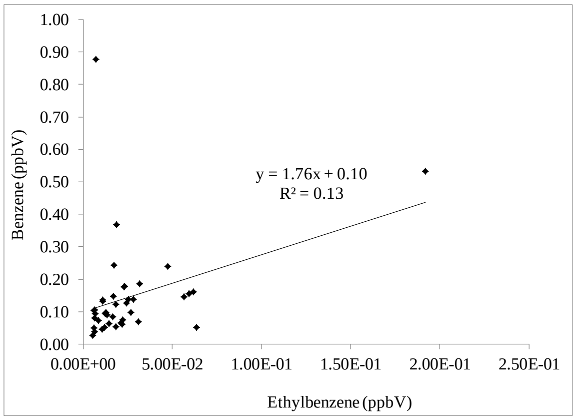
## D1: Egbert Samples

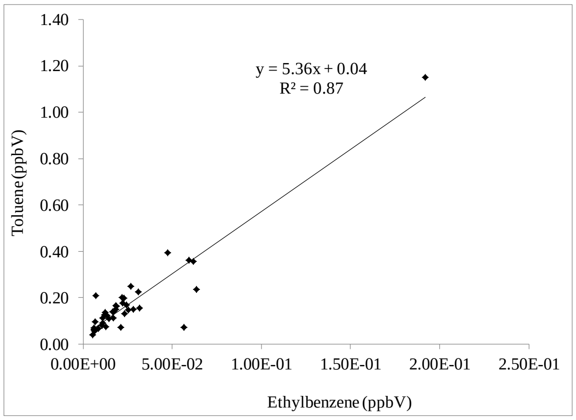


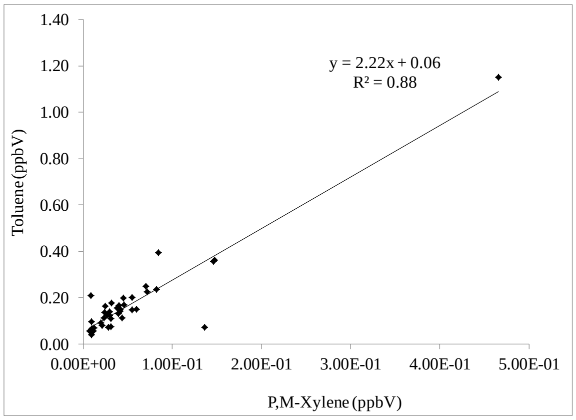




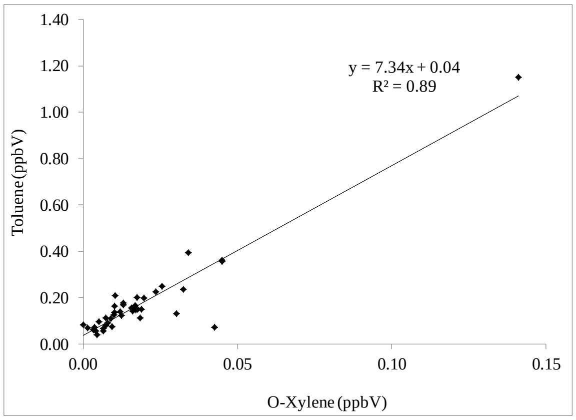






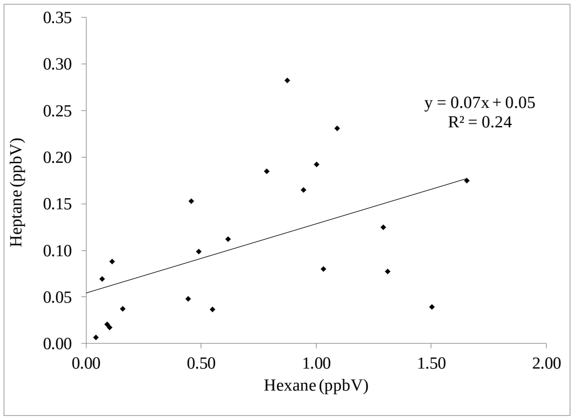


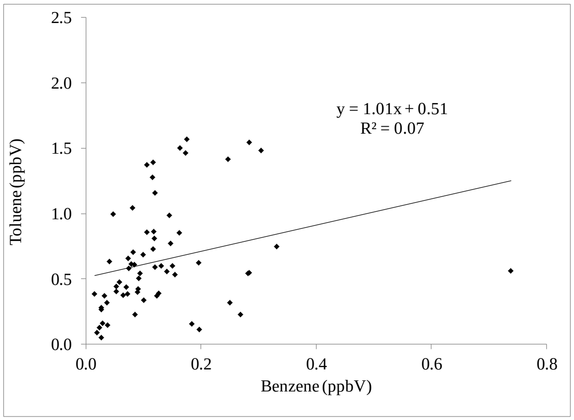
y = 2.22x + 0.06
R² = 0.88
Toluene (ppbV)
P,M-Xylene (ppbV)
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0.00E+00
1.00E-01
2.00E-01
3.00E-01
4.00E-01
5.00E-01

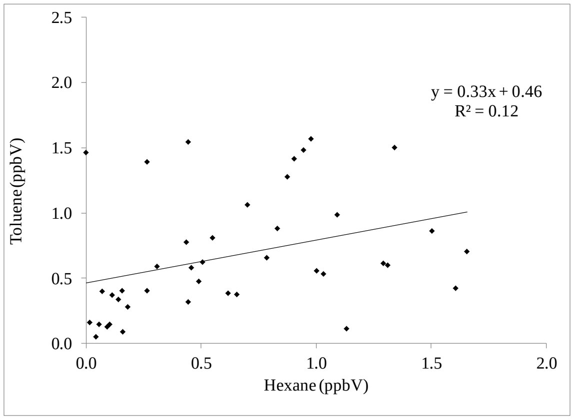


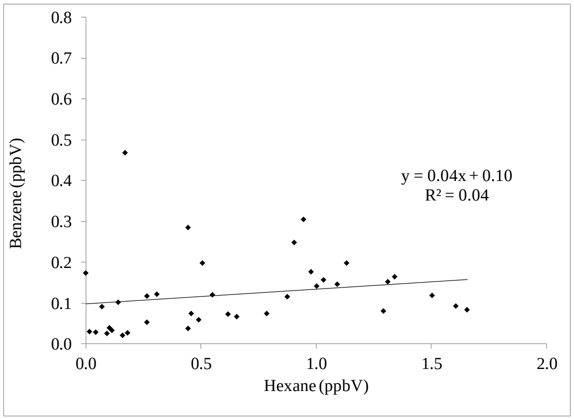
y = 7.34x + 0.04
R² = 0.89
Toluene (ppbV)
O-Xylene (ppbV)
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0.00
0.05
0.10
0.15

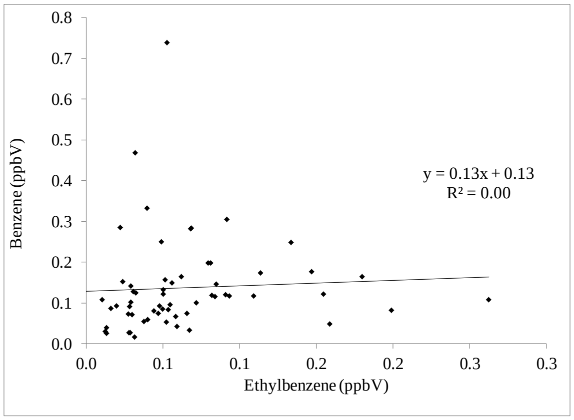
# D2: Toronto Samples

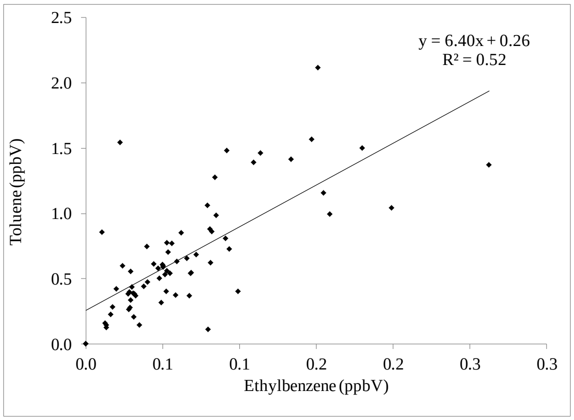


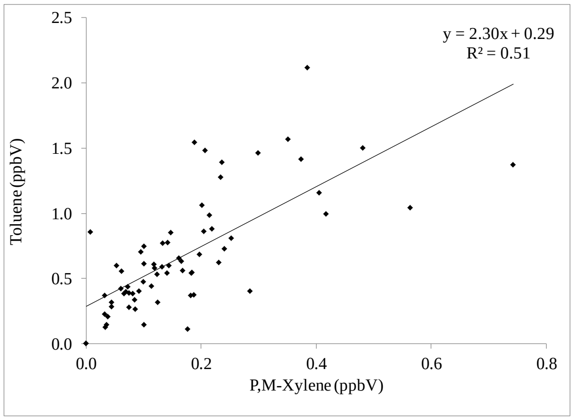


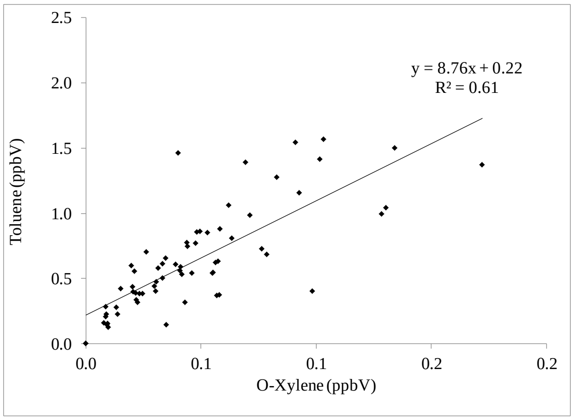






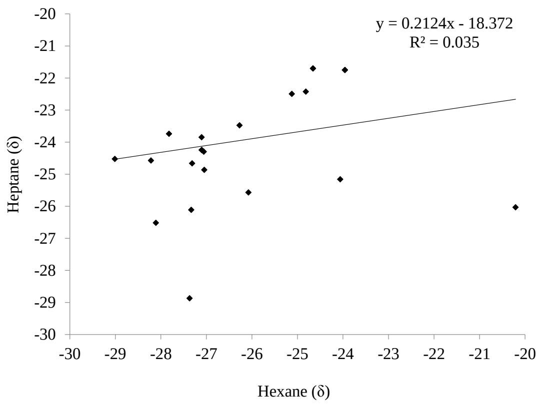


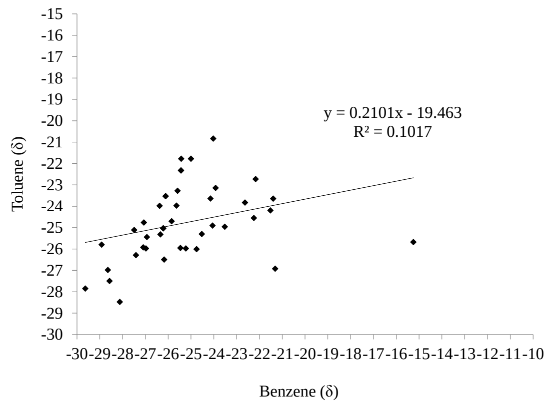

y = 2.30x + 0.29
R² = 0.51
Toluene (ppbV)
P,M-Xylene (ppbV)
0.0
0.5
1.0
1.5
2.0
2.5
0.0
0.2
0.4
0.6
0.8

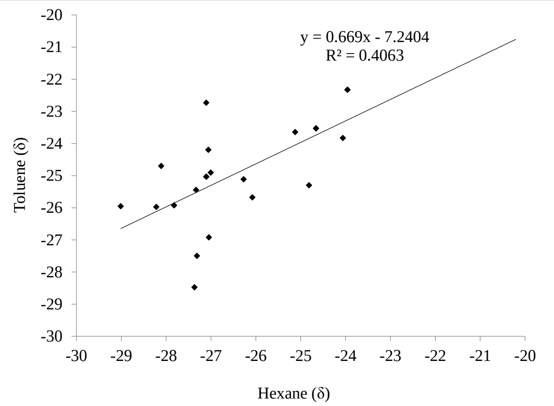

y = 8.76x + 0.22
R² = 0.61
Toluene (ppbV)
O-Xylene (ppbV)
0.0
0.5
1.0
1.5
2.0
2.5
0.0
0.1
0.1
0.2
0.2

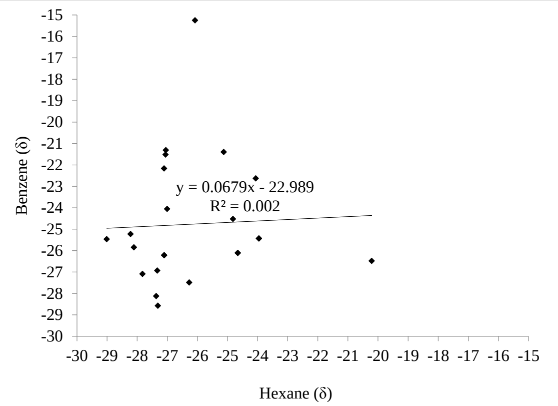
# Appendix E: Correlation of stable carbon isotope composition

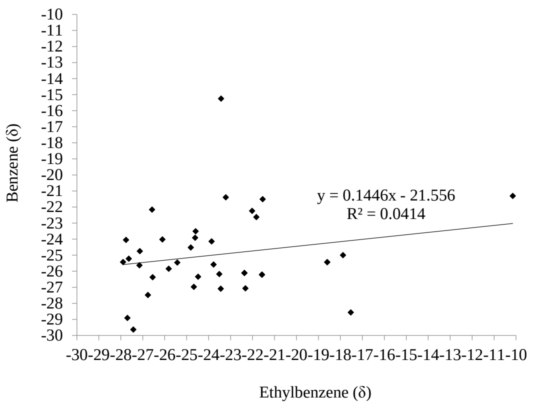
## E1: Egbert Samples

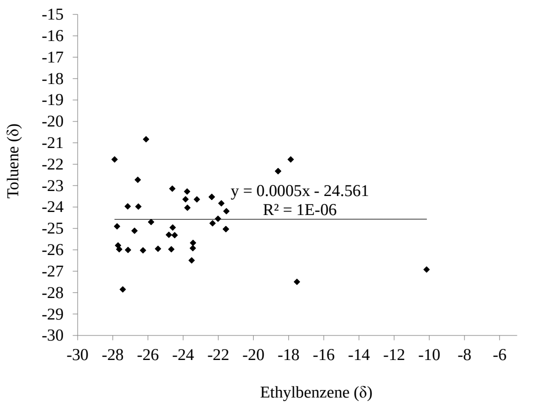


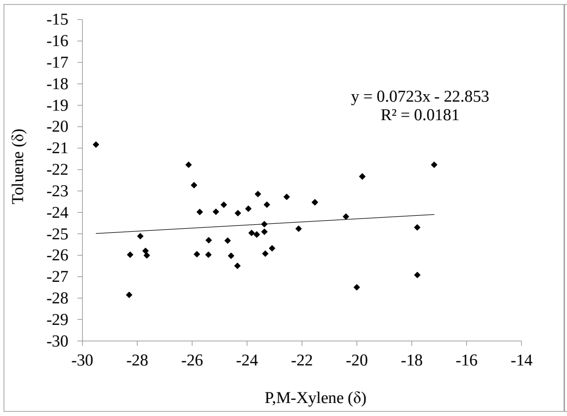


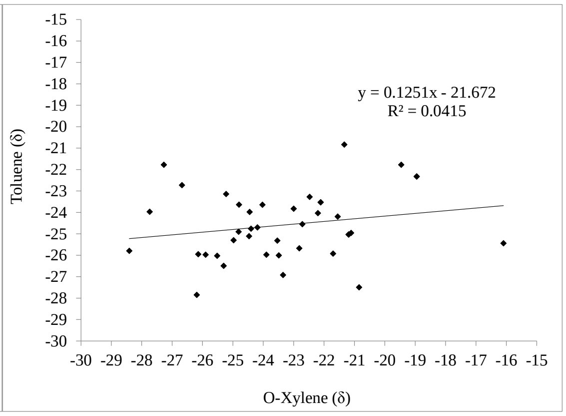




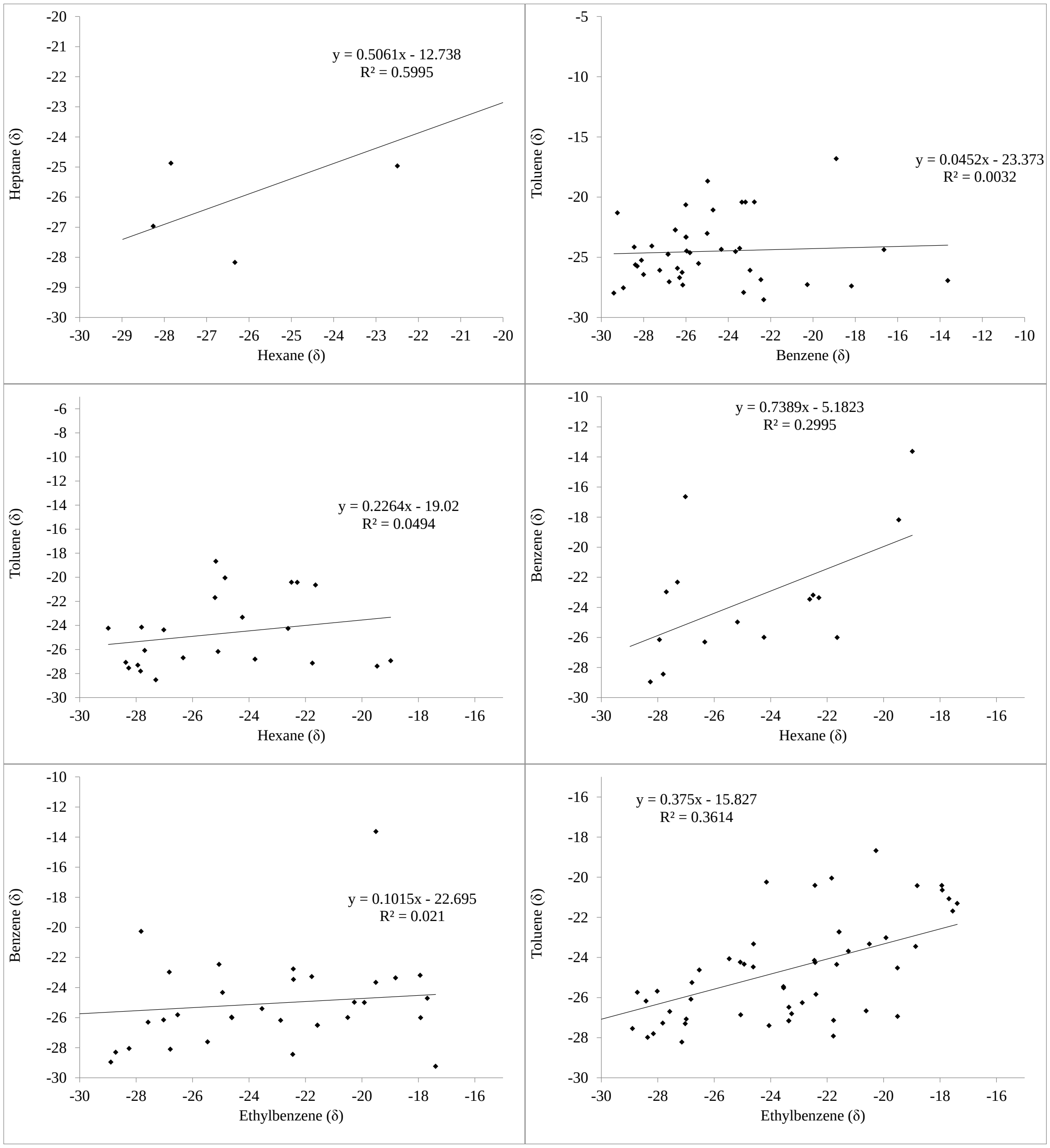


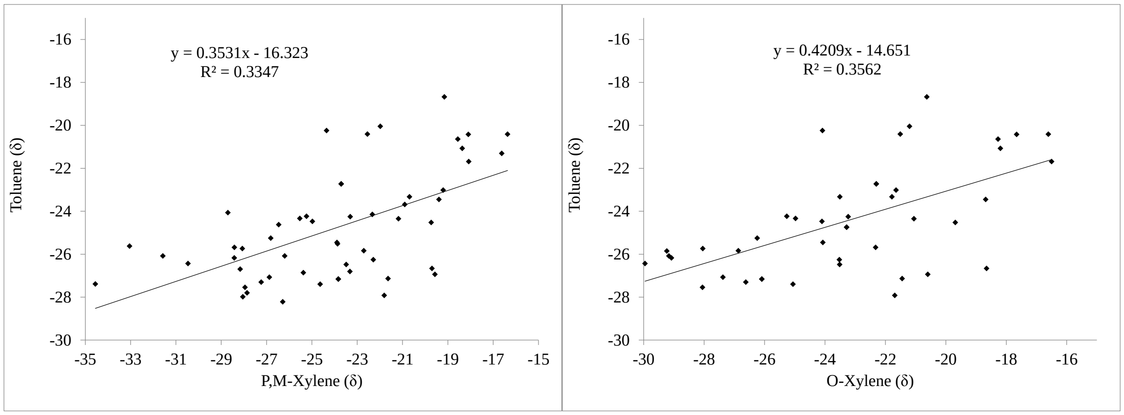



y = 0.0723x - 22.853
R² = 0.0181
Toluene (δ)
P,M-Xylene (δ)
-15
-16
-17
-18
-19
-20
-21
-22
-23
-24
-25
-26
-27
-28
-29
-30
-30
-28
-26
-24
-22
-20
-18
-16
-14


y = 0.1251x - 21.672
R² = 0.0415
Toluene (δ)
O-Xylene (δ)
-15
-16
-17
-18
-19
-20
-21
-22
-23
-24
-25
-26
-27
-28
-29
-30
-30
-29
-28
-27
-26
-25
-24
-23
-22
-21
-20
-19
-18
-17
-16
-15

## E2: Toronto Samples




y = 0.3531x - 16.323
R² = 0.3347
Toluene (δ)
P,M-Xylene (δ)
-16
-18
-20
-22
-24
-26
-28
-30
-35
-33
-31
-29
-27
-25
-23
-21
-19
-17
-15
y = 0.4209x - 14.651
R² = 0.3562
Toluene (δ)
O-Xylene (δ)
-16
-18
-20
-22
-24
-26
-28
-30
-30
-28
-26
-24
-22
-20
-18
-16

# APPENDIX F: Photochemical ages and dilution factors determined using VOC-$k_{OH}$ correlation.

## F1.1: Harrow samples

| Date and Time | $t[OH]\cdot 10^{-11}$ [a] s molecules $cm^{-3}$ | $s_{t[OH]}$ [b] s molecules $cm^{-3}$ | D [c] | $s_D$ [d] | $R^2$ [e] |
|---|---|---|---|---|---|
| 6/20/2007 13:57 | 1.21 | 0.47 | 0.29 | 0.20 | 0.42 |
| 6/20/2007 17:19 | 2.80 | 0.69 | 0.25 | 0.29 | 0.65 |
| 6/21/2007 10:09 | 1.41 | 0.42 | 0.58 | 0.18 | 0.56 |
| 6/21/2007 12:48 | 3.01 | 0.35 | 0.35 | 0.15 | 0.89 |
| 6/21/2007 17:39 | 1.69 | 0.27 | 0.27 | 0.15 | 0.80 |
| 6/22/2007 9:19 | 1.81 | 0.64 | 0.55 | 0.36 | 0.42 |
| 6/22/2007 12:24 | 1.38 | 0.43 | 0.37 | 0.25 | 0.51 |
| 6/23/2007 9:57 | 0.87 | 0.23 | 0.21 | 0.13 | 0.59 |
| 6/23/2007 12:43 | 2.51 | 0.37 | 0.22 | 0.21 | 0.72 |
| 6/23/2007 18:20 | 0.10 | 0.18 | 0.28 | 0.10 | 0.03 |
| 6/24/2007 10:02 | 2.07 | 0.33 | 0.71 | 0.14 | 0.81 |
| 6/24/2007 13:45 | 1.69 | 0.32 | 0.55 | 0.18 | 0.73 |
| 6/24/2007 19:34 | 2.00 | 0.32 | 0.50 | 0.18 | 0.80 |
| 6/25/2007 9:00 | 0.31 | 0.18 | 0.92 | 0.10 | 0.23 |
| 6/25/2007 13:36 | 2.84 | 0.47 | 0.73 | 0.20 | 0.80 |
| 6/25/2007 17:55 | 2.45 | 0.37 | 0.44 | 0.16 | 0.83 |
| 6/26/2007 8:52 | 0.47 | 0.30 | 0.97 | 0.20 | 0.20 |
| 6/26/2007 14:17 | 2.50 | 0.44 | 0.47 | 0.19 | 0.78 |
| 6/26/2007 21:08 | 1.40 | 0.34 | 0.32 | 0.14 | 0.66 |
| 6/27/2007 8:48 | 0.64 | 0.51 | 1.00 | 0.29 | 0.14 |
| 6/27/2007 14:43 | 1.41 | 0.27 | 0.50 | 0.19 | 0.73 |
| 6/27/2007 17:39 | 0.35 | 0.31 | 0.36 | 0.17 | 0.11 |
| 6/28/2007 9:10 | 0.35 | 0.29 | 0.34 | 0.16 | 0.13 |
| 6/28/2007 14:30 | 1.54 | 0.62 | 0.36 | 0.27 | 0.41 |
| 6/28/2007 18:30 | 1.26 | 0.66 | 1.00 | 0.37 | 0.27 |
| 7/3/2007 8:44 | 0.88 | 0.27 | 0.63 | 0.15 | 0.51 |
| 7/3/2007 14:07 | 0.57 | 0.47 | 0.18 | 0.27 | 0.13 |
| 7/3/2007 18:51 | 1.32 | 0.50 | 0.18 | 0.28 | 0.41 |
| 7/4/2007 9:08 | 1.39 | 0.22 | 0.52 | 0.09 | 0.82 |
| 7/4/2007 13:50 | 2.36 | 0.22 | 0.38 | 0.12 | 0.92 |
| 7/4/2007 17:30 | 1.68 | 0.20 | 0.34 | 0.12 | 0.87 |

| Date and Time | $t[OH] \cdot 10^{-11}$ [a] s molecules $cm^{-3}$ | $s_{t[OH]}$ [b] s molecules $cm^{-3}$ | D [c] | $s_D$ [d] | $R^2$ [e] |
|---|---|---|---|---|---|
| 7/5/2007 8:48 | 0.52 | 0.22 | 0.76 | 0.13 | 0.35 |
| 7/5/2007 13:43 | 1.45 | 0.20 | 0.53 | 0.12 | 0.83 |
| 7/5/2007 18:58 | -0.25 | 0.31 | 0.17 | 0.17 | 0.06 |

## F1.2: Ridgetown samples

| Date and Time | $t[OH]\cdot10^{-11}$ s molecules $cm^{-3}$ | $S_{t[OH]}$ s molecules $cm^{-3}$ | D | $S_D$ | $R^2$ |
|---|---|---|---|---|---|
| 6/18/2007 20:05 | 1.55 | 0.30 | 0.42 | 0.17 | 0.73 |
| 6/19/2007 9:25 | 0.58 | 0.38 | 0.37 | 0.22 | 0.19 |
| 6/19/2007 14:15 | 1.69 | 0.27 | 0.23 | 0.12 | 0.81 |
| 6/19/2007 18:05 | 1.24 | 0.35 | 0.32 | 0.20 | 0.55 |
| 6/19/2007 21:09 | 0.26 | 0.09 | 0.22 | 0.06 | 0.46 |
| 6/19/2007 23:45 | 1.38 | 0.32 | 0.22 | 0.14 | 0.68 |
| 6/20/2007 8:45 | 0.30 | 0.92 | 0.81 | 0.39 | 0.01 |
| 6/20/2007 11:21 | 1.25 | 0.44 | 0.26 | 0.25 | 0.45 |
| 6/20/2007 13:52 | 2.02 | 0.36 | 0.50 | 0.20 | 0.76 |
| 6/20/2007 21:21 | -0.79 | 0.25 | 0.27 | 0.18 | 0.16 |
| 6/21/2007 8:20 | 0.97 | 0.20 | 0.77 | 0.11 | 0.70 |
| 6/21/2007 11:52 | 1.50 | 0.39 | 0.34 | 0.17 | 0.61 |
| 6/21/2007 14:37 | 0.26 | 0.44 | 0.49 | 0.19 | 0.04 |
| 6/21/2007 20:50 | 1.75 | 0.60 | 0.15 | 0.37 | 0.47 |
| 6/22/2007 8:20 | -0.25 | 0.35 | 0.21 | 0.22 | 0.06 |
| 6/22/2007 10:45 | 2.36 | 0.99 | 0.16 | 0.42 | 0.39 |
| 6/22/2007 13:35 | 0.52 | 1.10 | 0.06 | 0.47 | 0.02 |
| 6/22/2007 16:00 | 1.51 | 0.77 | 0.31 | 0.58 | 0.26 |
| 6/23/2007 8:16 | 0.90 | 0.45 | 0.12 | 0.28 | 0.11 |
| 6/23/2007 11:09 | -0.13 | 1.36 | 0.08 | 0.58 | 0.00 |
| 6/23/2007 13:52 | 1.24 | 0.67 | 0.13 | 0.29 | 0.27 |
| 6/23/2007 16:15 | 1.45 | 0.42 | 0.13 | 0.24 | 0.54 |
| 6/24/2007 8:09 | 0.80 | 0.45 | 0.32 | 0.19 | 0.26 |
| 6/24/2007 13:10 | 1.77 | 0.17 | 0.31 | 0.10 | 0.91 |
| 6/24/2007 16:04 | 1.94 | 0.46 | 0.54 | 0.20 | 0.66 |
| 6/24/2007 21:39 | 1.47 | 0.26 | 0.46 | 0.15 | 0.77 |
| 6/25/2007 8:16 | 0.66 | 0.31 | 0.93 | 0.13 | 0.33 |
| 6/25/2007 11:02 | 1.29 | 0.35 | 0.56 | 0.28 | 0.62 |
| 6/25/2007 14:18 | 1.44 | 0.85 | 0.45 | 0.47 | 0.22 |
| 6/25/2007 17:02 | 1.97 | 0.26 | 0.44 | 0.11 | 0.87 |
| 6/25/2007 21:07 | 2.25 | 0.43 | 0.53 | 0.18 | 0.76 |
| 6/26/2007 8:39 | 0.64 | 0.26 | 1.04 | 0.15 | 0.37 |
| 6/26/2007 11:10 | 1.61 | 0.45 | 0.54 | 0.26 | 0.56 |
| 6/26/2007 15:10 | 1.88 | 0.43 | 0.31 | 0.18 | 0.68 |
| 6/27/2007 8:26 | 1.19 | 0.16 | 0.62 | 0.09 | 0.85 |

| Date and Time | $t[OH]\cdot10^{-11}$ s molecules cm$^{-3}$ | $S_{t[OH]}$ s molecules cm$^{-3}$ | D | $S_D$ | $R^2$ |
|---|---|---|---|---|---|
| 6/27/2007 10:55 | 1.64 | 0.20 | 0.40 | 0.11 | 0.75 |
| 6/27/2007 16:00 | 1.10 | 0.26 | 0.25 | 0.15 | 0.64 |
| 6/28/2007 8:13 | -0.35 | 0.27 | 0.19 | 0.15 | 0.14 |
| 6/28/2007 12:54 | 1.23 | 0.61 | 0.15 | 0.35 | 0.29 |
| 6/28/2007 16:36 | 2.35 | 0.76 | 0.27 | 0.42 | 0.57 |
| 6/29/2007 8:00 | 1.12 | 0.92 | 0.13 | 0.39 | 0.14 |
| 6/29/2007 11:40 | 0.96 | 0.80 | 0.12 | 0.34 | 0.14 |
| 6/29/2007 16:08 | 0.73 | 0.81 | 0.12 | 0.35 | 0.08 |
| 6/29/2007 21:11 | 0.92 | 0.94 | 0.12 | 0.40 | 0.10 |
| 6/30/2007 8:10 | 0.45 | 0.21 | 0.22 | 0.12 | 0.31 |
| 6/30/2007 17:40 | 0.53 | 0.87 | 0.04 | 0.49 | 0.04 |
| 6/30/2007 19:35 | 0.70 | 0.82 | 0.04 | 0.51 | 0.07 |
| 6/30/2007 22:00 | 0.05 | 0.29 | 0.14 | 0.23 | 0.00 |
| 7/1/2007 8:14 | 1.33 | 0.26 | 0.09 | 0.26 | 0.09 |
| 7/1/2007 16:30 | 1.09 | 1.32 | 0.04 | 0.57 | 0.07 |
| 7/1/2007 21:10 | 1.29 | 0.33 | 0.04 | 0.28 | 0.31 |
| 7/2/2007 8:07 | 0.86 | 0.70 | 0.17 | 0.39 | 0.13 |
| 7/2/2007 11:30 | 1.34 | 1.25 | 0.07 | 0.53 | 0.11 |
| 7/2/2007 14:56 | 1.40 | 0.27 | 0.05 | 0.26 | 0.40 |
| 7/2/2007 17:05 | 1.64 | 1.14 | 0.05 | 1.65 | 0.16 |
| 7/3/2007 8:14 | 1.33 | 0.28 | 0.08 | 0.27 | 0.35 |
| 7/3/2007 10:55 | 2.10 | 1.13 | 0.17 | 0.48 | 0.28 |
| 7/3/2007 15:15 | 1.41 | 0.81 | 0.11 | 1.17 | 0.22 |
| 7/3/2007 17:49 | 2.58 | 1.06 | 0.24 | 1.53 | 0.30 |
| 7/3/2007 21:15 | 0.90 | 0.81 | 0.19 | 0.46 | 0.11 |
| 7/4/2007 8:25 | 1.16 | 0.30 | 0.57 | 0.17 | 0.60 |
| 7/4/2007 11:04 | 1.35 | 0.28 | 0.45 | 0.16 | 0.70 |
| 7/4/2007 16:15 | 1.84 | 0.20 | 0.56 | 0.11 | 0.90 |
| 7/5/2007 7:58 | 0.98 | 0.20 | 0.62 | 0.11 | 0.70 |
| 7/5/2007 12:00 | 0.98 | 0.24 | 0.56 | 0.17 | 0.82 |
| 7/5/2007 15:40 | 1.83 | 0.55 | 0.28 | 0.24 | 0.55 |
| 7/5/2007 18:05 | 1.35 | 0.43 | 0.51 | 0.18 | 0.52 |
| 7/6/2007 8:15 | 0.59 | 0.99 | 1.16 | 0.42 | 0.04 |
| 7/6/2007 12:25 | 1.76 | 0.55 | 0.31 | 0.24 | 0.53 |
| 7/6/2007 15:49 | 1.19 | 0.36 | 0.35 | 0.20 | 0.52 |
| 7/6/2007 19:05 | 3.12 | 1.07 | 0.25 | 0.46 | 0.48 |

| Date and Time | $t[OH]\cdot 10^{-11}$ s molecules cm$^{-3}$ | $S_{t[OH]}$ s molecules cm$^{-3}$ | D | $S_D$ | $R^2$ |
|---|---|---|---|---|---|
| 7/7/2007 7:55 | 0.67 | 0.21 | 0.48 | 0.12 | 0.49 |
| 7/7/2007 11:25 | 1.41 | 0.47 | 0.47 | 0.26 | 0.42 |
| 7/7/2007 15:34 | 2.32 | 1.82 | 0.50 | 0.78 | 0.15 |
| 7/7/2007 18:05 | 0.94 | 1.15 | 0.25 | 0.49 | 0.07 |
| 7/7/2007 21:00 | 0.44 | 0.85 | 0.25 | 0.36 | 0.03 |
| 7/8/2007 8:14 | 1.21 | 0.44 | 0.37 | 0.19 | 0.46 |
| 7/8/2007 12:45 | 0.98 | 0.13 | 0.45 | 0.08 | 0.84 |
| 7/8/2007 15:30 | 1.02 | 0.19 | 0.36 | 0.11 | 0.75 |
| 7/8/2007 18:05 | 0.71 | 0.37 | 0.24 | 0.16 | 0.29 |
| 7/8/2007 21:15 | 0.34 | 0.53 | 0.15 | 0.23 | 0.04 |
| 7/8/2007 23:30 | 0.45 | 0.28 | 0.18 | 0.16 | 0.21 |
| 7/9/2007 8:05 | 1.00 | 0.24 | 0.39 | 0.13 | 0.64 |
| 7/9/2007 10:30 | 0.34 | 0.37 | 0.24 | 0.16 | 0.09 |
| 7/9/2007 16:03 | 0.81 | 0.40 | 0.28 | 0.17 | 0.31 |
| 7/9/2007 23:50 | 0.86 | 0.48 | 0.30 | 0.21 | 0.26 |
| 7/10/2007 8:07 | 0.50 | 0.57 | 0.67 | 0.24 | 0.08 |
| 7/10/2007 11:10 | 0.90 | 0.18 | 0.45 | 0.10 | 0.71 |

## F1.3: Egbert

| Start Date | End Date | Crtdg | $t[OH]\cdot10^{-11}$ s molecules $cm^{-3}$ | $s_{t[OH]}$ s molecules $cm^{-3}$ | D | $s_D$ | $R^2$ |
|---|---|---|---|---|---|---|---|
| 10/19/2009 | 10/20/2009 | 49 | 0.35 | 0.21 | 0.05 | 0.23 | 0.48 |
| 10/22/2009 | 10/23/2009 | 128 | 0.47 | 0.24 | 0.04 | 0.26 | 0.57 |
| 10/23/2009 | 10/24/2009 | 132 | 2.07 | 0.83 | 0.44 | 0.92 | 0.68 |
| 10/23/2009 | 10/26/2009 | 108 | 0.96 | 0.45 | 0.05 | 0.48 | 0.53 |
| 10/26/2009 | 10/26/2009 | 106 | 0.06 | 0.10 | 0.07 | 0.11 | 0.09 |
| 10/30/2009 | 10/30/2009 | 54 | 1.06 | 1.06 | 0.72 | 1.33 | 0.33 |
| 11/4/2009 | 11/5/2009 | 16 | 0.90 | 1.78 | 0.27 | 1.73 | 0.04 |
| 11/5/2009 | 11/6/2009 | 11 | 0.44 | 0.23 | 0.03 | 0.26 | 0.54 |
| 11/6/2009 | 11/6/2009 | 116 | 0.58 | 0.49 | 0.07 | 0.52 | 0.27 |
| 11/6/2009 | 11/7/2009 | 133 | 0.45 | 0.26 | 0.11 | 0.28 | 0.51 |
| 11/7/2009 | 11/8/2009 | 123 | 0.47 | 0.19 | 0.09 | 0.21 | 0.67 |
| 11/9/2009 | 11/10/2009 | 22 | 0.34 | 2.37 | 0.26 | 1.80 | 0.01 |
| 11/10/2009 | 11/12/2009 | 36 | 0.94 | 1.05 | 0.30 | 1.04 | 0.12 |
| 11/13/2009 | 11/13/2009 | 123 | 0.47 | 0.19 | 0.25 | 0.21 | 0.67 |
| 11/13/2009 | 11/16/2009 | 27 | 0.31 | 0.09 | 0.06 | 0.10 | 0.74 |
| 11/16/2009 | 11/17/2009 | 115 | 1.17 | 0.46 | 0.08 | 0.51 | 0.69 |
| 11/17/2009 | 11/18/2009 | 109 | 0.25 | 1.20 | 0.51 | 1.22 | 0.01 |
| 11/18/2009 | 11/19/2009 | 113 | 0.48 | 0.41 | 0.14 | 0.44 | 0.25 |
| 11/19/2009 | 11/20/2009 | 47 | 0.06 | 0.08 | 0.08 | 0.08 | 0.17 |
| 11/20/2009 | 11/21/2009 | 122 | 1.11 | 0.31 | 0.08 | 0.35 | 0.81 |
| 11/23/2009 | 11/25/2009 | 33 | 0.62 | 0.23 | 0.09 | 0.26 | 0.70 |
| 11/26/2009 | 11/27/2009 | 60 | 0.30 | 0.31 | 0.11 | 0.33 | 0.18 |
| 12/1/2009 | 12/2/2009 | 20 | 0.49 | 0.26 | 0.12 | 0.28 | 0.47 |
| 12/2/2009 | 12/3/2009 | 12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.21 |
| 12/3/2009 | 12/4/2009 | 104 | 0.84 | 0.44 | 0.10 | 0.49 | 0.55 |
| 12/4/2009 | 12/7/2009 | 119 | 0.58 | 0.31 | 0.16 | 0.42 | 0.54 |
| 12/7/2009 | 12/8/2009 | 137 | 0.40 | 0.40 | 0.07 | 0.42 | 0.21 |
| 12/9/2009 | 12/10/2009 | 154 | 0.34 | 0.46 | 0.09 | 0.49 | 0.12 |
| 12/10/2009 | 12/11/2009 | 111 | 0.80 | 1.51 | 0.12 | 2.23 | 0.08 |
| 12/11/2009 | 12/11/2009 | 146 | 0.83 | 0.37 | 0.11 | 0.40 | 0.55 |
| 12/14/2009 | 12/15/2009 | 149 | 0.06 | 0.91 | 0.36 | 0.93 | 0.00 |
| 12/15/2009 | 12/16/2009 | 79 | 1.15 | 0.33 | 0.07 | 0.35 | 0.75 |
| 12/16/2009 | 12/17/2009 | 100 | 0.34 | 0.33 | 0.11 | 0.35 | 0.21 |
| 12/17/2009 | 12/21/2009 | 142 | 0.68 | 0.45 | 0.15 | 0.48 | 0.37 |

| Start Date | End Date | Crtdg | $t[OH]\cdot 10^{-11}$ s molecules $cm^{-3}$ | $s_{t[OH]}$ s molecules $cm^{-3}$ | D | $s_D$ | $R^2$ |
|---|---|---|---|---|---|---|---|
| 1/18/2010 | 1/19/2010 | 158 | 0.72 | 0.33 | 0.17 | 0.35 | 0.55 |
| 1/19/2010 | 1/20/2010 | 113 | 0.45 | 0.31 | 0.08 | 0.47 | 0.51 |
| 1/21/2010 | 1/22/2010 | 165 | 1.27 | 0.52 | 0.25 | 0.57 | 0.67 |
| 1/22/2010 | 1/25/2010 | 118 | 0.45 | 0.12 | 0.10 | 0.14 | 0.82 |
| 1/25/2010 | 1/26/2010 | 115 | 2.17 | 1.60 | 0.62 | 1.59 | 0.27 |

## F1.4: Toronto

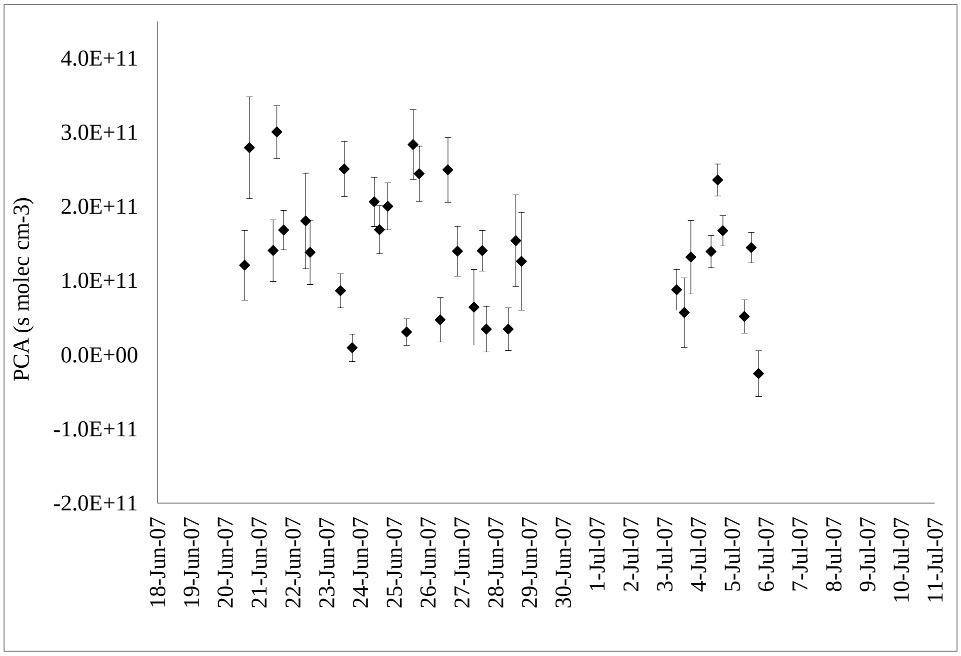
| Start Date | End Date | Crtdg | t[OH]·$10^{-11}$ s molecules $cm^{-3}$ | $s_{t[OH]}$ s molecules $cm^{-3}$ | D | $s_D$ | $R^2$ |
|---|---|---|---|---|---|---|---|
| 10/13/2009 | 10/14/2009 | 117 | 0.97 | 0.24 | 0.61 | 0.35 | 0.67 |
| 10/19/2009 | 10/20/2009 | 100 | 0.19 | 0.77 | 0.71 | 0.75 | 0.01 |
| 10/21/2009 | 10/22/2009 | 84 | 0.01 | 0.86 | 0.67 | 0.84 | 0.00 |
| 10/22/2009 | 10/23/2009 | 25 | 0.85 | 0.54 | 0.72 | 0.63 | 0.45 |
| 10/23/2009 | 10/23/2009 | 125 | 1.08 | 0.41 | 0.34 | 0.51 | 0.87 |
| 10/23/2009 | 10/26/2009 | 105 | 0.10 | 0.37 | 0.17 | 0.43 | 0.03 |
| 10/26/2009 | 10/27/2009 | 127 | 0.78 | 0.69 | 0.82 | 0.81 | 0.30 |
| 10/28/2009 | 10/29/2009 | 118 | 0.12 | 0.41 | 0.15 | 0.51 | 0.08 |
| 10/30/2009 | 10/30/2009 | 103 | 0.15 | 1.30 | 0.32 | 1.24 | 0.00 |
| 11/2/2009 | 11/3/2009 | 48 | 0.61 | 0.41 | 0.90 | 0.48 | 0.43 |
| 11/3/2009 | 11/4/2009 | 23 | 1.29 | 1.32 | 0.59 | 1.39 | 0.16 |
| 11/4/2009 | 11/5/2009 | 120 | 0.76 | 0.73 | 0.67 | 0.91 | 0.35 |
| 11/5/2009 | 11/6/2009 | 21 | 0.26 | 1.51 | 0.21 | 1.76 | 0.01 |
| 11/6/2009 | 11/6/2009 | 114 | 0.80 | 0.99 | 0.61 | 1.26 | 0.25 |
| 11/7/2009 | 11/8/2009 | 18 | 0.95 | 0.86 | 1.00 | 1.08 | 0.38 |
| 11/8/2009 | 11/9/2009 | 130 | 0.51 | 0.68 | 0.69 | 0.87 | 0.22 |
| 11/9/2009 | 11/10/2009 | 107 | 1.08 | 0.81 | 0.68 | 0.79 | 0.23 |
| 11/10/2009 | 11/11/2009 | 13 | 1.16 | 0.84 | 0.57 | 0.83 | 0.27 |
| 11/11/2009 | 11/12/2009 | 10 | 0.56 | 0.79 | 0.44 | 0.77 | 0.08 |
| 11/12/2009 | 11/13/2009 | 18 | 0.19 | 0.91 | 0.47 | 0.94 | 0.01 |
| 11/13/2009 | 11/16/2009 | 14 | 1.42 | 0.88 | 0.83 | 0.96 | 0.40 |
| 11/16/2009 | 11/17/2009 | 55 | 0.75 | 0.87 | 0.55 | 0.85 | 0.11 |
| 11/17/2009 | 11/18/2009 | 126 | 0.56 | 0.63 | 0.48 | 0.61 | 0.11 |
| 11/24/2009 | 11/26/2009 | 15 | 1.20 | 1.13 | 0.65 | 1.33 | 0.27 |
| 11/27/2009 | 11/30/2009 | 44 | 0.71 | 1.11 | 0.62 | 1.44 | 0.17 |
| 11/30/2009 | 12/1/2009 | 124 | 0.04 | 0.72 | 0.86 | 0.73 | 0.00 |
| 12/1/2009 | 12/2/2009 | 102 | 0.83 | 0.72 | 1.11 | 0.78 | 0.25 |
| 12/2/2009 | 12/3/2009 | 39 | 0.79 | 0.50 | 0.36 | 0.59 | 0.45 |
| 12/3/2009 | 12/4/2009 | 30 | 0.33 | 0.66 | 0.36 | 0.64 | 0.04 |
| 12/4/2009 | 12/7/2009 | 8 | 1.15 | 0.81 | 0.97 | 0.87 | 0.29 |
| 12/7/2009 | 12/8/2009 | 46 | 0.89 | 0.75 | 1.05 | 0.80 | 0.22 |
| 12/8/2009 | 12/9/2009 | 59 | 0.28 | 1.17 | 0.38 | 1.35 | 0.01 |
| 12/9/2009 | 12/10/2009 | 112 | 0.08 | 0.78 | 0.56 | 0.78 | 0.00 |
| 12/10/2009 | 12/11/2009 | 148 | 0.64 | 1.18 | 0.74 | 1.44 | 0.09 |

| Start Date | End Date | Crtdg | $t[OH]\cdot10^{-11}$ s molecules cm$^{-3}$ | $s_{t[OH]}$ s molecules cm$^{-3}$ | D | $s_D$ | $R^2$ |
|---|---|---|---|---|---|---|---|
| 12/11/2009 | 12/14/2009 | 140 | 0.25 | 1.51 | 0.27 | 1.85 | 0.01 |
| 12/14/2009 | 12/15/2009 | 24 | 0.25 | 0.77 | 0.59 | 0.78 | 0.02 |
| 12/16/2009 | 12/17/2009 | 155 | 0.25 | 0.77 | 0.59 | 0.78 | 0.02 |
| 12/17/2009 | 12/18/2009 | 145 | 0.50 | 0.95 | 0.59 | 0.93 | 0.04 |
| 1/18/2010 | 1/19/2010 | 166 | 0.26 | 0.85 | 0.42 | 1.07 | 0.02 |
| 1/19/2010 | 1/20/2010 | 139 | 0.56 | 0.74 | 0.78 | 0.82 | 0.12 |
| 1/20/2010 | 1/21/2010 | 110 | 0.65 | 0.41 | 0.27 | 0.45 | 0.39 |
| 1/21/2010 | 1/25/2010 | 32 | 0.32 | 0.41 | 0.07 | 0.57 | 0.38 |
| 1/22/2010 | 1/25/2010 | 85 | 0.92 | 0.78 | 0.25 | 0.84 | 0.22 |
| 1/25/2010 | 1/26/2010 | 105 | 0.10 | 0.37 | 0.49 | 0.43 | 0.03 |
| 1/26/2010 | 1/27/2010 | 109 | 1.12 | 0.92 | 0.99 | 1.01 | 0.27 |
| 06-Mar-10 | 07-Mar-10 | 103 | 0.10 | 0.30 | 0.81 | 0.37 | 0.03 |
| 12-Mar-10 | 13-Mar-10 | 114 | 0.79 | 1.23 | 0.47 | 1.26 | 0.08 |
| 13-Mar-10 | 14-Mar-10 | 101 | 0.42 | 0.99 | 0.56 | 1.15 | 0.06 |
| 19-Mar-10 | 20-Mar-10 | 152 | 0.57 | 0.52 | 0.26 | 0.64 | 0.38 |
| 21-Mar-10 | 22-Mar-10 | 168 | 0.87 | 0.61 | 0.32 | 0.71 | 0.40 |
| 22-Mar-10 | 23-Mar-10 | 159 | 0.42 | 0.75 | 0.23 | 0.75 | 0.05 |
| 30-Aug-10 | 31-Aug-10 | 111 | 0.48 | 0.57 | 0.82 | 0.52 | 0.15 |
| 31-Aug-10 | 01-Sep-10 | 68 | 0.32 | 0.49 | 1.04 | 0.55 | 0.17 |
| 09-Sep-10 | 10-Sep-10 | 109 | 0.77 | 0.80 | 0.16 | 1.12 | 0.48 |
| 09-Sep-10 | 10-Sep-10 | 123 | 0.14 | 0.64 | 0.06 | 0.89 | 0.05 |
| 13-Sep-10 | 14-Sep-10 | 11 | 0.09 | 0.12 | 0.12 | 0.15 | 0.21 |
| 13-Sep-10 | 14-Sep-10 | 131 | 0.71 | 0.61 | 0.13 | 0.67 | 0.25 |
| 14-Sep-10 | 15-Sep-10 | 36 | 0.25 | 0.68 | 0.48 | 0.73 | 0.03 |
| 16-Sep-10 | 17-Sep-10 | 22 | 0.34 | 0.41 | 0.05 | 0.38 | 0.41 |
| 17-Sep-10 | 20-Sep-10 | 144 | 0.67 | 0.54 | 0.32 | 0.67 | 0.44 |

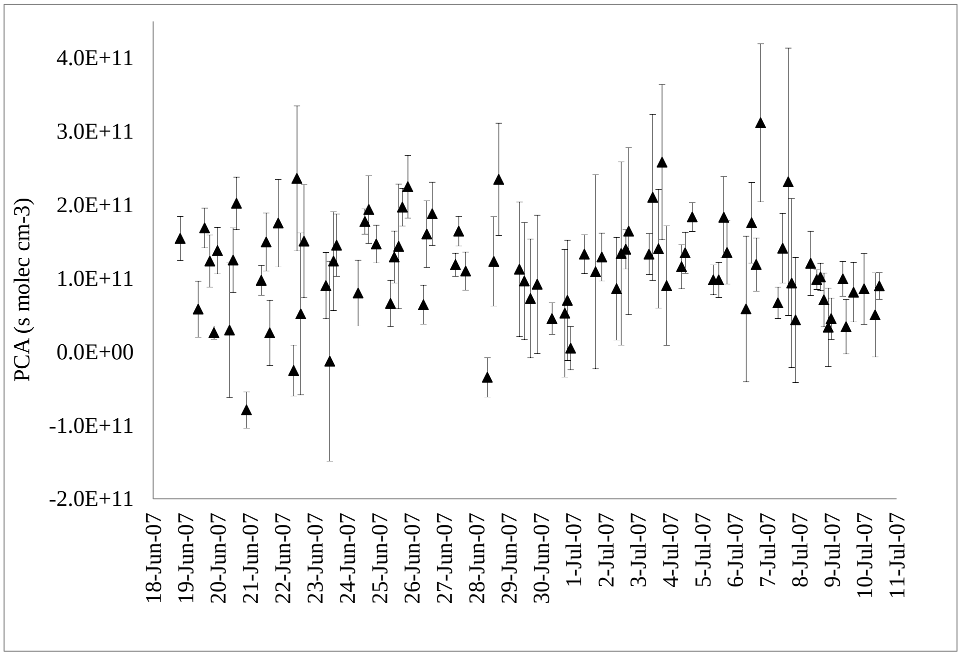
(a) $t[OH]\cdot10^{-11}$ – Photochemical age (PCA), (b) $s_{t[OH]}$ - error in the slope of the linear regression line, (c) D- dilution factor (d) $s_D$- error in the intercept of the linear regression line, (e) $R^2$- correlation

## F2: Time series for the determined photochemical ages and dilution factors using VOC-$k_{OH}$ correlation. Error bars represent an error in the slope of the linear regression line.

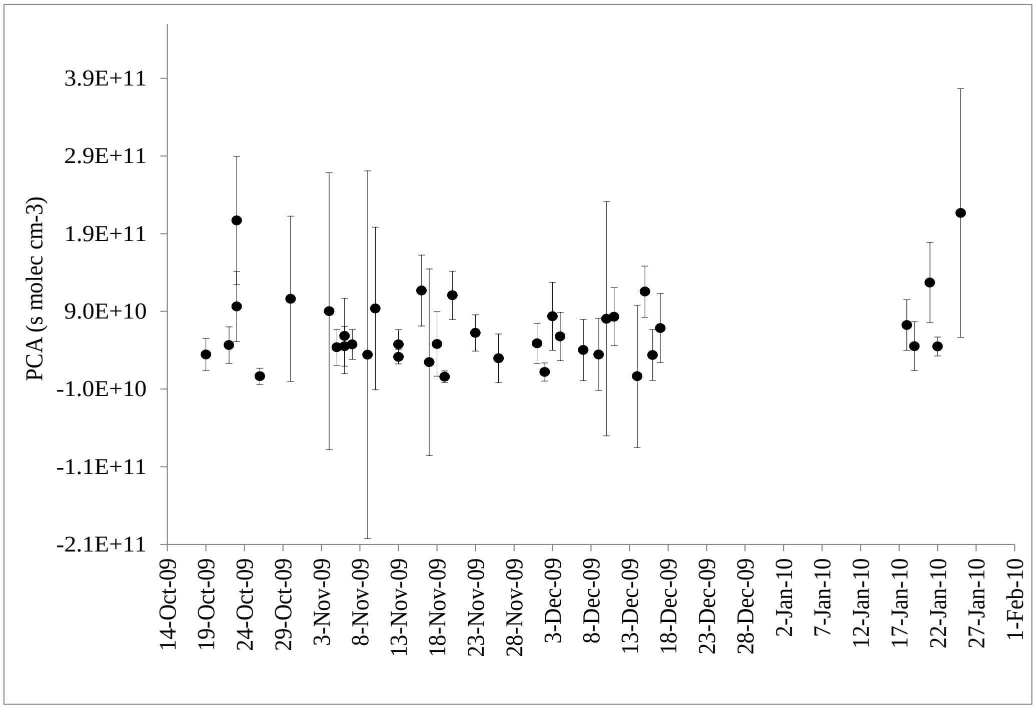
### F2.1 Harrow



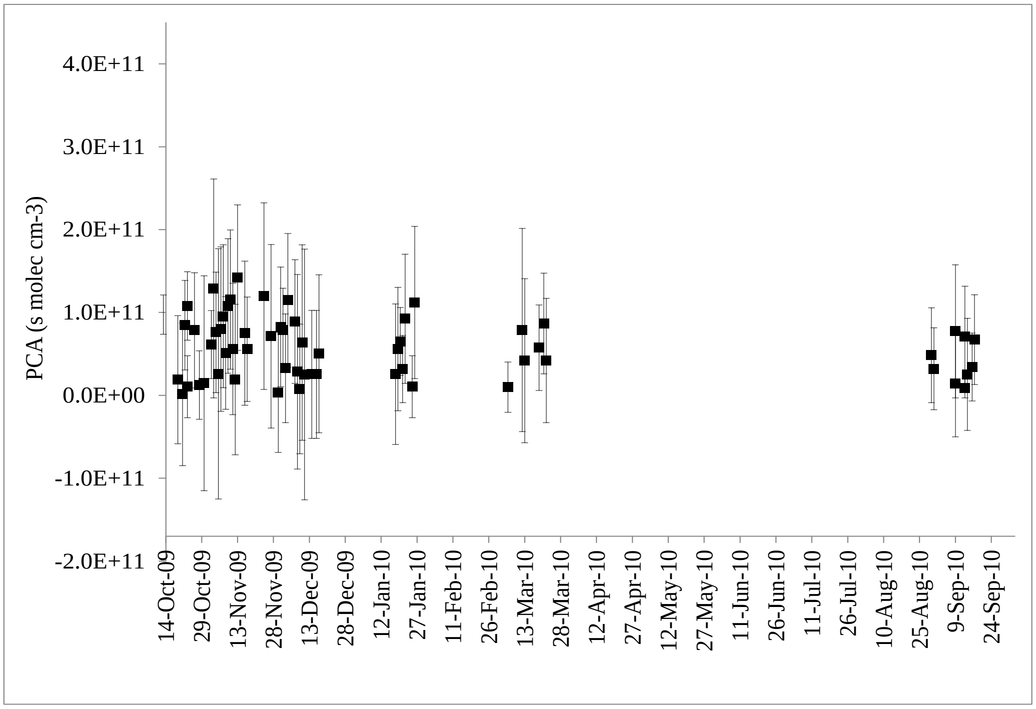
## F2.2: Ridgetown



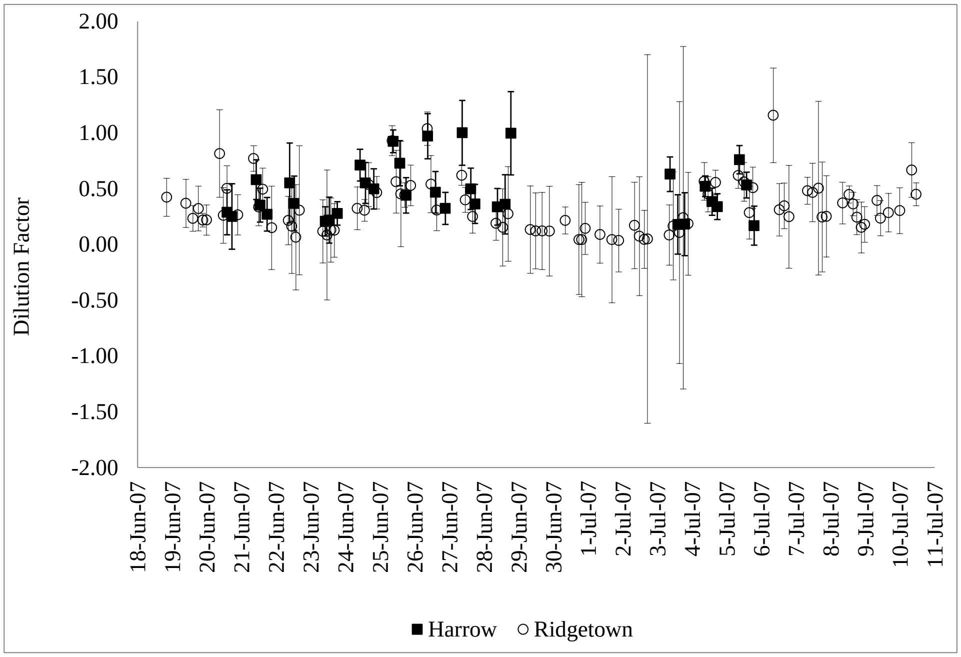
## F2.3: Egbert



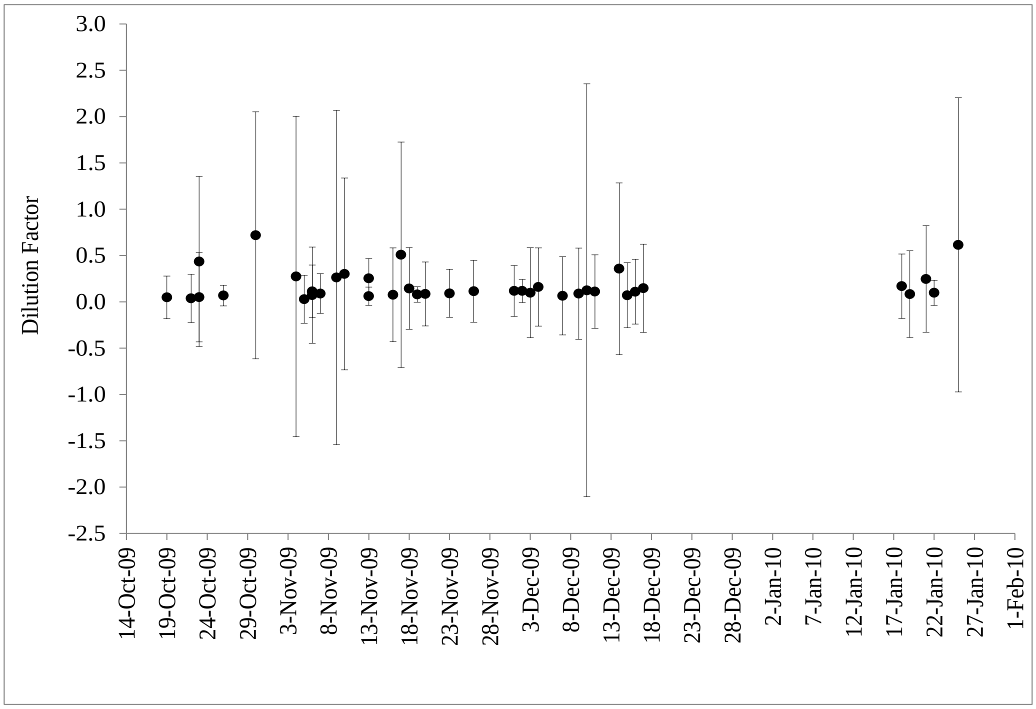
## F2.4 Toronto


PCA (s molec cm-3)
4.0E+11
3.0E+11
2.0E+11
1.0E+11
0.0E+00
-1.0E+11
-2.0E+11
14-Oct-09
29-Oct-09
13-Nov-09
28-Nov-09
13-Dec-09
28-Dec-09
12-Jan-10
27-Jan-10
11-Feb-10
26-Feb-10
13-Mar-10
28-Mar-10
12-Apr-10
27-Apr-10
12-May-10
27-May-10
11-Jun-10
26-Jun-10
11-Jul-10
26-Jul-10
10-Aug-10
25-Aug-10
9-Sep-10
24-Sep-10

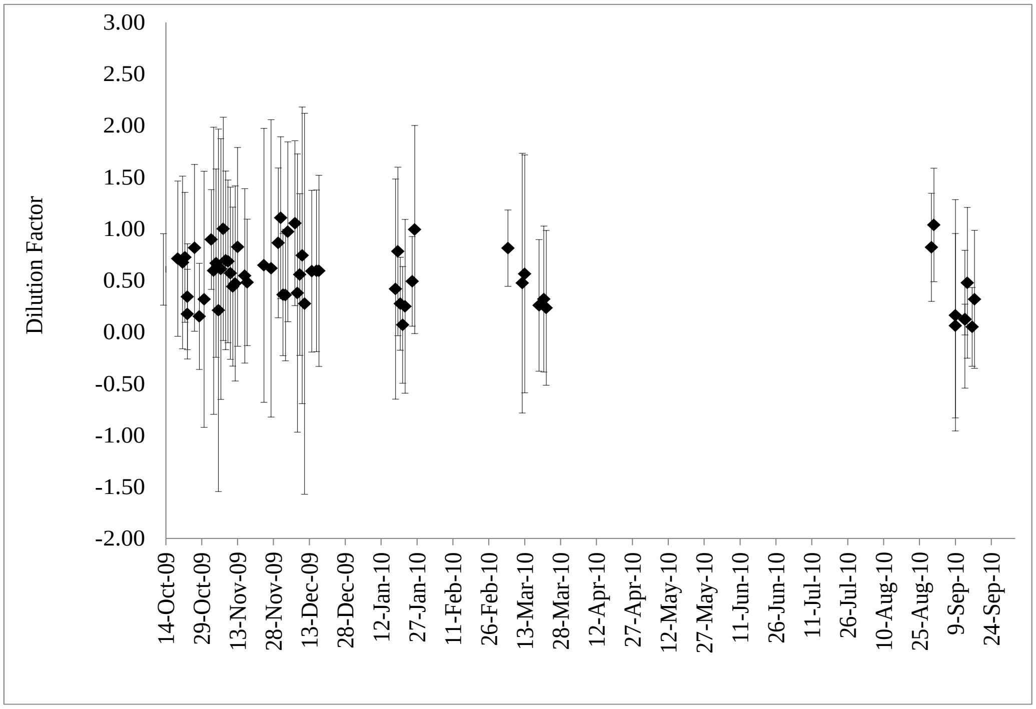
## F3.1 Harrow and Ridgetown



## F3.2 Egbert



### F3.3 Toronto


3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
Dilution Factor
14-Oct-09
29-Oct-09
13-Nov-09
28-Nov-09
13-Dec-09
28-Dec-09
12-Jan-10
27-Jan-10
11-Feb-10
26-Feb-10
13-Mar-10
28-Mar-10
12-Apr-10
27-Apr-10
12-May-10
27-May-10
11-Jun-10
26-Jun-10
11-Jul-10
26-Jul-10
10-Aug-10
25-Aug-10
9-Sep-10
24-Sep-10

# APPENDIX G: Photochemical ages determined using VOC ratios.

## G1.1: Harrow samples

| Date and Time | $t[OH]\cdot10^{-11}$ [a]<br>s molecules $cm^{-3}$ | $s_{t[OH]}$ [b]<br>s molecules $cm^{-3}$ |
|---|---|---|
| 6/20/2007 13:57 | 1.45 | 0.32 |
| 6/20/2007 17:19 | 3.25 | 0.73 |
| 6/21/2007 10:09 | 0.73 | 0.16 |
| 6/21/2007 12:48 | 2.43 | 0.54 |
| 6/21/2007 17:39 | 1.06 | 0.24 |
| 6/22/2007 9:19 | 1.80 | 0.40 |
| 6/22/2007 12:24 | 2.24 | 0.50 |
| 6/23/2007 9:57 | 0.92 | 0.21 |
| 6/23/2007 12:43 | 2.06 | 0.46 |
| 6/23/2007 18:20 | -0.44 | 0.10 |
| 6/24/2007 10:02 | 1.69 | 0.38 |
| 6/24/2007 13:45 | 2.47 | 0.55 |
| 6/24/2007 19:34 | 2.68 | 0.60 |
| 6/25/2007 9:00 | -0.24 | 0.05 |
| 6/25/2007 13:36 | 2.26 | 0.51 |
| 6/25/2007 17:55 | 0.87 | 0.19 |
| 6/26/2007 8:52 | 0.80 | 0.18 |
| 6/26/2007 14:17 | 1.74 | 0.39 |
| 6/26/2007 21:08 | 0.26 | 0.06 |
| 6/27/2007 8:48 | -0.13 | 0.03 |
| 6/27/2007 14:43 | -1.42 | 0.32 |
| 6/27/2007 17:39 | -2.49 | 0.56 |
| 6/28/2007 9:10 | -2.12 | 0.47 |
| 6/28/2007 14:30 | -1.03 | 0.23 |
| 6/28/2007 18:30 | -0.70 | 0.16 |
| 7/3/2007 8:44 | -0.93 | 0.21 |
| 7/3/2007 14:07 | -0.18 | 0.04 |
| 7/3/2007 18:51 | -0.17 | 0.04 |
| 7/4/2007 9:08 | -0.33 | 0.07 |
| 7/4/2007 13:50 | 0.06 | 0.01 |
| 7/4/2007 17:30 | -0.12 | 0.03 |
| 7/5/2007 8:48 | -0.74 | 0.17 |

| Date and Time | $t[OH]\cdot10^{-11}$ [a] s molecules $cm^{-3}$ | $s_{t[OH]}$ [b] s molecules $cm^{-3}$ |
|---|---|---|
| 7/5/2007 13:43 | -0.79 | 0.18 |
| 7/5/2007 18:58 | -2.22 | 0.50 |

## G1.2: Ridgetown

| Date and Time | $t[OH]\cdot10^{-11}$ s molecules cm$^{-3}$ | $s_{t[OH]}$ s molecules cm$^{-3}$ |
|---|---|---|
| 6/18/2007 20:05 | 2.22 | 0.50 |
| 6/19/2007 9:25 | 0.56 | 0.12 |
| 6/19/2007 14:15 | 0.98 | 0.22 |
| 6/19/2007 18:05 | 2.30 | 0.51 |
| 6/19/2007 21:09 | -0.56 | 0.12 |
| 6/19/2007 23:45 | 0.04 | 0.01 |
| 6/20/2007 8:45 | -0.55 | 0.12 |
| 6/20/2007 11:21 | -2.86 | 0.64 |
| 6/20/2007 13:52 | 0.02 | 0.00 |
| 6/20/2007 21:21 | -1.79 | 0.40 |
| 6/21/2007 8:20 | 0.17 | 0.04 |
| 6/21/2007 11:52 | 0.55 | 0.12 |
| 6/21/2007 14:37 | -0.83 | 0.19 |
| 6/21/2007 20:50 | 0.27 | 0.06 |
| 6/22/2007 8:20 | -1.85 | 0.41 |
| 6/22/2007 10:45 | -0.38 | 0.08 |
| 6/22/2007 13:35 | -1.22 | 0.27 |
| 6/23/2007 8:16 | -2.50 | 0.56 |
| 6/23/2007 11:09 | -0.24 | 0.05 |
| 6/23/2007 13:52 | -2.02 | 0.45 |
| 6/23/2007 16:15 | -2.49 | 0.56 |
| 6/24/2007 8:09 | -2.06 | 0.46 |
| 6/24/2007 13:10 | -0.35 | 0.08 |
| 6/24/2007 16:04 | 0.89 | 0.20 |
| 6/24/2007 21:39 | -0.04 | 0.01 |
| 6/25/2007 8:16 | -0.84 | 0.19 |
| 6/25/2007 11:02 | 1.11 | 0.25 |
| 6/25/2007 14:18 | 0.29 | 0.06 |
| 6/25/2007 17:02 | 0.15 | 0.03 |
| 6/25/2007 21:07 | 0.79 | 0.18 |
| 6/26/2007 8:39 | -0.38 | 0.08 |
| 6/26/2007 11:10 | 0.69 | 0.16 |
| 6/26/2007 15:10 | 0.26 | 0.06 |
| 6/27/2007 8:26 | -0.60 | 0.13 |

| Date and Time | $t[OH]\cdot10^{-11}$ s molecules cm$^{-3}$ | $s_{t[OH]}$ s molecules cm$^{-3}$ |
|---|---|---|
| 6/27/2007 10:55 | -0.36 | 0.08 |
| 6/27/2007 16:00 | -0.63 | 0.14 |
| 6/28/2007 8:13 | -1.83 | 0.41 |
| 6/28/2007 12:54 | -1.22 | 0.27 |
| 6/28/2007 16:36 | 0.74 | 0.17 |
| 6/29/2007 8:00 | -2.21 | 0.49 |
| 6/29/2007 11:40 | -2.33 | 0.52 |
| 6/29/2007 16:08 | -1.71 | 0.38 |
| 6/29/2007 21:11 | -1.99 | 0.44 |
| 6/30/2007 8:10 | -1.70 | 0.38 |
| 6/30/2007 17:40 | -2.29 | 0.51 |
| 6/30/2007 19:35 | -2.15 | 0.48 |
| 6/30/2007 22:00 | -2.11 | 0.47 |
| 7/1/2007 8:14 | -2.46 | 0.55 |
| 7/1/2007 16:30 | -2.46 | 0.55 |
| 7/2/2007 8:07 | -1.99 | 0.44 |
| 7/3/2007 10:55 | -2.05 | 0.46 |
| 7/3/2007 17:49 | -2.12 | 0.47 |
| 7/3/2007 21:15 | -2.44 | 0.55 |
| 7/4/2007 8:25 | -2.25 | 0.50 |
| 7/4/2007 11:04 | -1.77 | 0.40 |
| 7/4/2007 16:15 | -0.31 | 0.07 |
| 7/5/2007 7:58 | -1.12 | 0.25 |
| 7/5/2007 12:00 | -0.72 | 0.16 |
| 7/5/2007 15:40 | -1.39 | 0.31 |
| 7/5/2007 18:05 | -0.31 | 0.07 |
| 7/6/2007 8:15 | -0.44 | 0.10 |
| 7/6/2007 12:25 | -1.19 | 0.27 |
| 7/6/2007 15:49 | -1.09 | 0.24 |
| 7/6/2007 19:05 | -0.53 | 0.12 |
| 7/7/2007 7:55 | -1.33 | 0.30 |
| 7/7/2007 11:25 | -0.97 | 0.22 |
| 7/7/2007 18:05 | -1.59 | 0.36 |
| 7/7/2007 21:00 | -1.07 | 0.24 |
| 7/8/2007 8:14 | -1.84 | 0.41 |
| 7/8/2007 12:45 | -0.94 | 0.21 |

| Date and Time | $t[OH]\cdot10^{-11}$ s molecules $cm^{-3}$ | $s_{t[OH]}$ s molecules $cm^{-3}$ |
|---|---|---|
| 7/8/2007 15:30 | -0.73 | 0.16 |
| 7/8/2007 18:05 | -1.72 | 0.39 |
| 7/8/2007 21:15 | -2.83 | 0.63 |
| 7/8/2007 23:30 | -2.26 | 0.51 |
| 7/9/2007 8:05 | -1.34 | 0.30 |
| 7/9/2007 10:30 | -1.47 | 0.33 |
| 7/9/2007 16:03 | -1.89 | 0.42 |
| 7/9/2007 23:50 | -1.82 | 0.41 |
| 7/10/2007 8:07 | -0.71 | 0.16 |
| 7/10/2007 11:10 | -0.63 | 0.14 |

## G1.3: Egbert

| Start Date | End Date | Crtrdg | $t[OH]\cdot 10^{-11}$ s molecules cm$^{-3}$ | $s_{t[OH]}$ s molecules cm$^{-3}$ |
|---|---|---|---|---|
| 10/19/2009 | 10/20/2009 | 49 | 0.34 | 0.05 |
| 10/21/2009 | 10/22/2009 | 144 | 0.00 | 0.00 |
| 10/22/2009 | 10/23/2009 | 128 | 0.58 | 0.08 |
| 10/23/2009 | 10/24/2009 | 132 | 4.78 | 0.68 |
| 10/23/2009 | 10/26/2009 | 108 | 0.83 | 0.12 |
| 10/26/2009 | 10/26/2009 | 106 | -0.82 | -0.12 |
| 11/2/2009 | 11/3/2009 | 103 | 0.52 | 0.07 |
| 11/4/2009 | 11/5/2009 | 16 | -1.92 | -0.27 |
| 11/5/2009 | 11/6/2009 | 11 | 0.68 | 0.10 |
| 11/6/2009 | 11/6/2009 | 116 | 1.27 | 0.18 |
| 11/6/2009 | 11/7/2009 | 133 | 0.82 | 0.12 |
| 11/7/2009 | 11/8/2009 | 123 | 0.41 | 0.06 |
| 11/9/2009 | 11/10/2009 | 22 | 0.87 | 0.12 |
| 11/10/2009 | 11/12/2009 | 36 | 0.32 | 0.05 |
| 11/12/2009 | 11/13/2009 | 40 | -1.16 | -0.17 |
| 11/13/2009 | 11/13/2009 | 123 | 0.41 | 0.06 |
| 11/13/2009 | 11/16/2009 | 27 | -0.43 | -0.06 |
| 11/16/2009 | 11/17/2009 | 115 | 2.69 | 0.38 |
| 11/17/2009 | 11/18/2009 | 109 | -0.26 | -0.04 |
| 11/18/2009 | 11/19/2009 | 113 | 2.23 | 0.32 |
| 11/19/2009 | 11/20/2009 | 47 | -1.12 | -0.16 |
| 11/20/2009 | 11/21/2009 | 122 | 1.45 | 0.21 |
| 11/23/2009 | 11/25/2009 | 33 | 0.67 | 0.10 |
| 11/26/2009 | 11/27/2009 | 60 | 1.35 | 0.19 |
| 11/27/2009 | 11/27/2009 | 133 | -0.21 | -0.03 |
| 11/30/2009 | 31/11/2009 | 51 | 3.15 | 0.45 |
| 12/1/2009 | 12/2/2009 | 20 | 0.89 | 0.13 |
| 12/2/2009 | 12/3/2009 | 12 | -0.57 | -0.08 |
| 12/3/2009 | 12/4/2009 | 104 | 2.45 | 0.35 |
| 12/4/2009 | 12/7/2009 | 119 | 1.28 | 0.18 |
| 12/7/2009 | 12/8/2009 | 137 | 2.15 | 0.31 |
| 12/9/2009 | 12/10/2009 | 154 | 2.16 | 0.31 |
| 12/10/2009 | 12/11/2009 | 111 | 1.75 | 0.25 |
| 12/11/2009 | 12/11/2009 | 146 | 1.88 | 0.27 |
| 12/11/2009 | 11/14/2009 | 136 | 2.86 | 0.41 |

| Start Date | End Date | Crtrdg | $t[OH]\cdot 10^{-11}$ s molecules $cm^{-3}$ | $s_{t[OH]}$ s molecules $cm^{-3}$ |
|---|---|---|---|---|
| 12/14/2009 | 12/15/2009 | 149 | -0.39 | -0.06 |
| 12/15/2009 | 12/16/2009 | 79 | 2.37 | 0.34 |
| 12/16/2009 | 12/17/2009 | 100 | 1.38 | 0.20 |
| 12/17/2009 | 12/21/2009 | 142 | 2.77 | 0.40 |
| 1/18/2010 | 1/19/2010 | 158 | 1.94 | 0.28 |
| 1/19/2010 | 1/20/2010 | 113 | 0.82 | 0.12 |
| 1/21/2010 | 1/22/2010 | 165 | 3.36 | 0.48 |
| 1/22/2010 | 1/25/2010 | 118 | -0.41 | -0.06 |
| 1/25/2010 | 1/26/2010 | 115 | 2.69 | 0.38 |

## G1.4: Toronto

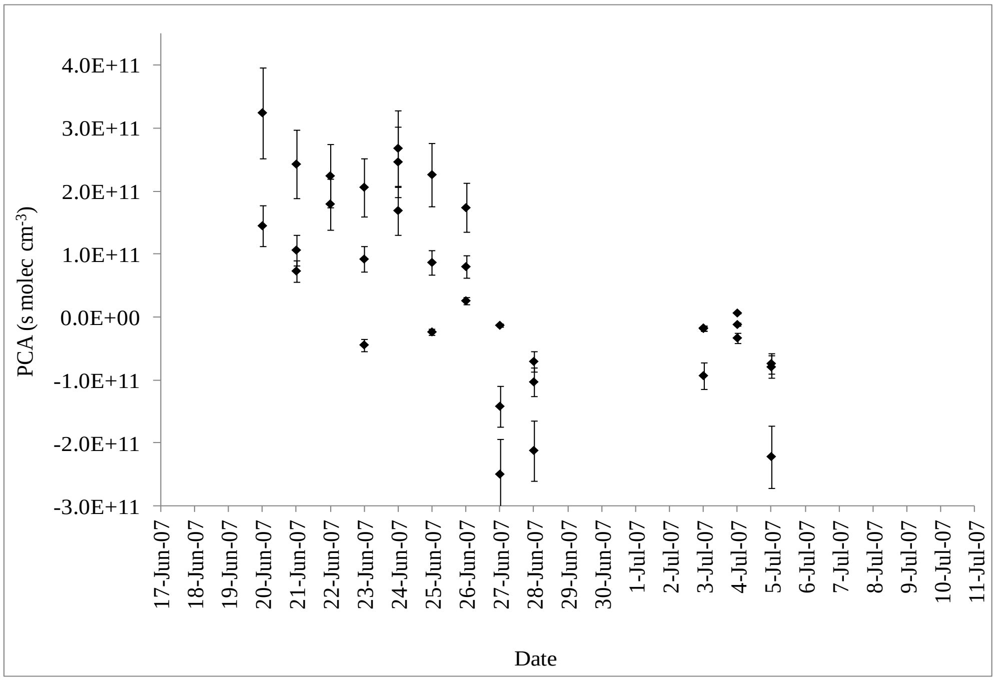
| Start Date | End Date | Crtdg | $t[OH]\cdot10^{-11}$ s molecules $cm^{-3}$ | $s_{t[OH]}$ s molecules $cm^{-3}$ |
|---|---|---|---|---|
| 10/13/2009 | 10/14/2009 | 117 | 0.60 | 0.09 |
| 10/19/2009 | 10/20/2009 | 100 | 1.78 | 0.25 |
| 10/20/2009 | 10/21/2009 | 29 | 0.47 | 0.07 |
| 10/21/2009 | 10/22/2009 | 84 | 0.69 | 0.10 |
| 10/22/2009 | 10/23/2009 | 25 | -5.06 | 0.72 |
| 10/23/2009 | 10/26/2009 | 105 | -0.58 | 0.08 |
| 10/26/2009 | 10/27/2009 | 127 | 2.82 | 0.40 |
| 10/30/2009 | 10/30/2009 | 103 | 6.80 | 0.97 |
| 11/5/2009 | 11/6/2009 | 21 | 0.24 | 0.03 |
| 11/9/2009 | 11/10/2009 | 107 | 2.88 | 0.41 |
| 11/10/2009 | 11/11/2009 | 13 | 3.33 | 0.48 |
| 11/11/2009 | 11/12/2009 | 10 | 3.24 | 0.46 |
| 11/13/2009 | 11/16/2009 | 14 | 2.63 | 0.38 |
| 11/16/2009 | 11/17/2009 | 55 | 3.48 | 0.50 |
| 11/17/2009 | 11/18/2009 | 126 | 3.05 | 0.44 |
| 11/19/2009 | 11/20/2009 | 134 | -17.74 | 2.54 |
| 11/26/2009 | 11/27/2009 | 81 | 1.28 | 0.18 |
| 11/30/2009 | 31/11/2009 | 124 | 0.53 | 0.08 |
| 12/1/2009 | 12/2/2009 | 102 | 1.41 | 0.20 |
| 12/3/2009 | 12/4/2009 | 30 | 1.01 | 0.14 |
| 12/4/2009 | 12/7/2009 | 8 | 1.61 | 0.23 |
| 12/7/2009 | 12/8/2009 | 46 | 0.61 | 0.09 |
| 12/9/2009 | 12/10/2009 | 112 | 1.07 | 0.15 |
| 12/17/2009 | 12/18/2009 | 145 | 0.07 | 0.01 |
| 1/18/2010 | 1/19/2010 | 166 | 2.81 | 0.40 |
| 1/19/2010 | 1/20/2010 | 139 | 0.66 | 0.09 |
| 1/20/2010 | 1/21/2010 | 110 | -2.38 | 0.34 |
| 1/22/2010 | 1/25/2010 | 85 | 0.85 | 0.12 |
| 1/25/2010 | 1/26/2010 | 105 | -0.58 | 0.08 |
| 1/26/2010 | 1/27/2010 | 109 | 1.95 | 0.28 |
| 12-Mar-10 | 13-Mar-10 | 114 | 4.58 | 0.65 |
| 13-Mar-10 | 14-Mar-10 | 101 | -1.28 | 0.18 |
| 19-Mar-10 | 20-Mar-10 | 152 | -0.41 | 0.06 |
| 20-Mar-10 | 21-Mar-10 | 112 | -2.21 | 0.32 |
| 21-Mar-10 | 22-Mar-10 | 168 | 0.59 | 0.08 |

| Start Date | End Date | Crtdg | $t[OH]\cdot10^{-11}$ s molecules $cm^{-3}$ | $s_{t[OH]}$ s molecules $cm^{-3}$ |
|---|---|---|---|---|
| 22-Mar-10 | 23-Mar-10 | 159 | 2.29 | 0.33 |
| 30-Aug-10 | 31-Aug-10 | 111 | 0.53 | 0.08 |
| 13-Sep-10 | 14-Sep-10 | 131 | 0.77 | 0.11 |
| 14-Sep-10 | 15-Sep-10 | 36 | -1.13 | 0.16 |
| 14-Sep-10 | 15-Sep-10 | 77 | 2.90 | 0.42 |
| 16-Sep-10 | 17-Sep-10 | 22 | -3.64 | 0.52 |
| 16-Sep-10 | 17-Sep-10 | 54 | 1.31 | 0.19 |

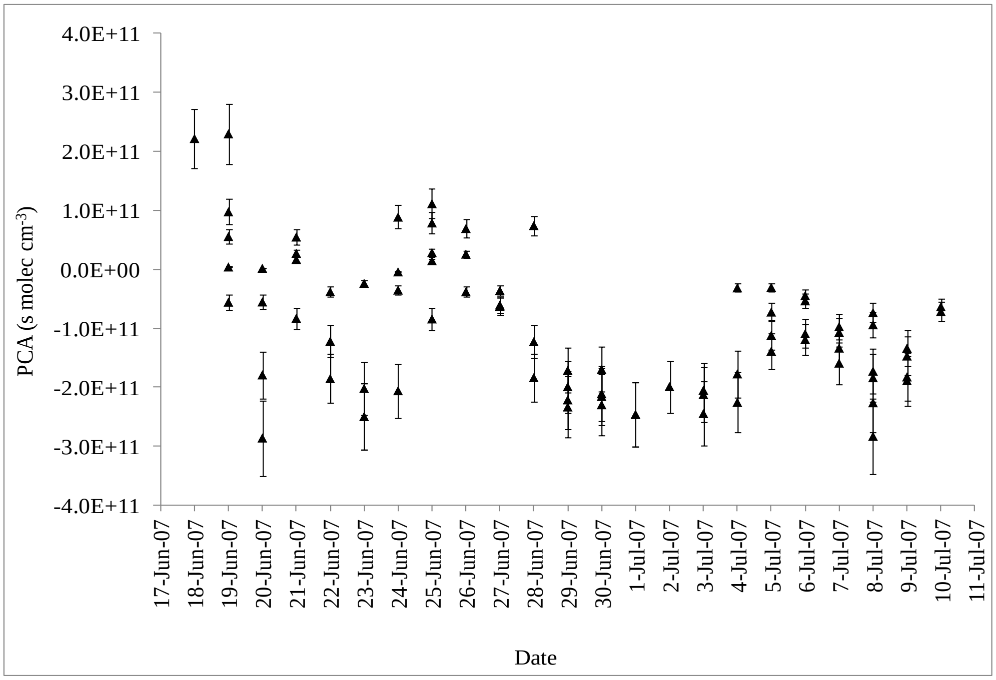
(a) $t[OH]\cdot10^{-11}$ – Photochemical age (PCA), (b) $s_{t[OH]}$ - error determined by the propagation of errors

## G2: Time series for the determined photochemical ages and dilution factors using VOC ratios.

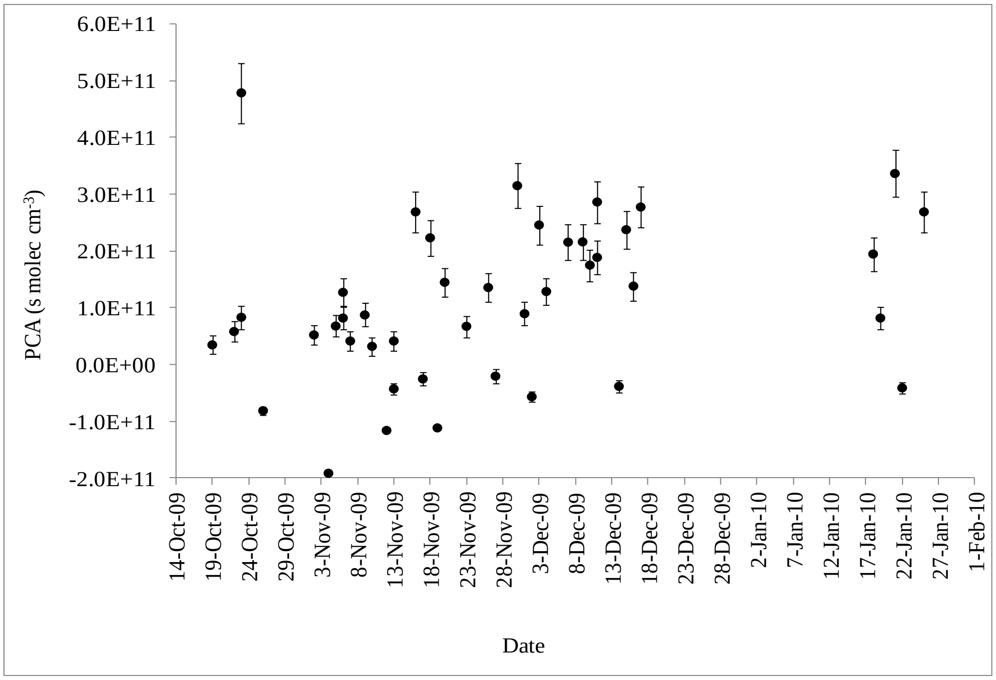
### G2.1: Harrow



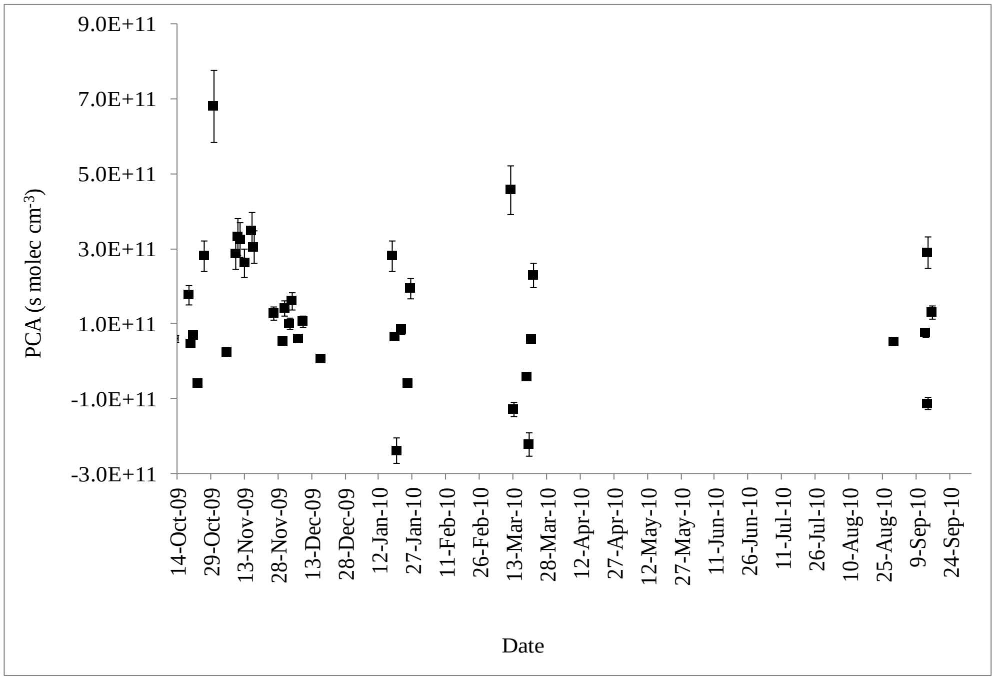
## G2.2: Ridgetown



## G2.3: Egbert



## G2.4: Toronto


9.0E+11
7.0E+11
5.0E+11
3.0E+11
1.0E+11
-1.0E+11
-3.0E+11
PCA (s molec cm$^{-3}$)
14-Oct-09
29-Oct-09
13-Nov-09
28-Nov-09
13-Dec-09
28-Dec-09
12-Jan-10
27-Jan-10
11-Feb-10
26-Feb-10
13-Mar-10
28-Mar-10
12-Apr-10
27-Apr-10
12-May-10
27-May-10
11-Jun-10
26-Jun-10
11-Jul-10
26-Jul-10
10-Aug-10
25-Aug-10
9-Sep-10
24-Sep-10
Date

# APPENDIX H: Photochemical determined using stable carbon isotope composition

## H1.1: Egbert

| | | | hexane | | benzene | | heptane | | toluene | | ethylbenzene | | p,m-xylene | | o-xylene | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Start Date | End Date | Crtdg | t[OH][a] | $s_{t[OH]}$[b] | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ |
| 10/19/2009 | 10/20/2009 | 49 | 1.36 | 0.58 | 5.96 | 1.90 | 2.70 | 1.11 | 1.07 | 0.31 | 1.10 | 0.57 | 0.27 | 0.08 | 0.34 | 0.31 |
| 10/21/2009 | 10/22/2009 | 144 | | | | | | | | | | | | | | |
| 10/22/2009 | 10/23/2009 | 128 | -0.38 | 0.58 | 5.15 | 1.89 | 1.67 | 1.08 | 1.34 | 0.31 | -0.01 | 0.56 | 0.15 | 0.08 | -0.12 | 0.31 |
| 10/23/2009 | 10/24/2009 | 132 | -1.00 | 0.58 | -0.01 | 1.87 | 1.76 | 1.08 | 0.39 | 0.30 | 1.02 | 0.57 | 0.43 | 0.08 | 0.74 | 0.31 |
| 10/23/2009 | 10/26/2009 | 108 | -1.25 | 0.58 | 1.29 | 1.87 | -0.34 | 1.05 | 0.75 | 0.30 | 0.24 | 0.56 | 1.05 | 0.08 | 0.31 | 0.31 |
| 10/26/2009 | 10/26/2009 | 106 | 0.52 | 0.58 | 12.39 | 1.99 | 0.37 | 1.05 | 0.46 | 0.30 | 1.03 | 0.57 | 0.46 | 0.08 | 0.55 | 0.31 |
| 10/27/2009 | 10/28/2009 | 141 | | | 5.07 | 1.89 | -8.34 | 1.53 | | | | | | | | |
| 10/28/2009 | 10/29/2009 | 65 | | | | | | | | | | | | | | |
| 10/29/2009 | 10/30/2009 | 41 | | | | | | | | | | | | | | |
| 10/30/2009 | 10/30/2009 | 54 | | | | | -2.73 | 1.11 | | | | | | | | |
| 10/30/2009 | 11/2/2009 | 52 | | | | | | | | | | | | | | |
| 11/2/2009 | 11/3/2009 | 103 | -0.61 | 0.58 | -1.09 | 1.87 | -2.12 | 1.09 | -0.38 | 0.30 | | | | | | |
| 11/3/2009 | 11/4/2009 | 80 | | | -0.27 | 1.87 | | | | | | | | | | |
| 11/4/2009 | 11/5/2009 | 16 | -0.33 | 0.58 | 6.05 | 1.90 | 0.91 | 1.06 | 0.09 | 0.30 | 5.40 | 0.66 | 1.05 | 0.08 | 0.46 | 0.31 |
| 11/5/2009 | 11/6/2009 | 11 | -0.33 | 0.58 | 5.83 | 1.90 | 1.34 | 1.07 | 0.90 | 0.30 | 1.65 | 0.57 | 0.76 | 0.08 | 0.77 | 0.31 |
| 11/6/2009 | 11/6/2009 | 116 | -0.56 | 0.58 | -1.56 | 1.87 | 1.06 | 1.06 | -0.08 | 0.30 | 2.97 | 0.60 | 0.80 | 0.08 | 0.89 | 0.31 |
| 11/6/2009 | 11/7/2009 | 133 | 2.38 | 0.58 | 1.73 | 1.87 | 3.26 | 1.14 | 1.46 | 0.31 | 2.62 | 0.59 | 0.82 | 0.08 | 1.21 | 0.31 |
| 11/7/2009 | 11/8/2009 | 123 | -0.37 | 0.58 | 0.91 | 1.87 | 1.37 | 1.07 | 0.65 | 0.30 | 1.64 | 0.57 | 0.40 | 0.08 | 0.83 | 0.31 |
| 11/8/2009 | 11/9/2009 | 131 | | | | | | | | | | | | | | |
| 11/9/2009 | 11/10/2009 | 22 | -0.57 | 0.58 | 0.16 | 1.87 | -0.03 | 1.05 | 0.53 | 0.30 | | | | | 1.71 | 0.31 |
| 11/10/2009 | 11/12/2009 | 36 | -2.04 | 0.58 | 1.70 | 1.87 | 1.16 | 1.06 | 0.38 | 0.30 | 0.37 | 0.56 | 0.16 | 0.08 | -0.02 | 0.31 |

| Start Date | End Date | Crtdg | hexane |  | benzene |  | heptane |  | toluene |  | ethylbenzene |  | p,m-xylene |  | o-xylene |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | t[OH][a] | $s_{t[OH]}$[b] | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ |
| 11/12/2009 | 11/13/2009 | 40 | -1.35 | 0.58 | 1.95 | 1.87 | 1.13 | 1.06 | 0.37 | 0.30 | -0.35 | 0.56 | -0.11 | 0.08 | 0.36 | 0.31 |
| 11/13/2009 | 11/13/2009 | 123 | -0.37 | 0.58 | 0.91 | 1.87 | 1.37 | 1.07 | 0.65 | 0.30 | 1.64 | 0.57 | 0.40 | 0.08 | 0.83 | 0.31 |
| 11/13/2009 | 11/16/2009 | 27 | 0.35 | 0.58 | -0.42 | 1.87 | 1.95 | 1.09 | 0.63 | 0.30 | -0.07 | 0.56 | -0.07 | 0.08 | 0.26 | 0.31 |
| 11/16/2009 | 11/17/2009 | 115 | 1.76 | 0.58 | 1.02 | 1.87 | 3.29 | 1.14 | 1.10 | 0.31 | 1.38 | 0.57 | 0.63 | 0.08 | 0.67 | 0.31 |
| 11/17/2009 | 11/18/2009 | 109 |  |  | 3.21 | 1.88 | 3.59 | 1.16 | 1.90 | 0.31 | 0.15 | 0.56 | -0.25 | 0.08 | 0.80 | 0.31 |
| 11/18/2009 | 11/19/2009 | 113 |  |  | 3.08 | 1.88 |  |  | 1.07 | 0.31 | 0.89 | 0.57 | 0.44 | 0.08 | 0.21 | 0.31 |
| 11/19/2009 | 11/20/2009 | 47 | -0.29 | 0.58 | 3.17 | 1.88 | 6.31 | 1.35 | 0.69 | 0.30 | -0.39 | 0.56 | 0.43 | 0.08 | 0.20 | 0.31 |
| 11/20/2009 | 11/21/2009 | 122 |  |  | 3.31 | 1.88 | 1.13 | 1.06 | 1.22 | 0.31 | 0.64 | 0.57 | 0.40 | 0.08 | 0.13 | 0.31 |
| 11/23/2009 | 11/25/2009 | 33 |  |  | 1.52 | 1.87 | 0.80 | 1.06 | 0.97 | 0.30 | -0.19 | 0.56 | 0.23 | 0.08 | -0.30 | 0.31 |
| 11/26/2009 | 11/27/2009 | 60 |  |  | -1.92 | 1.87 | 1.00 | 1.06 | 0.42 | 0.30 | -0.37 | 0.56 | -0.05 | 0.08 | -0.41 | 0.31 |
| 11/27/2009 | 11/27/2009 | 133 |  |  | 1.73 | 1.87 | 3.76 | 1.17 | 1.62 | 0.31 | -0.44 | 0.56 | 0.12 | 0.08 | -0.22 | 0.31 |
| 11/30/2009 | 31/11/2009 | 51 |  |  | 0.74 | 1.87 | 2.53 | 1.11 | 0.97 | 0.30 | 0.00 | 0.56 | 0.17 | 0.08 | 0.27 | 0.31 |
| 12/1/2009 | 12/2/2009 | 20 |  |  | 3.74 | 1.88 | 1.68 | 1.08 | 0.67 | 0.30 | 0.65 | 0.57 | 0.38 | 0.08 | 0.84 | 0.31 |
| 12/2/2009 | 12/3/2009 | 12 |  |  | 0.78 | 1.87 | 0.84 | 1.06 | 0.57 | 0.30 | 0.68 | 0.57 | 0.28 | 0.08 | 0.42 | 0.31 |
| 12/3/2009 | 12/4/2009 | 104 |  |  | 2.44 | 1.88 | 0.99 | 1.06 | 0.36 | 0.30 | -0.19 | 0.56 | -0.05 | 0.08 | 0.43 | 0.31 |
| 12/4/2009 | 12/7/2009 | 119 |  |  |  |  | 2.71 | 1.11 | 0.36 | 0.30 | 0.09 | 0.56 | 0.29 | 0.08 | 0.08 | 0.31 |
| 12/7/2009 | 12/8/2009 | 137 |  |  | -2.67 | 1.88 | -0.38 | 1.05 | -0.19 | 0.30 | -0.29 | 0.56 | -0.12 | 0.08 | -0.03 | 0.31 |
| 12/8/2009 | 12/9/2009 | 153 | 5.65 | 0.61 | 0.63 | 1.87 | 0.03 | 1.05 |  |  |  |  |  |  |  |  |
| 12/9/2009 | 12/10/2009 | 154 |  |  | 1.57 | 1.87 | 1.84 | 1.08 | 1.18 | 0.31 | 0.92 | 0.57 | 0.52 | 0.08 | 0.61 | 0.31 |
| 12/10/2009 | 12/11/2009 | 111 |  |  | 0.02 | 1.87 | 1.87 | 1.08 | 0.73 | 0.30 | 1.39 | 0.57 | 0.57 | 0.08 | 0.28 | 0.31 |
| 12/11/2009 | 12/11/2009 | 146 |  |  | -1.63 | 1.87 | 1.20 | 1.07 | 0.07 | 0.30 |  |  |  |  |  |  |
| 12/11/2009 | 11/14/2009 | 136 |  |  | -0.34 | 1.87 | 2.05 | 1.09 | 0.28 | 0.30 |  |  |  |  |  |  |
| 12/14/2009 | 12/15/2009 | 149 |  |  | 2.18 | 1.88 | 3.76 | 1.17 | 1.62 | 0.31 | 2.86 | 0.59 | 1.11 | 0.08 | 1.13 | 0.31 |
| 12/15/2009 | 12/16/2009 | 79 | 1.62 | 0.58 | 2.68 | 1.88 | 2.75 | 1.11 | 0.57 | 0.30 | 0.58 | 0.56 | 0.20 | 0.08 | 0.18 | 0.31 |

| Start Date | End Date | Crtdg | hexane |  | benzene |  | heptane |  | toluene |  | ethylbenzene |  | p,m-xylene |  | o-xylene |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | t[OH][a] | $s_{t[OH]}$[b] | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ |
| 12/16/2009 | 12/17/2009 | 100 |  |  | 0.11 | 1.87 | 1.26 | 1.07 | 0.37 | 0.30 | 0.62 | 0.57 | 0.20 | 0.08 | 0.02 | 0.31 |
| 12/17/2009 | 12/21/2009 | 142 | 2.29 | 0.58 | 4.66 | 1.89 | 0.68 | 1.06 | 1.01 | 0.30 | 1.56 | 0.57 | 0.36 | 0.08 | 0.52 | 0.31 |
| 1/18/2010 | 1/19/2010 | 158 |  |  | 5.07 | 1.89 | -23.38 | 3.27 | 0.80 | 0.30 | 1.50 | 0.57 | 0.43 | 0.08 | 0.57 | 0.31 |
| 1/19/2010 | 1/20/2010 | 113 | 2.38 | 0.58 | 1.73 | 1.87 | 3.26 | 1.14 | 1.46 | 0.31 | 2.62 | 0.59 | 0.82 | 0.08 | 1.21 | 0.31 |
| 1/20/2010 | 1/21/2010 | 163 |  |  |  |  |  |  | 0.90 | 0.30 |  |  |  |  |  |  |
| 1/21/2010 | 1/22/2010 | 165 |  |  | 0.95 | 1.87 |  |  | 0.21 | 0.30 | 1.00 | 0.57 | 0.32 | 0.08 | 0.12 | 0.31 |
| 1/22/2010 | 1/25/2010 | 118 |  |  |  |  |  |  | 0.95 | 0.30 | 0.92 | 0.57 | 0.32 | 0.08 | 0.65 | 0.31 |
| 1/25/2010 | 1/26/2010 | 115 | 1.76 | 0.58 | 1.02 | 1.87 | 3.29 | 1.14 | 1.10 | 0.31 | 1.38 | 0.57 | 0.63 | 0.08 | 0.67 | 0.31 |

Empty cells- data is not available

## H1.2: Toronto

| | | | hexane | | benzene | | heptane | | toluene | | octane | | ethylbenzene | | p,m-xylene | | o-xylene | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Start Date | End Date | Crtdg | t[OH][a] | $s_{t[OH]}$[b] | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ |
| 10/13/2009 | 10/14/2009 | 117 | 4.40 | 0.60 | 1.13 | 1.87 | | | 1.96 | 0.31 | | | 2.84 | 0.59 | 0.96 | 0.08 | 1.33 | 0.31 |
| 10/19/2009 | 10/20/2009 | 100 | 3.83 | 0.59 | 3.90 | 1.88 | | | 2.03 | 0.32 | 5.60 | 1.17 | 2.55 | 0.59 | 1.01 | 0.08 | 1.44 | 0.31 |
| 10/20/2009 | 10/21/2009 | 29 | 2.13 | 0.58 | 1.14 | 1.87 | | | 1.16 | 0.31 | 7.38 | 1.47 | 1.99 | 0.58 | 0.73 | 0.08 | 0.73 | 0.31 |
| 10/21/2009 | 10/22/2009 | 84 | 3.65 | 0.59 | 4.08 | 1.88 | 0.83 | 1.06 | 2.03 | 0.32 | 3.08 | 0.80 | 2.84 | 0.59 | 1.20 | 0.08 | 1.62 | 0.31 |
| 10/22/2009 | 10/23/2009 | 25 | 1.29 | 0.58 | | | | | 1.65 | 0.31 | 8.97 | 1.74 | 2.97 | 0.60 | 1.01 | 0.08 | 1.64 | 0.31 |
| 10/23/2009 | 10/23/2009 | 125 | | | -2.43 | 1.88 | | | -0.23 | 0.30 | | | | | | | | |
| 10/23/2009 | 10/26/2009 | 105 | 1.56 | 0.58 | | | | | | | 2.71 | 0.76 | | | | | | |
| 10/26/2009 | 10/27/2009 | 127 | 3.55 | 0.59 | 3.79 | 1.88 | | | 0.88 | 0.30 | -0.50 | 0.58 | 1.36 | 0.57 | 0.44 | 0.08 | 0.48 | 0.31 |
| 10/27/2009 | 10/28/2009 | 129 | | | 2.48 | 1.88 | | | 1.83 | 0.31 | 1.38 | 0.62 | 2.92 | 0.59 | 0.98 | 0.08 | 1.34 | 0.31 |
| 10/28/2009 | 10/29/2009 | 118 | | | -2.25 | 1.88 | | | 1.76 | 0.31 | -1.36 | 0.62 | 3.02 | 0.60 | 1.18 | 0.08 | 0.00 | 0.00 |
| 10/29/2009 | 10/30/2009 | 110 | | | | | | | 1.12 | 0.31 | -2.96 | 0.79 | 2.53 | 0.59 | 0.87 | 0.08 | 1.26 | 0.31 |
| 10/30/2009 | 10/30/2009 | 103 | -0.99 | 0.58 | -1.42 | 1.87 | | | 0.92 | 0.30 | | | 1.35 | 0.57 | 0.54 | 0.08 | | |
| 10/30/2009 | 11/2/2009 | 101 | | | | | | | | | | | | | | | | |
| 11/2/2009 | 11/3/2009 | 48 | | | -0.96 | 1.87 | 1.61 | 1.07 | 0.23 | 0.30 | -0.87 | 0.59 | -1.20 | 0.57 | -0.36 | 0.08 | -0.68 | 0.31 |
| 11/3/2009 | 11/4/2009 | 23 | | | -0.16 | 1.87 | | | 0.34 | 0.30 | 15.49 | 2.89 | -1.69 | 0.57 | -0.48 | 0.08 | -0.54 | 0.31 |
| 11/4/2009 | 11/5/2009 | 120 | | | -1.27 | 1.87 | | | 0.44 | 0.30 | | | -0.71 | 0.57 | -0.09 | 0.08 | -0.35 | 0.31 |
| 11/5/2009 | 11/6/2009 | 21 | -2.02 | 0.58 | | | | | 0.89 | 0.30 | | | 0.49 | 0.56 | 0.22 | 0.08 | 0.13 | 0.31 |
| 11/6/2009 | 11/6/2009 | 114 | | | -0.55 | 1.87 | | | 0.94 | 0.30 | -1.63 | 0.64 | 0.36 | 0.56 | -0.16 | 0.08 | | |
| 11/6/2009 | 11/7/2009 | 121 | | | -1.36 | 1.87 | | | 0.48 | 0.30 | | | -2.00 | 0.58 | -0.64 | 0.08 | | |
| 11/7/2009 | 11/8/2009 | 18 | | | 0.61 | 1.87 | 2.67 | 1.11 | 1.34 | 0.31 | | | 1.64 | 0.57 | 0.39 | 0.08 | 0.64 | 0.31 |
| 11/8/2009 | 11/9/2009 | 130 | | | 4.52 | 1.89 | | | 2.03 | 0.32 | | | 1.36 | 0.57 | 0.52 | 0.08 | 0.77 | 0.31 |
| 11/9/2009 | 11/10/2009 | 107 | -0.89 | 0.58 | 4.31 | 1.89 | | | 0.34 | 0.30 | | | -0.09 | 0.56 | 0.12 | 0.08 | | |

| | | | hexane | | benzene | | heptane | | toluene | | octane | | ethylbenzene | | p,m-xylene | | o-xylene | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Start Date | End Date | Crtdg | t[OH][a] | $s_{t[OH]}$[b] | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ |
| 11/10/2009 | 11/11/2009 | 13 | | | 4.84 | 1.89 | | | 0.11 | 0.30 | | | 0.49 | 0.56 | 0.21 | 0.08 | | |
| 11/11/2009 | 11/12/2009 | 10 | | | | | | | -0.23 | 0.30 | | | -0.59 | 0.57 | -0.09 | 0.08 | | |
| 11/12/2009 | 11/13/2009 | 18 | | | | | 2.67 | 1.11 | 1.34 | 0.31 | | | 1.64 | 0.57 | 0.39 | 0.08 | 0.64 | 0.31 |
| 11/13/2009 | 11/16/2009 | 14 | 0.30 | 0.58 | 0.82 | 1.87 | -1.59 | 1.07 | 0.16 | 0.30 | | | -0.33 | 0.56 | -0.10 | 0.08 | | |
| 11/16/2009 | 11/17/2009 | 55 | -1.02 | 0.58 | | | 0.90 | 1.06 | -0.17 | 0.30 | | | -0.52 | 0.56 | -0.07 | 0.08 | | |
| 11/17/2009 | 11/18/2009 | 126 | | | 7.14 | 1.91 | 3.25 | 1.14 | -0.02 | 0.30 | | | -0.42 | 0.56 | | | | |
| 11/19/2009 | 11/20/2009 | 134 | | | 3.99 | 1.88 | | | -0.21 | 0.30 | 2.72 | 0.76 | 1.57 | 0.57 | 0.60 | 0.08 | 0.74 | 0.31 |
| 11/20/2009 | 11/23/2009 | 56 | | | | | | | | | | | | | | | | |
| 11/23/2009 | 11/24/2009 | 69 | | | | | | | 2.08 | 0.32 | | | 0.79 | 0.57 | 0.32 | 0.08 | 0.33 | 0.31 |
| 11/24/2009 | 11/26/2009 | 15 | | | | | 3.43 | 1.15 | 0.86 | 0.30 | | | 1.61 | 0.57 | 0.67 | 0.08 | 0.85 | 0.31 |
| 11/26/2009 | 11/27/2009 | 81 | 1.60 | 0.58 | | | | | 2.14 | 0.32 | 2.99 | 0.79 | 1.55 | 0.57 | 0.58 | 0.08 | 0.83 | 0.31 |
| 11/27/2009 | 11/30/2009 | 44 | | | 3.59 | 1.88 | | | 0.80 | 0.30 | | | 2.32 | 0.58 | 0.83 | 0.08 | 1.09 | 0.31 |
| 11/30/2009 | 31/11/2009 | 124 | -1.11 | 0.58 | 0.98 | 1.87 | | | -0.03 | 0.30 | 15.49 | 2.89 | -0.15 | 0.56 | 0.001 | 0.08 | -0.11 | 0.31 |
| 12/1/2009 | 12/2/2009 | 102 | | | | | | | 0.46 | 0.30 | | | -0.48 | 0.56 | -0.13 | 0.08 | 0.63 | 0.31 |
| 12/2/2009 | 12/3/2009 | 39 | | | | | | | 0.53 | 0.30 | | | 0.99 | 0.57 | 0.37 | 0.08 | 0.33 | 0.31 |
| 12/3/2009 | 12/4/2009 | 30 | | | | | | | 0.41 | 0.30 | | | 1.37 | 0.57 | 0.50 | 0.08 | -0.15 | 0.31 |
| 12/4/2009 | 12/7/2009 | 8 | | | 0.95 | 1.87 | | | 0.29 | 0.30 | | | 1.21 | 0.57 | 0.55 | 0.08 | 0.43 | 0.31 |
| 12/7/2009 | 12/8/2009 | 46 | 1.38 | 0.58 | | | | | 0.31 | 0.30 | -2.79 | 0.77 | -0.61 | 0.57 | -0.13 | 0.08 | -0.53 | 0.31 |
| 12/8/2009 | 12/9/2009 | 59 | | | | | -3.52 | -1.15 | 0.41 | 0.30 | | | | | | | -0.56 | 0.31 |
| 12/9/2009 | 12/10/2009 | 112 | 1.31 | 0.58 | 2.21 | 1.88 | | | 2.55 | 0.32 | 5.91 | 1.22 | 2.07 | 0.58 | 0.90 | 0.08 | 0.93 | 0.31 |
| 12/10/2009 | 12/11/2009 | 148 | | | 2.88 | 1.88 | | | 0.86 | 0.30 | | | 0.53 | 0.56 | 0.19 | 0.08 | 0.18 | 0.31 |
| 12/11/2009 | 12/14/2009 | 140 | | | 1.17 | 1.87 | | | 0.82 | 0.30 | | | 0.64 | 0.57 | 0.25 | 0.08 | 0.33 | 0.31 |
| 12/14/2009 | 12/15/2009 | 24 | | | | | | | 0.22 | 0.30 | | | 1.06 | 0.57 | 0.42 | 0.08 | 0.43 | 0.31 |
| 12/15/2009 | 12/16/2009 | 138 | | | | | | | | | | | | | | | | |

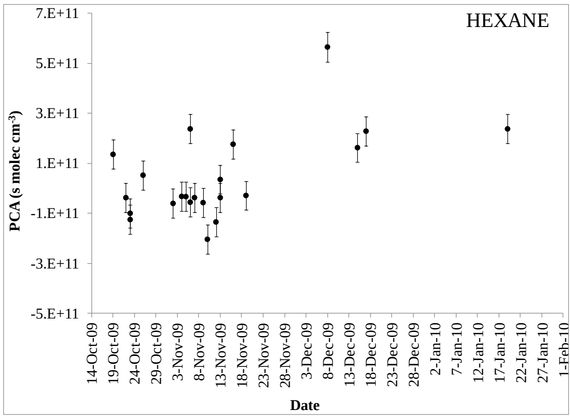
| | | | hexane | | benzene | | heptane | | toluene | | octane | | ethylbenzene | | p,m-xylene | | o-xylene | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Start Date | End Date | Crtdg | t[OH][a] | $s_{t[OH]}$[b] | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ |
| 12/16/2009 | 12/17/2009 | 155 | | | -1.06 | 1.87 | | | 0.59 | 0.30 | | | -0.08 | 0.56 | 0.05 | 0.08 | -0.04 | 0.31 |
| 12/17/2009 | 12/18/2009 | 145 | | | | | | | 0.16 | 0.30 | | | 1.96 | 0.58 | 0.84 | 0.08 | 1.27 | 0.31 |
| 1/18/2010 | 1/19/2010 | 166 | -1.48 | 0.58 | | | | | 0.04 | 0.30 | | | -0.14 | 0.56 | 0.04 | 0.08 | -0.24 | 0.31 |
| 1/19/2010 | 1/20/2010 | 139 | 2.52 | 0.58 | | | | | 0.12 | 0.30 | 3.40 | 0.84 | 1.09 | 0.57 | 0.43 | 0.08 | | |
| 1/20/2010 | 1/21/2010 | 110 | | | 1.33 | 1.87 | | | 0.77 | 0.30 | | | 0.01 | 0.56 | 0.09 | 0.08 | | |
| 1/21/2010 | 1/25/2010 | 32 | | | | | | | -0.05 | 0.30 | | | 0.82 | 0.57 | 0.29 | 0.08 | 0.16 | 0.31 |
| 1/22/2010 | 1/25/2010 | 85 | 6.31 | 0.61 | 9.32 | 1.94 | 3.32 | 1.14 | -0.05 | 0.30 | | | -2.70 | 0.59 | -0.81 | 0.08 | | |
| 1/25/2010 | 1/26/2010 | 105 | 1.56 | 0.58 | | | | | | | 2.71 | 0.76 | | | | | | |
| 1/26/2010 | 1/27/2010 | 109 | -1.39 | 0.58 | -1.96 | 1.87 | -0.68 | 1.06 | -0.10 | 0.30 | | | -0.77 | 0.57 | -0.08 | 0.08 | -0.35 | 0.31 |
| 3/06/2010 | 3/07/2010 | 103 | | | | | | | 0.02 | 0.30 | | | 1.05 | 0.57 | 0.38 | 0.08 | -0.02 | 0.31 |
| 3/07/2010 | 3/08/2010 | 104 | | | | | | | | | | | | | | | | |
| 3/12/2010 | 3/13/2010 | 114 | -0.55 | 0.58 | 4.98 | 1.89 | | | -0.39 | 0.30 | | | | | | | | |
| 3/13/2010 | 3/14/2010 | 101 | 6.73 | 0.62 | 14.08 | 2.02 | | | 0.08 | 0.30 | 5.60 | 1.17 | 2.32 | 0.58 | 0.85 | 0.08 | 0.93 | 0.31 |
| 3/14/2010 | 3/15/2010 | 113 | | | 0.25 | 1.87 | | | 0.74 | 0.30 | | | | | | | 0.47 | 0.31 |
| 3/15/2010 | 3/16/2010 | 42 | | | 2.18 | 1.88 | | | 1.25 | 0.31 | | | 2.19 | 0.58 | 0.89 | 0.08 | 0.75 | 0.31 |
| 3/19/2010 | 3/20/2010 | 152 | | | 0.31 | 1.87 | | | 0.05 | 0.30 | | | | | | | | |
| 3/20/2010 | 3/21/2010 | 112 | 4.30 | 0.60 | | | | | 0.02 | 0.30 | -0.97 | 0.60 | 1.58 | 0.57 | 0.62 | 0.08 | 0.78 | 0.31 |
| 3/21/2010 | 3/22/2010 | 168 | -0.30 | 0.58 | 10.93 | 1.96 | | | 0.85 | 0.30 | | | | | | | | |
| 3/22/2010 | 3/23/2010 | 159 | | | | | | | 0.11 | 0.30 | | | | | | | | |
| 08/30/2010 | 08/31/2010 | 111 | | | 1.76 | 1.87 | 0.54 | 1.06 | 0.51 | 0.30 | | | 0.99 | 0.57 | 0.37 | 0.08 | | |
| 08/31/2010 | 09/01/2010 | 68 | | | | | | | 1.05 | 0.30 | | | 1.75 | 0.57 | 0.70 | 0.08 | | |
| 09/01/2010 | 09/02/2010 | 104 | | | | | | | | | | | | | | | | |

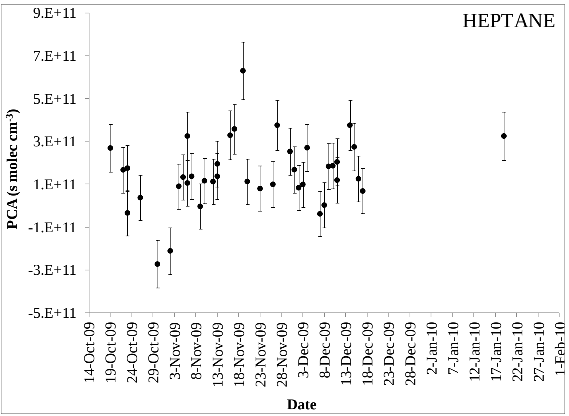
|  |  |  | hexane |  | benzene |  | heptane |  | toluene |  | octane |  | ethylbenzene |  | p,m-xylene |  | o-xylene |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Start Date | End Date | Crtdg | t[OH][a] | $s_{t[OH]}$[b] | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ | t[OH] | $s_{t[OH]}$ |
| 09/02/2010 | 09/03/2010 | 65 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 09/03/2010 | 09/04/2010 | 128 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 09/07/2010 | 09/08/2010 | 141 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 09/07/2010 | 09/08/2010 | 113 |  |  | 0.25 | 1.87 |  |  | 0.74 | 0.30 |  |  |  |  |  |  | 0.47 | 0.31 |
| 09/08/2010 | 09/09/2010 | 103 |  |  |  |  |  |  | 0.02 | 0.30 |  |  | 1.05 | 0.57 | 0.38 | 0.08 | -0.02 | 0.31 |
| 09/08/2010 | 09/09/2010 | 106 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 09/09/2010 | 09/10/2010 | 109 |  |  |  |  |  |  | 0.69 | 0.30 |  |  |  |  |  |  |  |  |
| 09/09/2010 | 09/10/2010 | 123 |  |  |  |  |  |  | 0.27 | 0.30 |  |  |  |  |  |  |  |  |
| 09/10/2010 | 09/13/2010 | 115 |  |  |  |  |  |  | 1.16 | 0.31 |  |  | 0.64 | 0.57 |  |  | 0.43 | 0.31 |
| 09/10/2010 | 09/13/2010 | 41 |  |  |  |  |  |  | -0.03 | 0.30 |  |  |  |  |  |  |  |  |
| 09/13/2010 | 09/14/2010 | 11 |  |  |  |  |  |  | -0.30 | 0.30 |  |  | -0.19 | 0.56 | 0.11 | 0.08 |  |  |
| 09/13/2010 | 09/14/2010 | 131 |  |  |  |  |  |  | -0.03 | 0.30 |  |  |  |  |  |  |  |  |
| 09/14/2010 | 09/15/2010 | 36 |  |  | 0.71 | 1.87 | -1.01 | -1.06 | 0.39 | 0.30 |  |  |  |  |  |  |  |  |
| 09/14/2010 | 09/15/2010 | 77 |  |  |  |  |  |  | 5.82 | 0.41 |  |  |  |  |  |  |  |  |
| 09/15/2010 | 09/16/2010 | 80 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 09/15/2010 | 09/16/2010 | 116 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 09/16/2010 | 09/17/2010 | 22 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 09/16/2010 | 09/17/2010 | 54 |  |  | 8.57 | 1.93 |  |  | 3.11 | 0.33 |  |  |  |  |  |  |  |  |
| 09/17/2010 | 09/20/2010 | 40 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 09/17/2010 | 09/20/2010 | 144 |  |  | -1.01 | 1.87 |  |  |  |  |  |  | -0.56 | 0.56 | -0.05 | 0.08 |  |  |

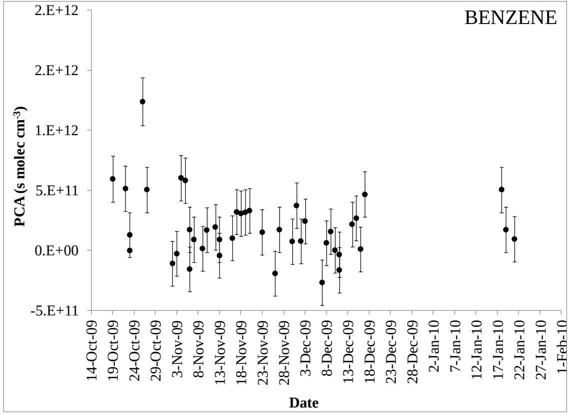
(a) $t[OH]\cdot 10^{-11}$ – Photochemical age (PCA), (b) $s_{t[OH]}$ - error determined by the propagation of errors. Empty cells- data is not available

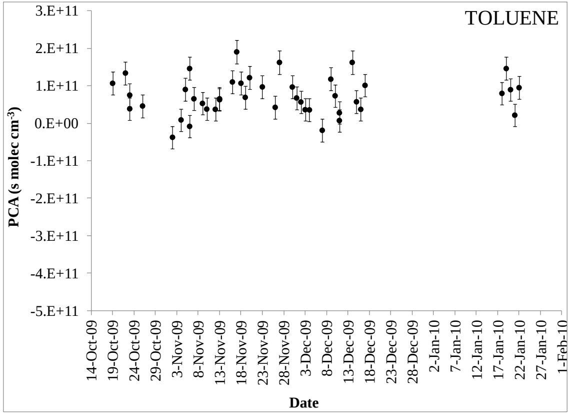
# H2: Time series for determined PCA per compound

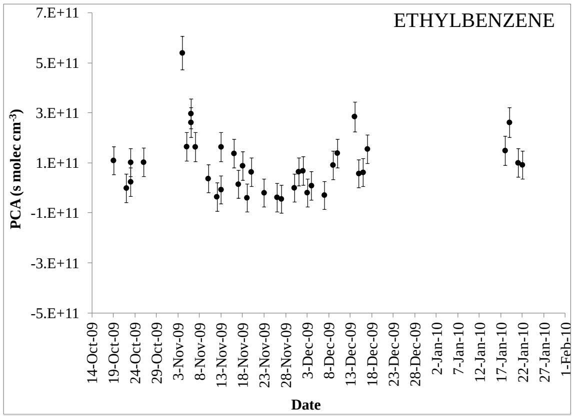
## H2.1: Egbert samples

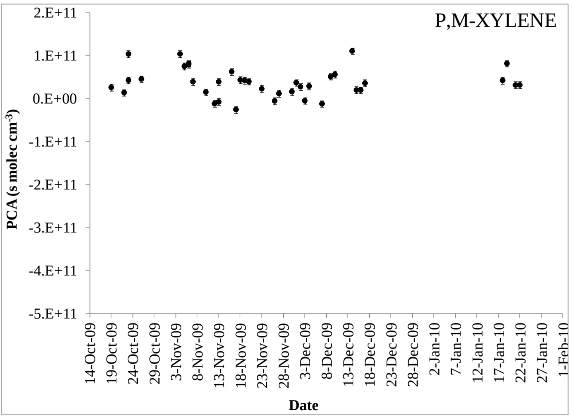


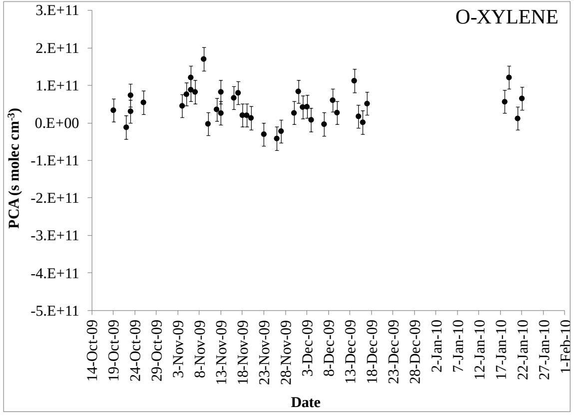




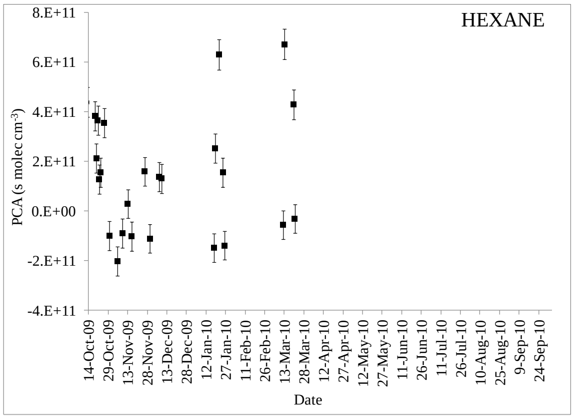


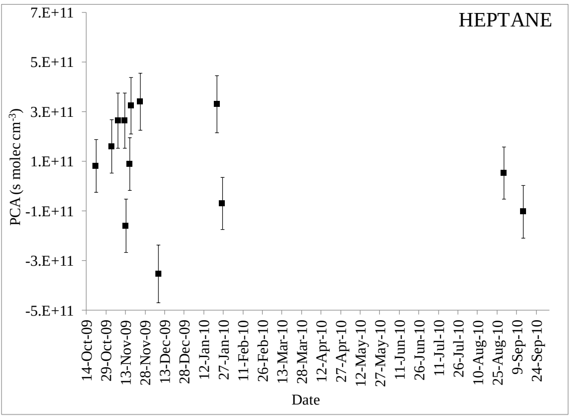

ETHYLBENZENE
PCA (s molec cm$^{-3}$)
7.E+11
5.E+11
3.E+11
1.E+11
-1.E+11
-3.E+11
-5.E+11
14-Oct-09
19-Oct-09
24-Oct-09
29-Oct-09
3-Nov-09
8-Nov-09
13-Nov-09
18-Nov-09
23-Nov-09
28-Nov-09
3-Dec-09
8-Dec-09
13-Dec-09
18-Dec-09
23-Dec-09
28-Dec-09
2-Jan-10
7-Jan-10
12-Jan-10
17-Jan-10
22-Jan-10
27-Jan-10
1-Feb-10
Date

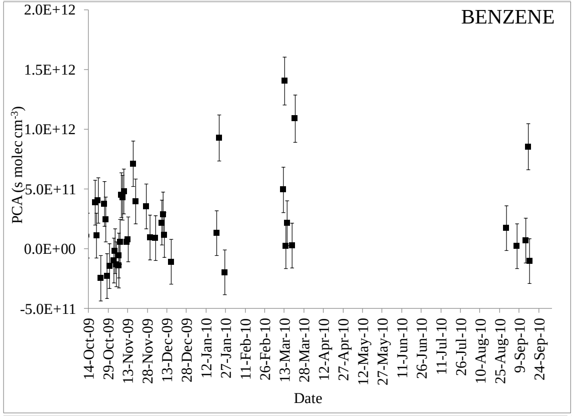

P,M-XYLENE
PCA (s molec cm$^{-3}$)
2.E+11
1.E+11
0.E+00
-1.E+11
-2.E+11
-3.E+11
-4.E+11
-5.E+11
14-Oct-09
19-Oct-09
24-Oct-09
29-Oct-09
3-Nov-09
8-Nov-09
13-Nov-09
18-Nov-09
23-Nov-09
28-Nov-09
3-Dec-09
8-Dec-09
13-Dec-09
18-Dec-09
23-Dec-09
28-Dec-09
2-Jan-10
7-Jan-10
12-Jan-10
17-Jan-10
22-Jan-10
27-Jan-10
1-Feb-10
Date

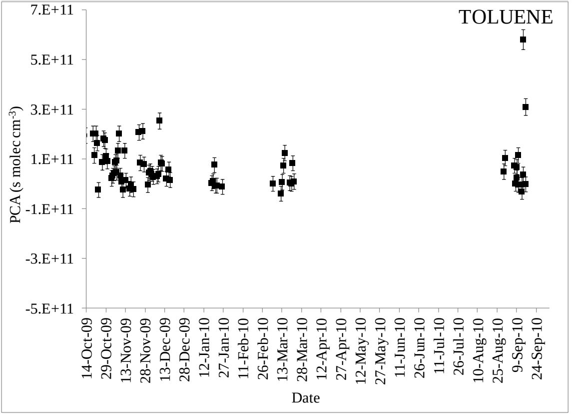

O-XYLENE
PCA (s molec cm$^{-3}$)
3.E+11
2.E+11
1.E+11
0.E+00
-1.E+11
-2.E+11
-3.E+11
-4.E+11
-5.E+11
14-Oct-09
19-Oct-09
24-Oct-09
29-Oct-09
3-Nov-09
8-Nov-09
13-Nov-09
18-Nov-09
23-Nov-09
28-Nov-09
3-Dec-09
8-Dec-09
13-Dec-09
18-Dec-09
23-Dec-09
28-Dec-09
2-Jan-10
7-Jan-10
12-Jan-10
17-Jan-10
22-Jan-10
27-Jan-10
1-Feb-10
Date

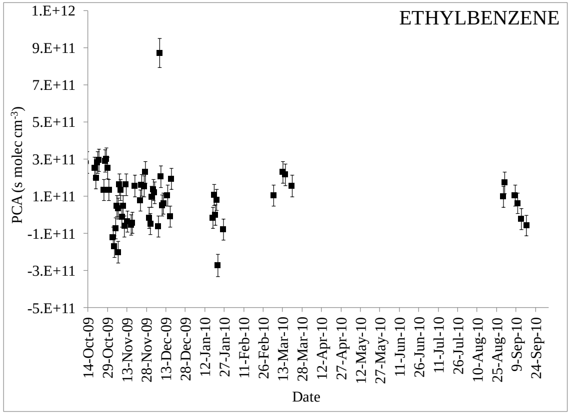
## H2.2: Toronto Samples

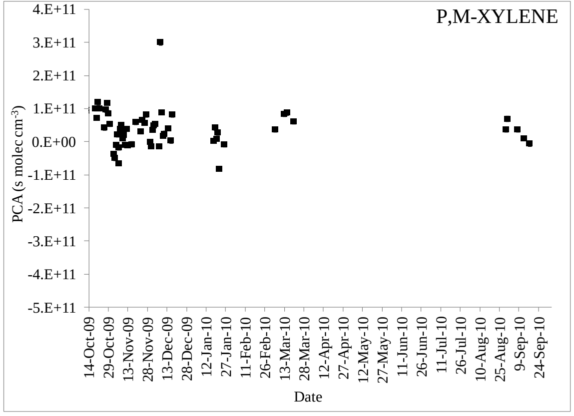


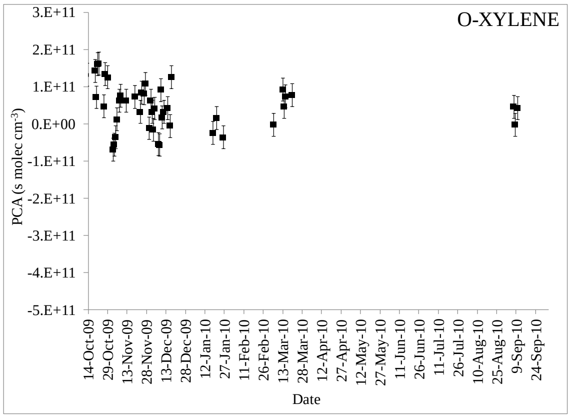


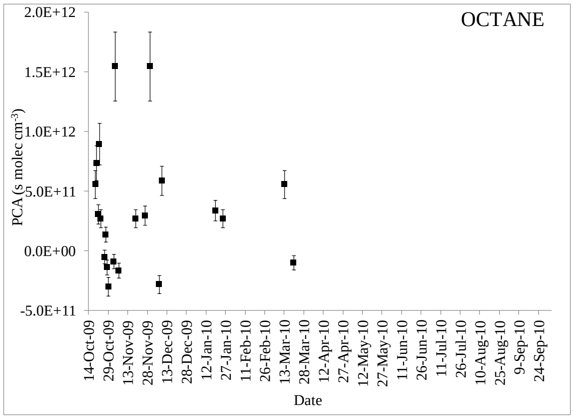






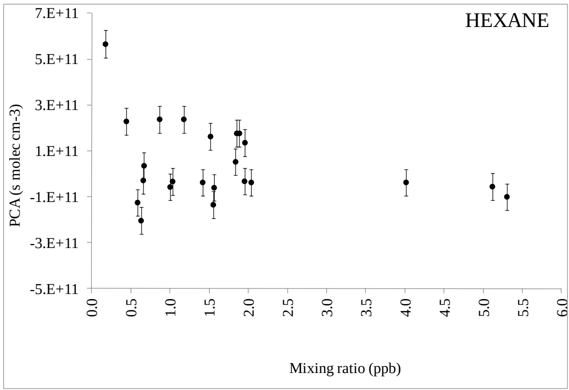


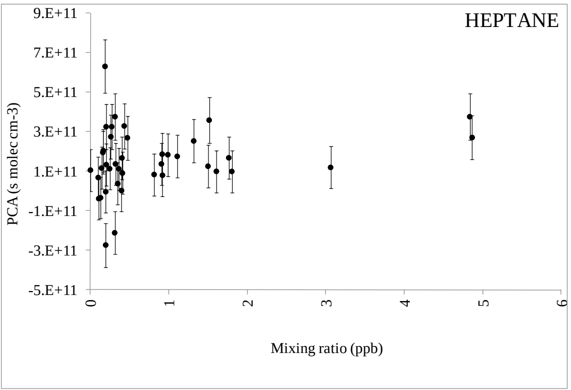

O-XYLENE
PCA (s molec cm$^{-3}$)
3.E+11
2.E+11
1.E+11
0.E+00
-1.E+11
-2.E+11
-3.E+11
-4.E+11
-5.E+11
14-Oct-09
29-Oct-09
13-Nov-09
28-Nov-09
13-Dec-09
28-Dec-09
12-Jan-10
27-Jan-10
11-Feb-10
26-Feb-10
13-Mar-10
28-Mar-10
12-Apr-10
27-Apr-10
12-May-10
27-May-10
11-Jun-10
26-Jun-10
11-Jul-10
26-Jul-10
10-Aug-10
25-Aug-10
9-Sep-10
24-Sep-10
Date

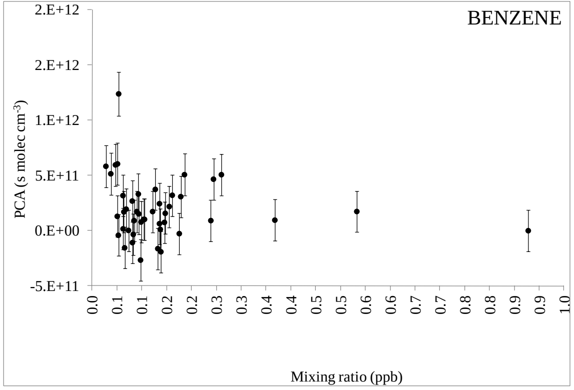

OCTANE
PCA (s molec cm$^{-3}$)
2.0E+12
1.5E+12
1.0E+12
5.0E+11
0.0E+00
-5.0E+11
14-Oct-09
29-Oct-09
13-Nov-09
28-Nov-09
13-Dec-09
28-Dec-09
12-Jan-10
27-Jan-10
11-Feb-10
26-Feb-10
13-Mar-10
28-Mar-10
12-Apr-10
27-Apr-10
12-May-10
27-May-10
11-Jun-10
26-Jun-10
11-Jul-10
26-Jul-10
10-Aug-10
25-Aug-10
9-Sep-10
24-Sep-10
Date

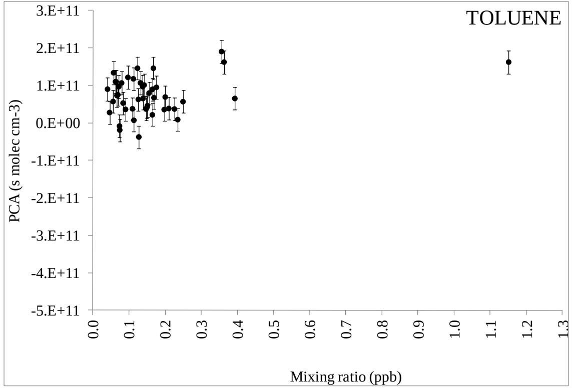
# APPENDIX I: Concentrations versus PCA determined from stable carbon isotope composition

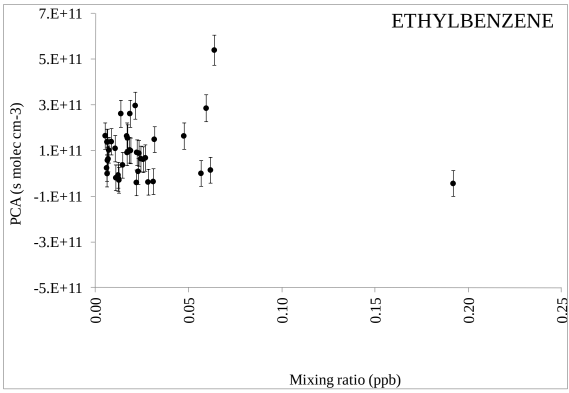
## I1: Egbert samples

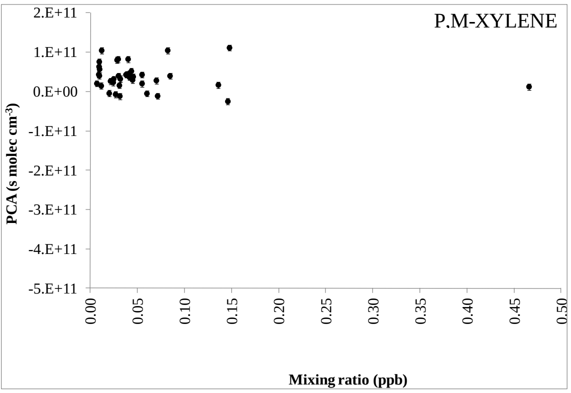


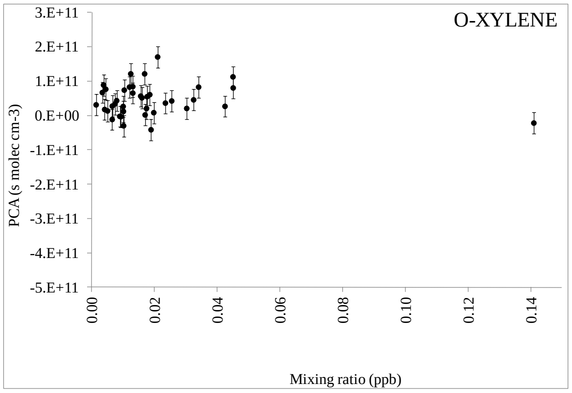




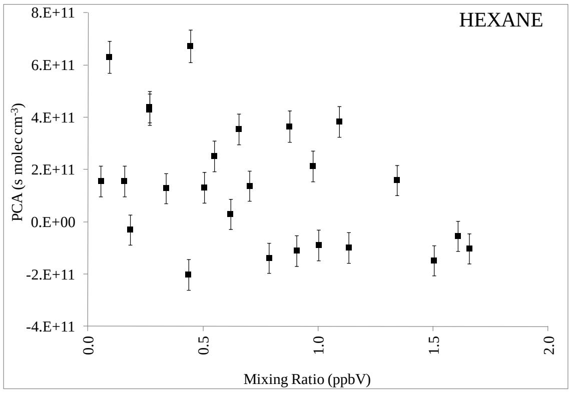


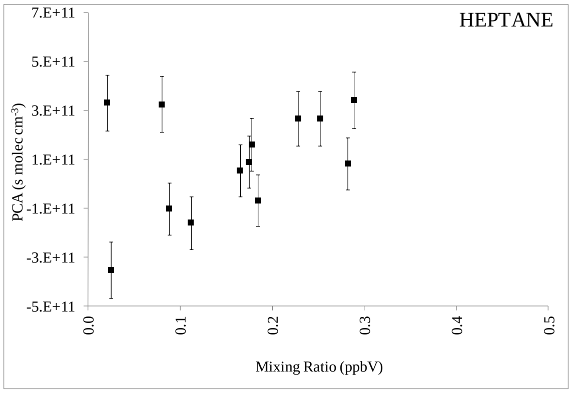


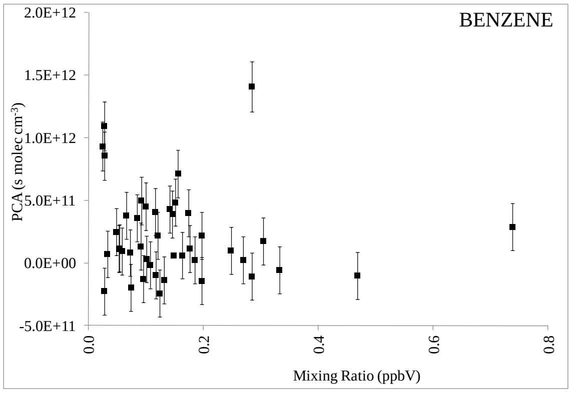


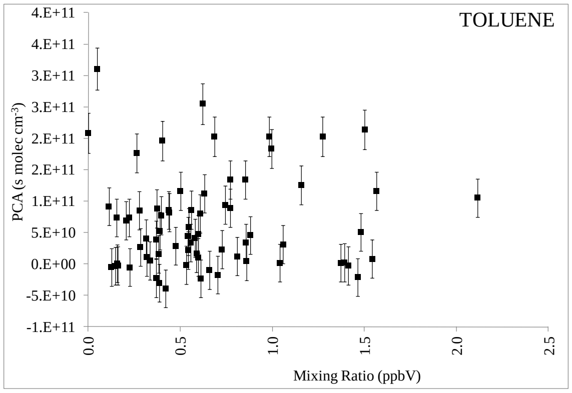

O-XYLENE
3.E+11
2.E+11
1.E+11
0.E+00
-1.E+11
-2.E+11
-3.E+11
-4.E+11
-5.E+11
PCA (s molec cm-3)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
Mixing ratio (ppb)

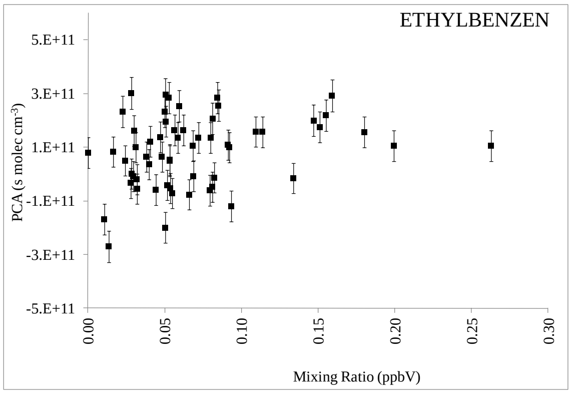
## I2: Toronto samples

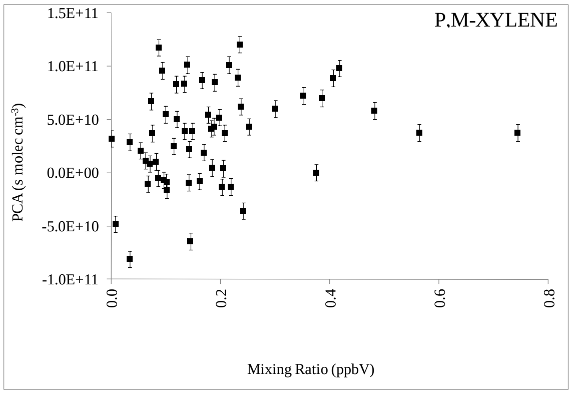


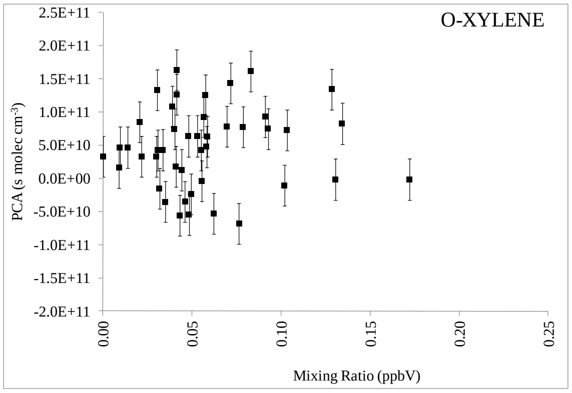






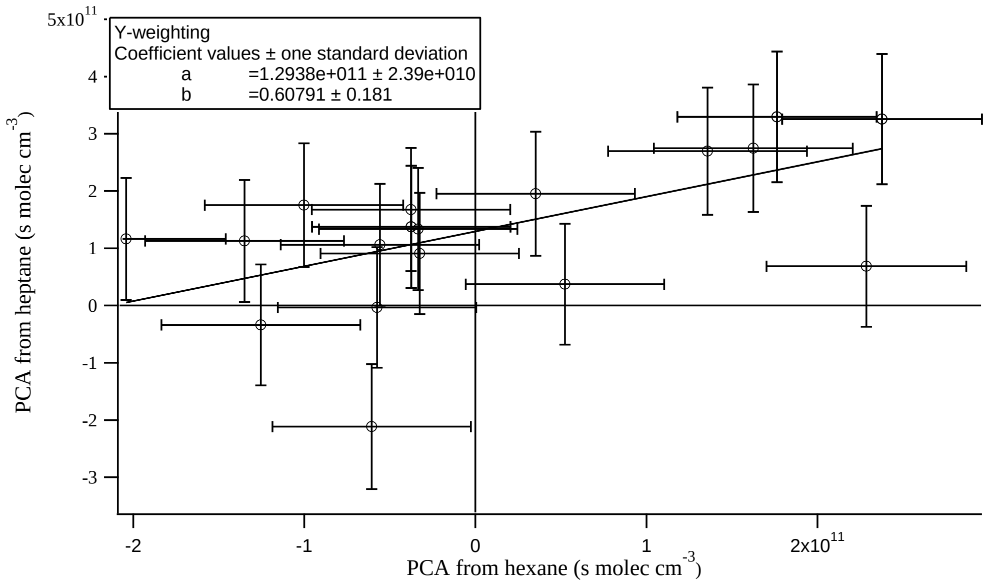


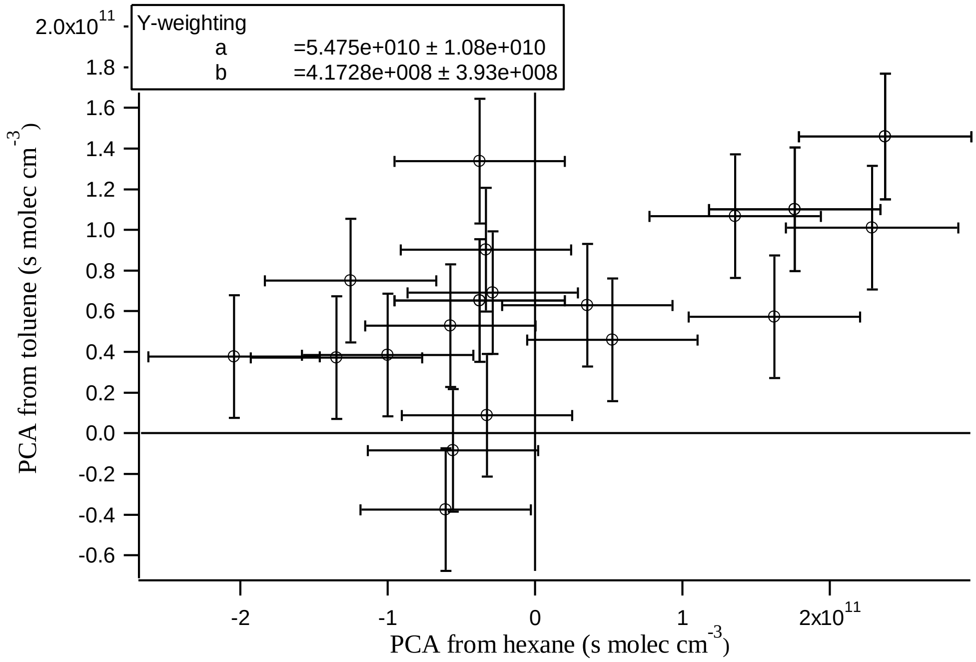


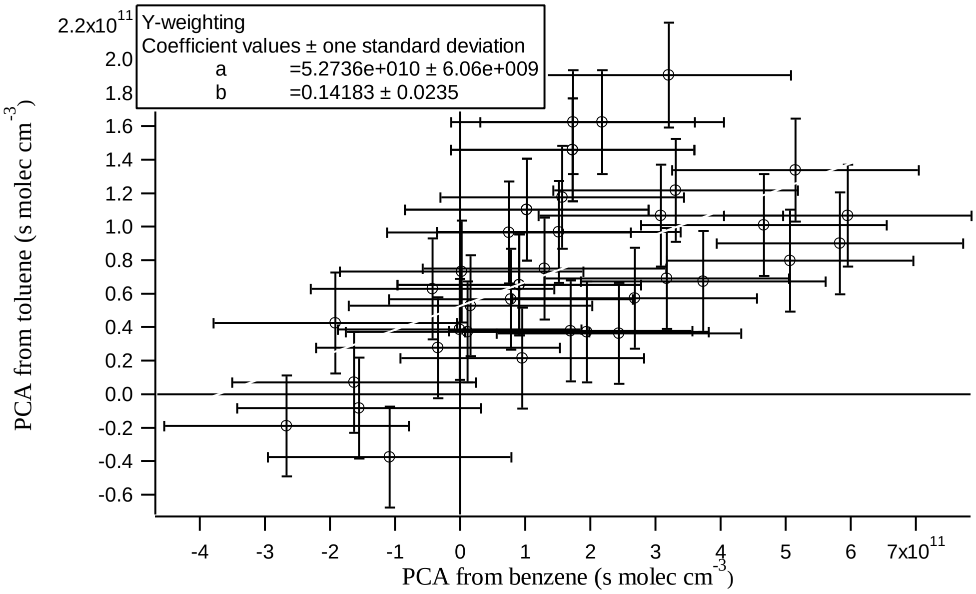

O-XYLENE
PCA (s molec cm$^{-3}$)
2.5E+11
2.0E+11
1.5E+11
1.0E+11
5.0E+10
0.0E+00
-5.0E+10
-1.0E+11
-1.5E+11
-2.0E+11
0.00
0.05
0.10
0.15
0.20
0.25
Mixing Ratio (ppbV)

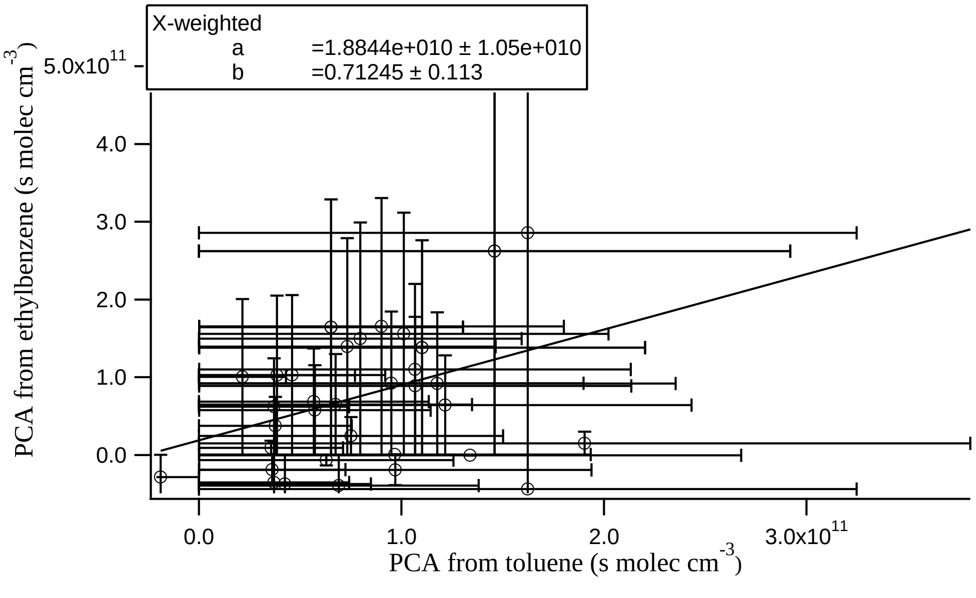
# Appendix J: Correlation of individual PCA using IGOR software (b-intercept, a- slope)

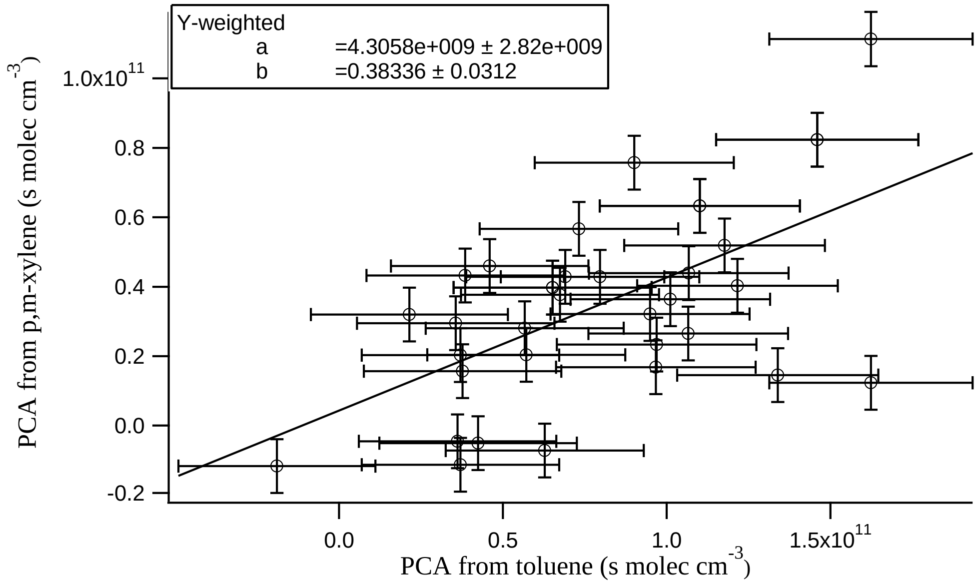
## J1: Egbert Samples, PCA correlations using IGOR using two variable analysis

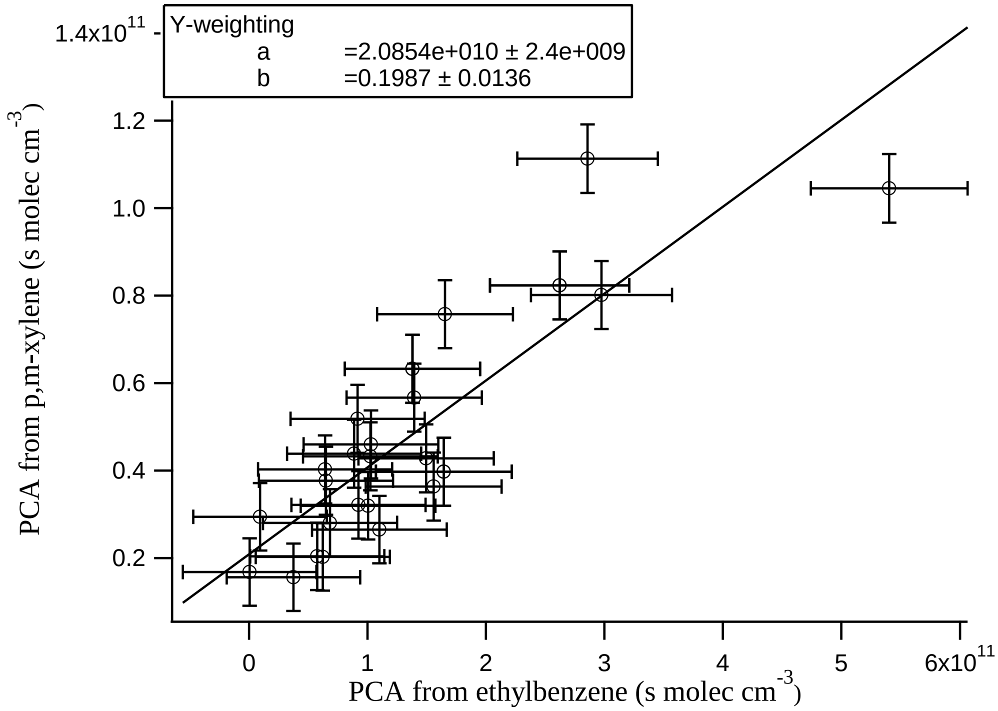


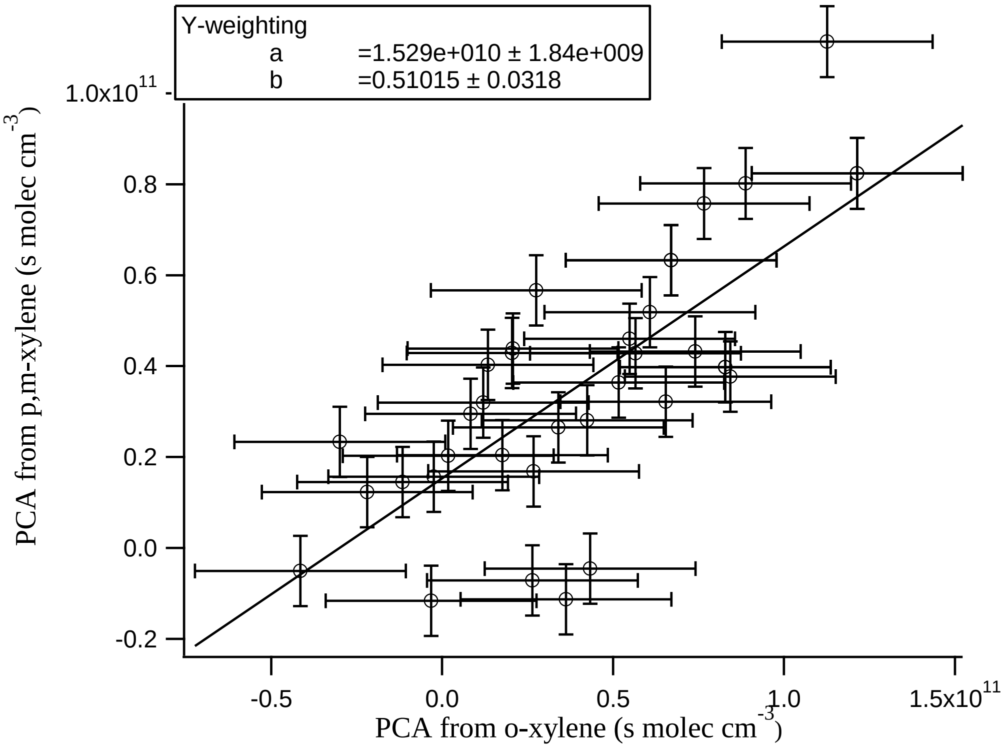



Y-weighting
Coefficient values ± one standard deviation
a =5.2736e+010 ± 6.06e+009
b =0.14183 ± 0.0235
2.2x10^11
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
PCA from toluene (s molec cm^-3)
-4
-3
-2
-1
0
1
2
3
4
5
6
7x10^11
PCA from benzene (s molec cm^-3)

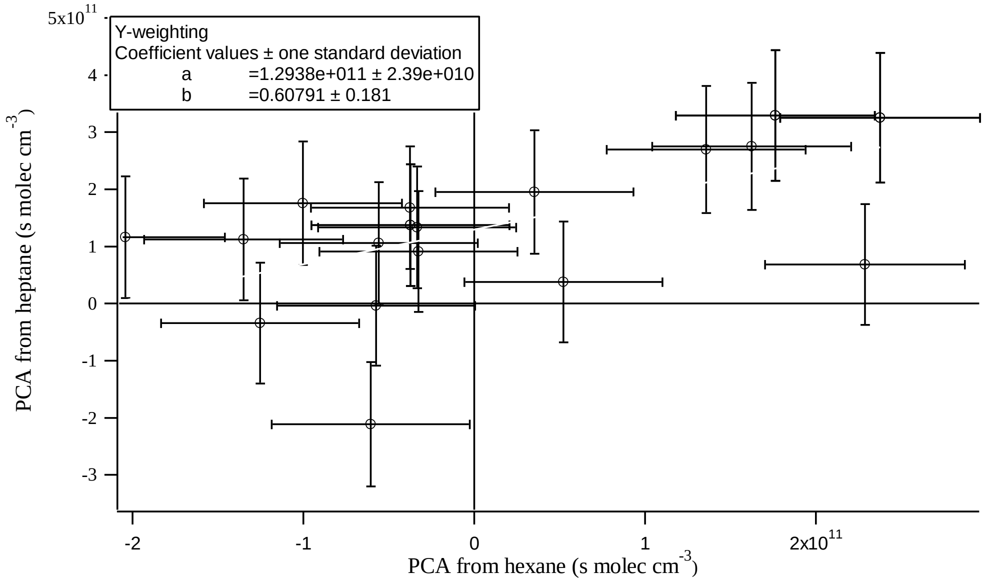

X-weighted
a =1.8844e+010 ± 1.05e+010
b =0.71245 ± 0.113
5.0x10^11
4.0
3.0
2.0
1.0
0.0
PCA from ethylbenzene (s molec cm^-3)
0.0
1.0
2.0
3.0x10^11
PCA from toluene (s molec cm^-3)

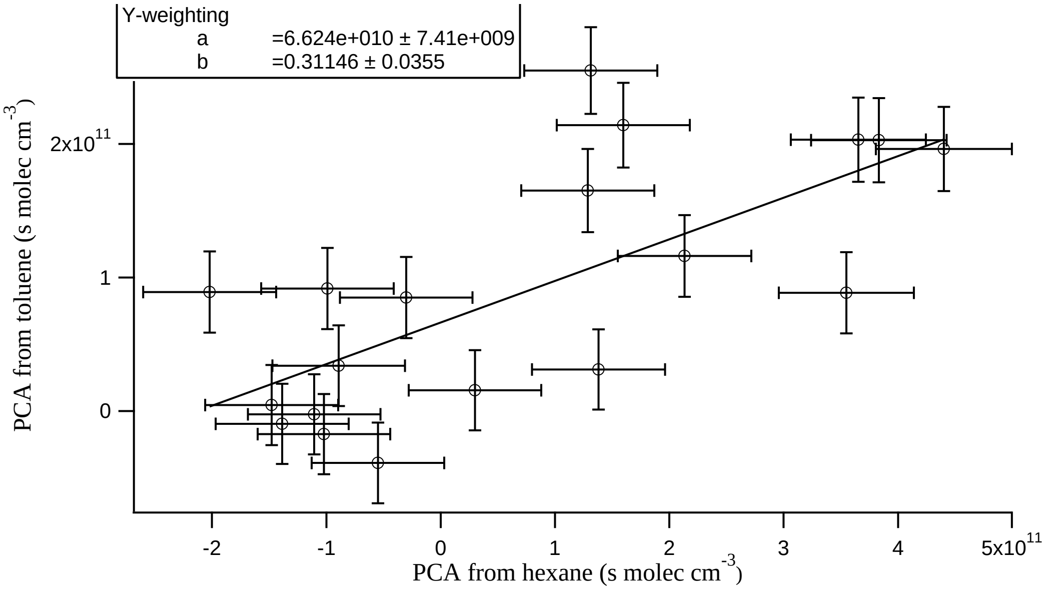

Y-weighted
a =4.3058e+009 ± 2.82e+009
b =0.38336 ± 0.0312
1.0x10^11
0.8
0.6
0.4
0.2
0.0
-0.2
PCA from p,m-xylene (s molec cm^-3)
0.0
0.5
1.0
1.5x10^11
PCA from toluene (s molec cm^-3)

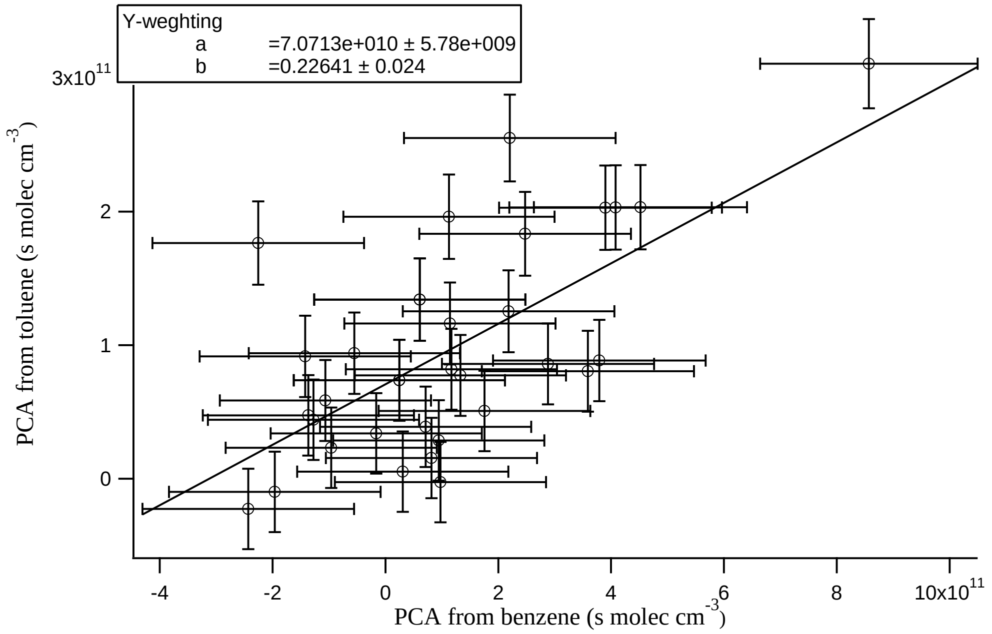

Y-weighting
a =2.0854e+010 ± 2.4e+009
b =0.1987 ± 0.0136
1.4x10^11
1.2
1.0
0.8
0.6
0.4
0.2
PCA from p,m-xylene (s molec cm^-3)
0
1
2
3
4
5
6x10^11
PCA from ethylbenzene (s molec cm^-3)

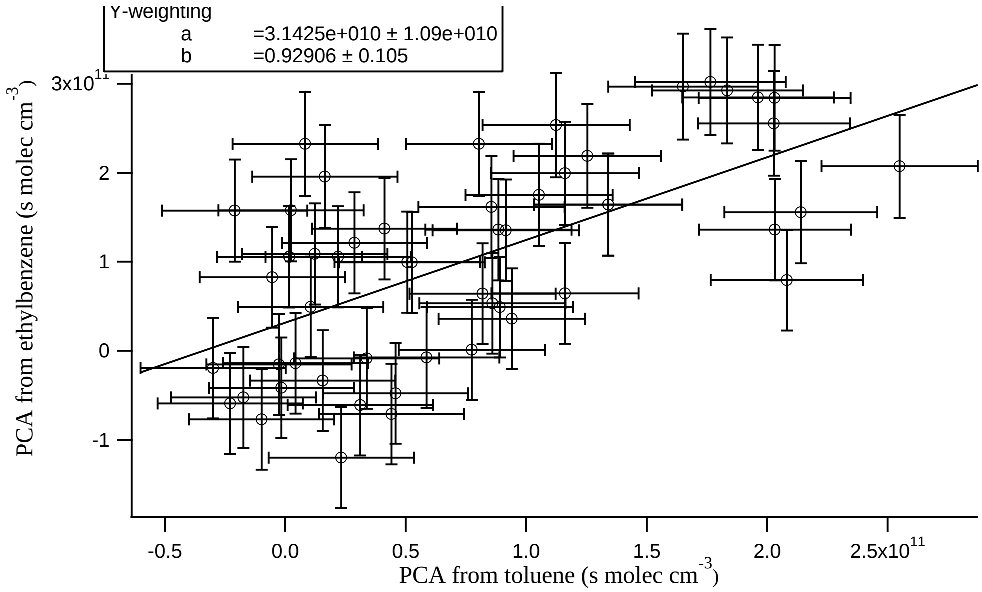

Y-weighting
a =1.529e+010 ± 1.84e+009
b =0.51015 ± 0.0318
1.0x10^11
0.8
0.6
0.4
0.2
0.0
-0.2
PCA from p,m-xylene (s molec cm^-3)
-0.5
0.0
0.5
1.0
1.5x10^11
PCA from o-xylene (s molec cm^-3)

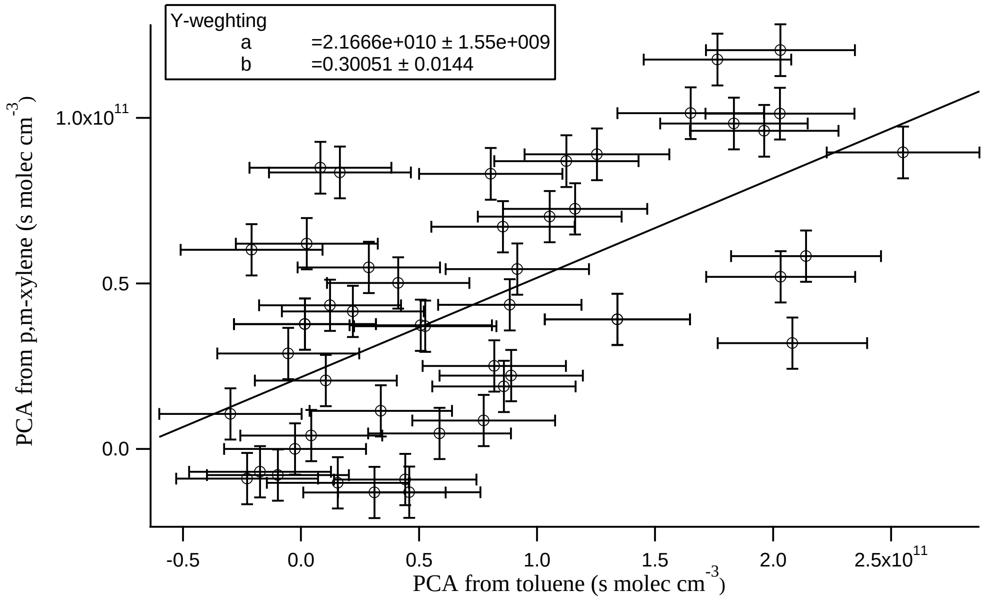
## J2: Toronto Samples, PCA correlations using IGOR using two variable analysis

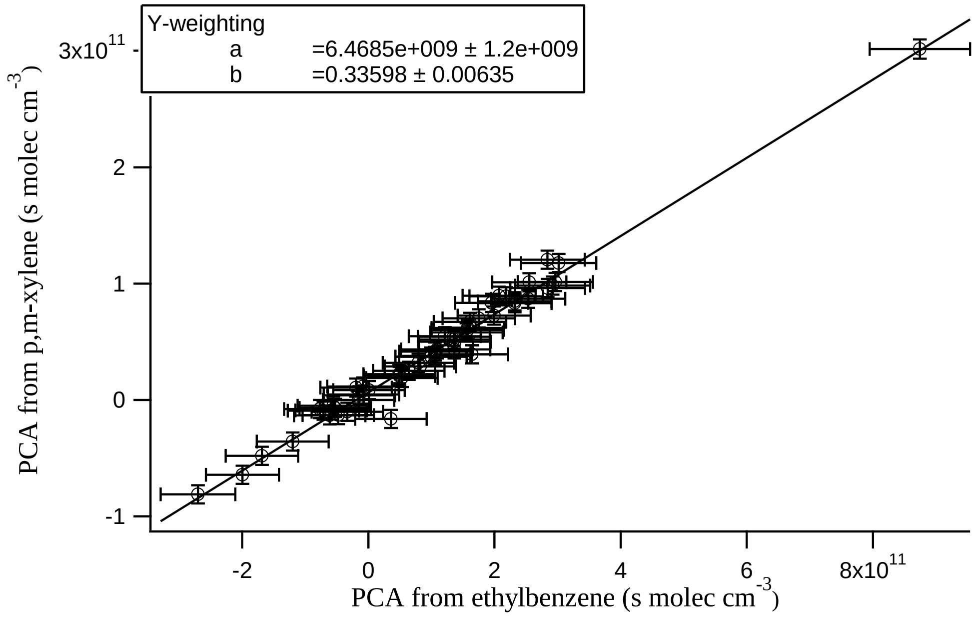


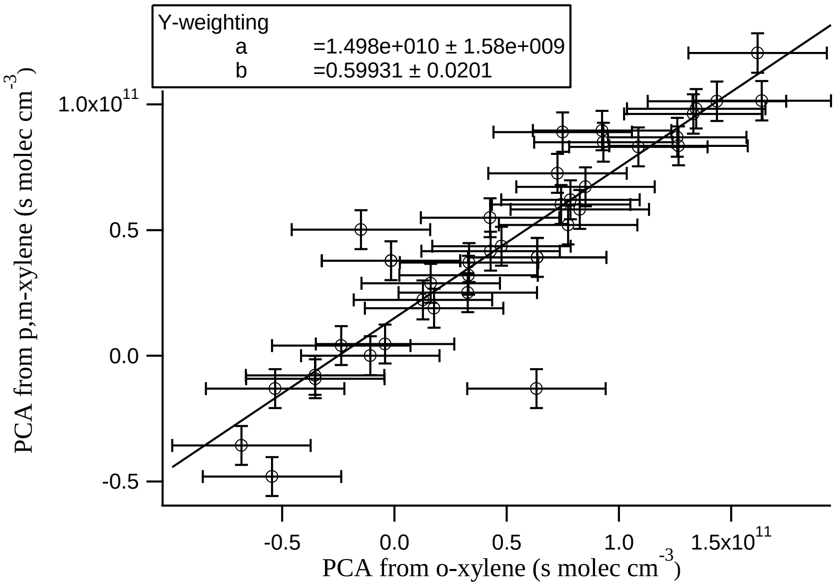



Y-weghting
a =7.0713e+010 ± 5.78e+009
b =0.22641 ± 0.024
3x10^11
2
1
0
PCA from toluene (s molec cm^-3)
-4
-2
0
2
4
6
8
10x10^11
PCA from benzene (s molec cm^-3)


Y-weighting
a =3.1425e+010 ± 1.09e+010
b =0.92906 ± 0.105
3x10^11
2
1
0
-1
PCA from ethylbenzene (s molec cm^-3)
-0.5
0.0
0.5
1.0
1.5
2.0
2.5x10^11
PCA from toluene (s molec cm^-3)

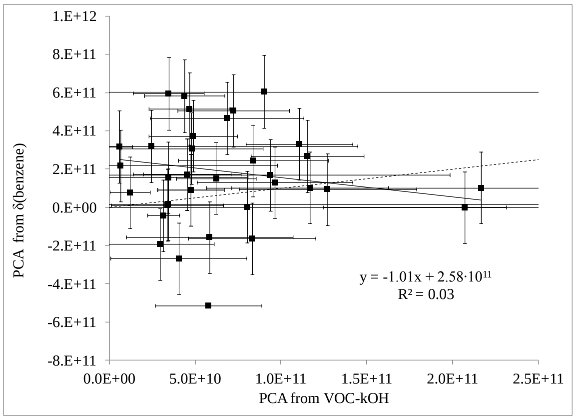

Y-weghting
a =2.1666e+010 ± 1.55e+009
b =0.30051 ± 0.0144
PCA from p,m-xylene (s molec cm-3)
1.0x10^11
0.5
0.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5x10^11
PCA from toluene (s molec cm-3)

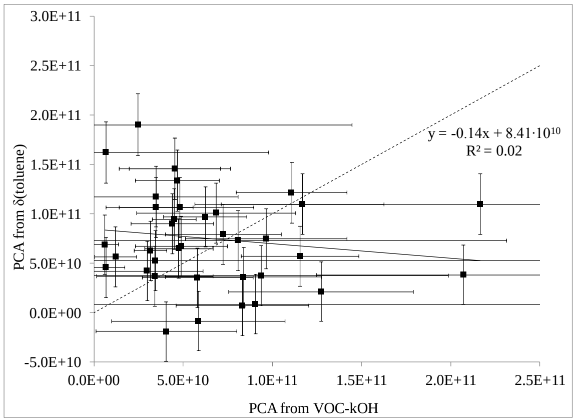

Y-weighting
a =6.4685e+009 ± 1.2e+009
b =0.33598 ± 0.00635
PCA from p,m-xylene (s molec cm-3)
3x10^11
2
1
0
-1
-2
0
2
4
6
8x10^11
PCA from ethylbenzene (s molec cm-3)

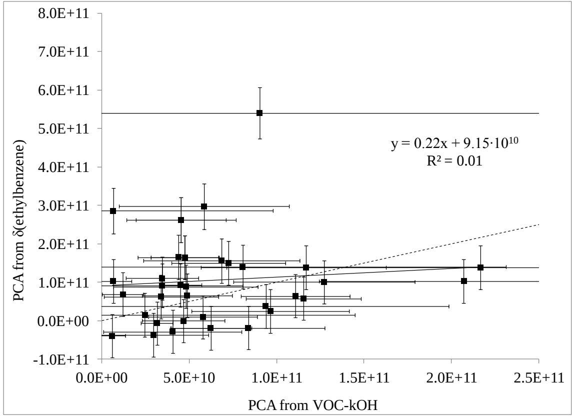

Y-weighting
a =1.498e+010 ± 1.58e+009
b =0.59931 ± 0.0201
1.0x10^11
0.5
0.0
-0.5
PCA from p,m-xylene (s molec cm^-3)
-0.5
0.0
0.5
1.0
1.5x10^11
PCA from o-xylene (s molec cm^-3)

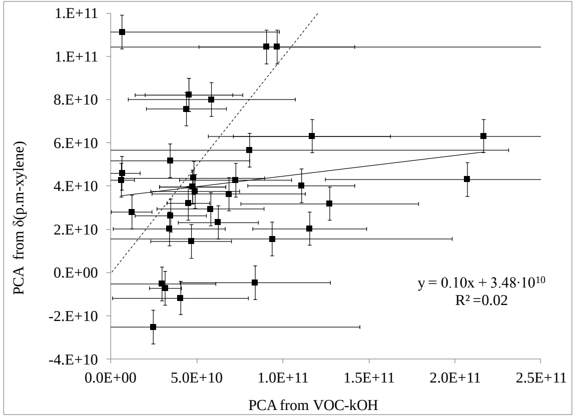
# Appendix K: Correlation of different PCA

## K1.1 PCA determined from mixing ratios of VOC and their rate constants (VOC) versus PCA determined from stable carbon isotope composition of various VOC (Egbert samples)

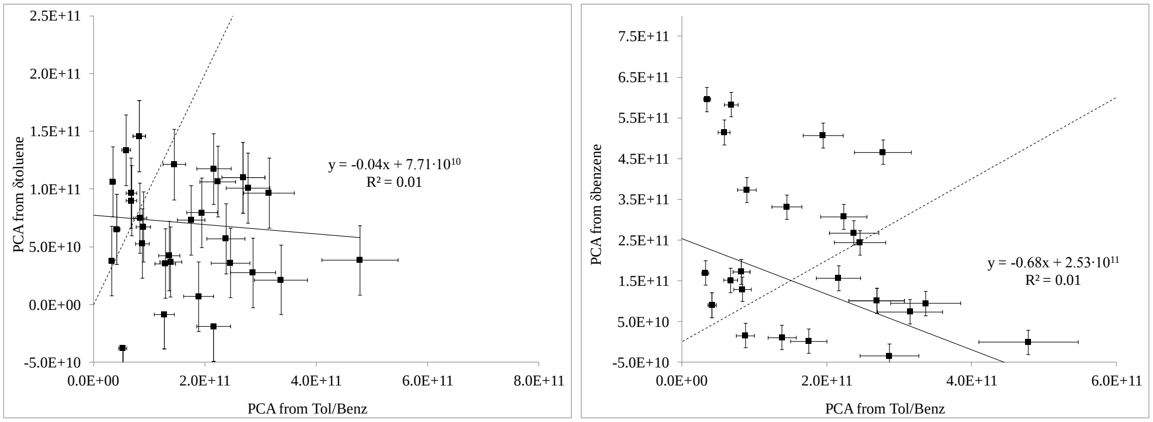




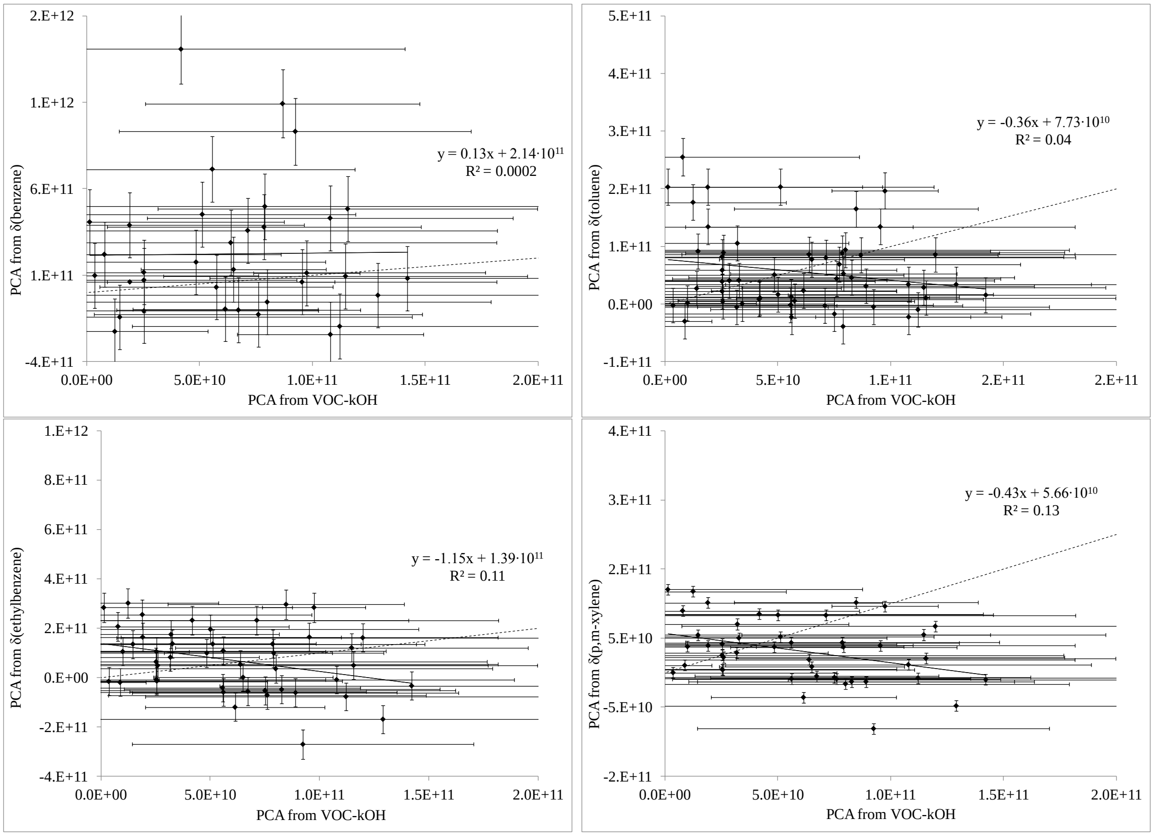




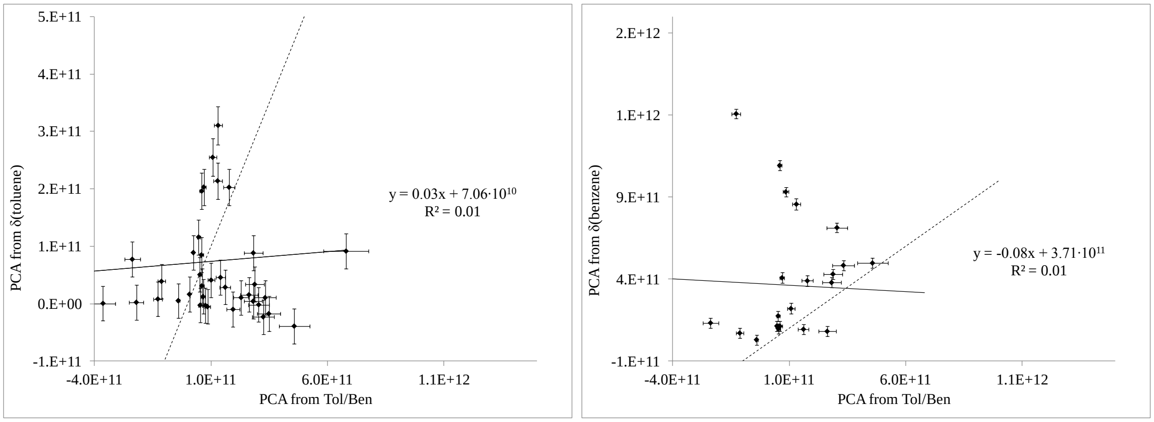
### K 1.2 PCA determined from toluene benzene ratio (using vehicle emission as a reference point) versus PCA from stable carbon isotope composition of various VOC (Egbert samples)



# K2.1 PCA determined from mixing ratios of VOC and their rate constants (VOC) versus PCA determined from stable carbon isotope composition of various VOC (Toronto samples)

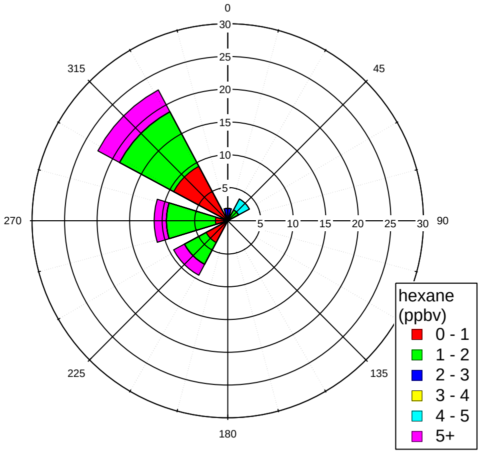


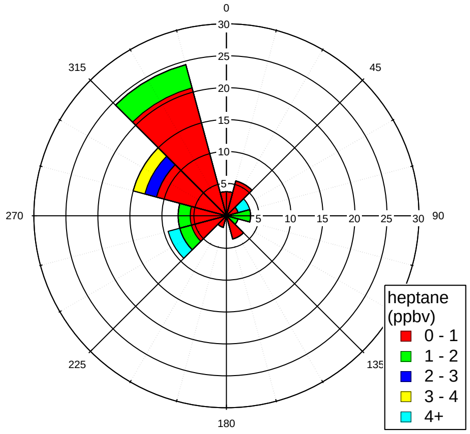
## K2.2 PCA determined from toluene benzene ratio (using vehicle emission as a reference point) versus PCA from stable carbon isotope composition of various VOC (Toronto samples)

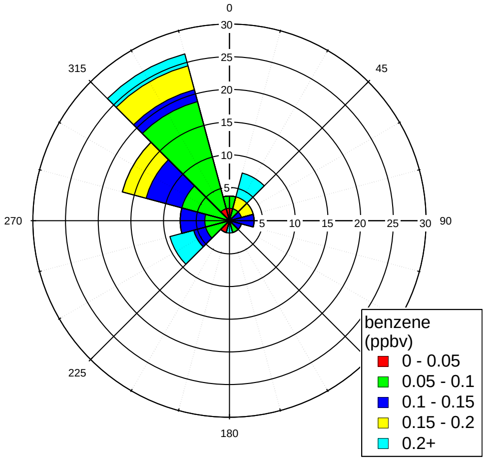


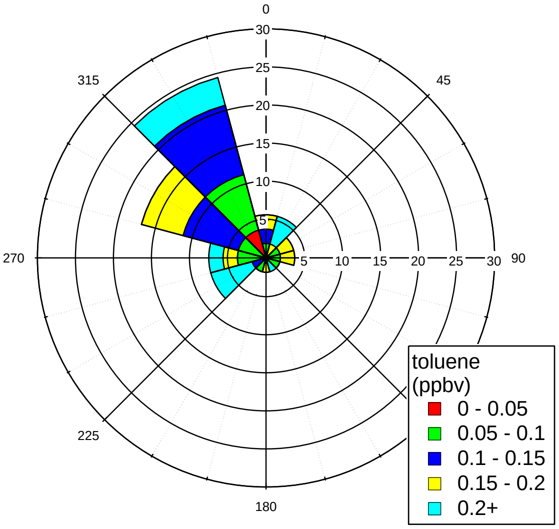
# APPENDIX L: Air parcel origins based on the air trajectory analysis and VOC concentrations

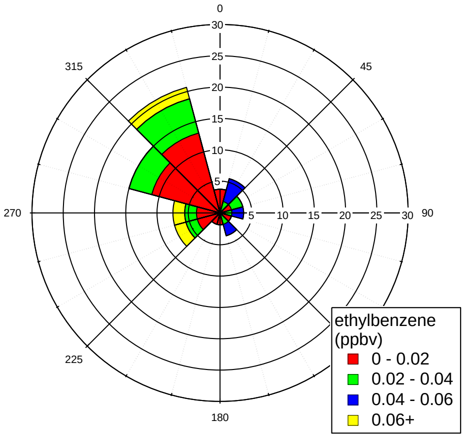
## L1: Egbert Samples

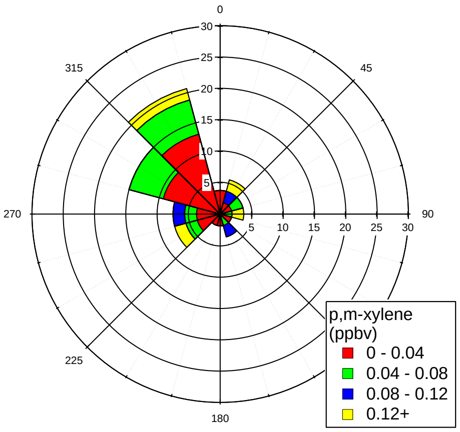




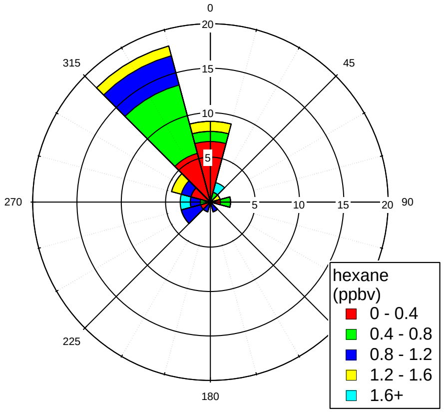


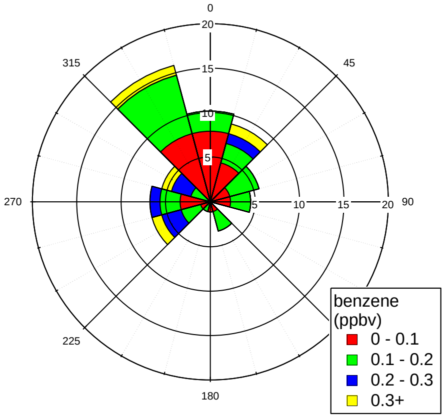


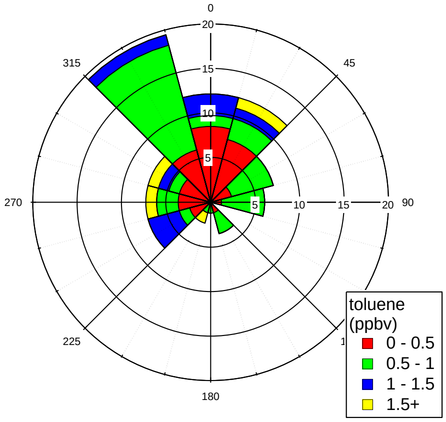

0
45
90
180
225
270
315
5
10
15
20
25
30
ethylbenzene (ppbv)
🟥 0 - 0.02
🟩 0.02 - 0.04
🟦 0.04 - 0.06
🟨 0.06+

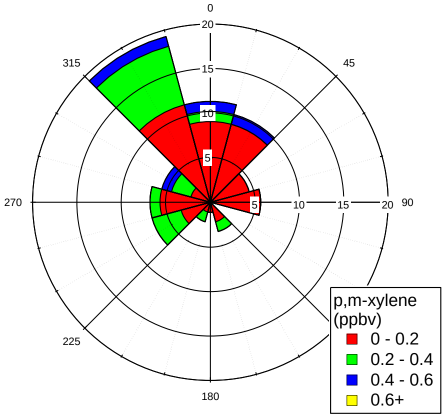

0
45
90
180
225
270
315
5
10
15
20
25
30
p,m-xylene (ppbv)
🟥 0 - 0.04
🟩 0.04 - 0.08
🟦 0.08 - 0.12
🟨 0.12+

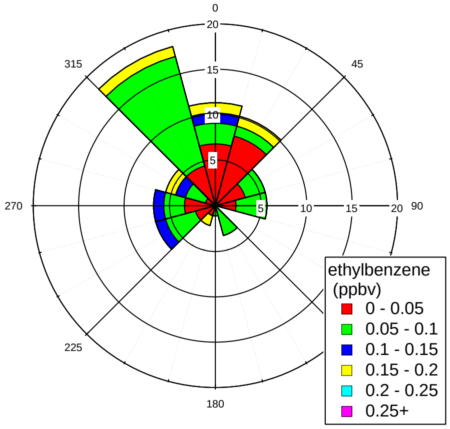
# L2: Toronto Samples





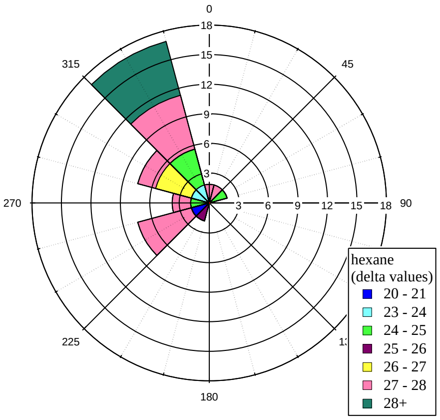


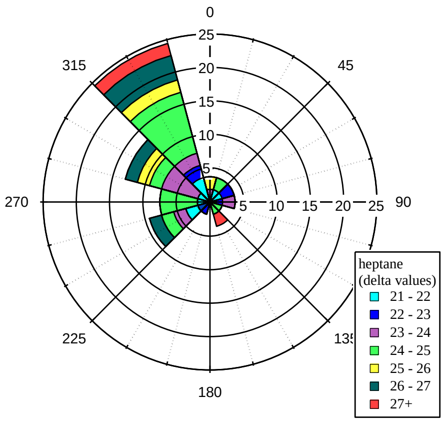


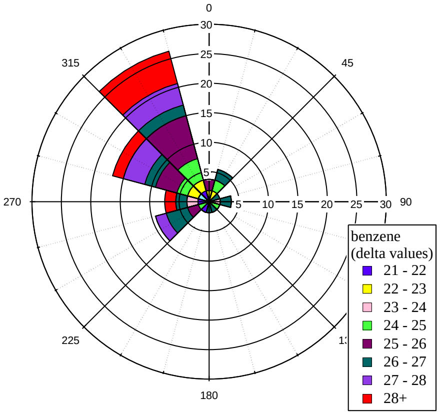


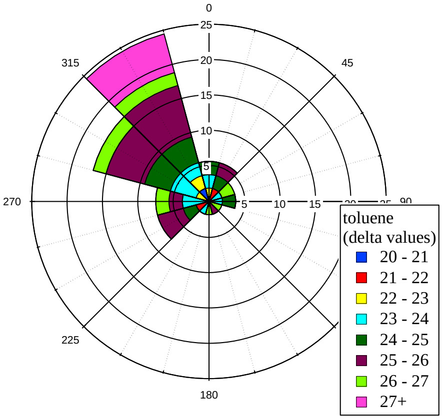
# APPENDIX M: Air parcel origins based on the air trajectory analysis and VOC isotope composition (all δ (‰) values are given as absolute numbers)

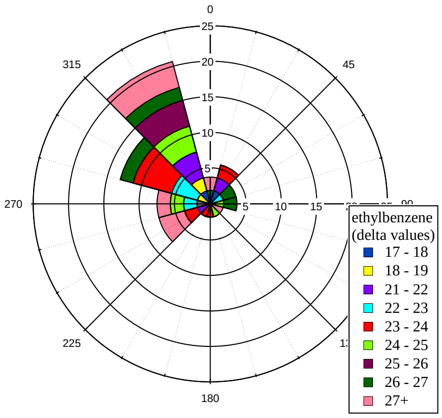
## M1: Egbert Samples

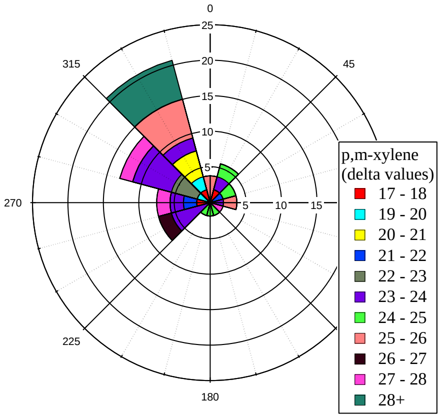


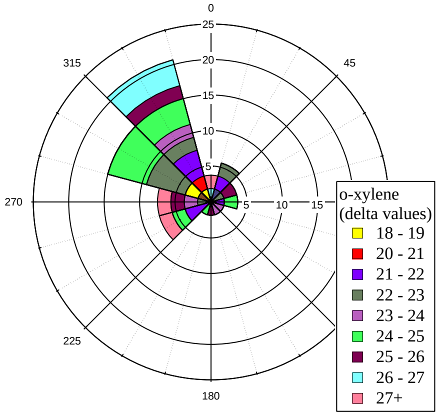




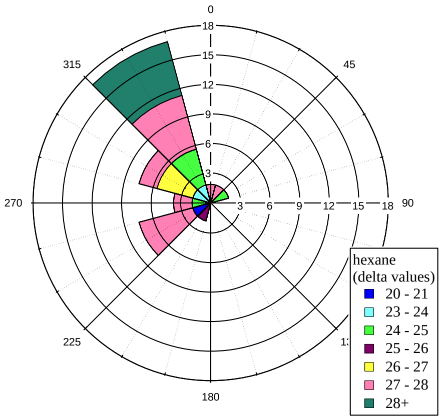


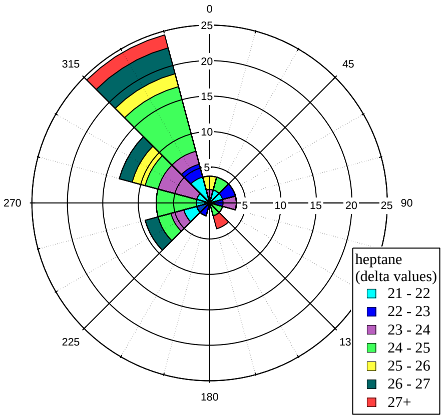

0
45
90
135
180
225
270
315
5
10
15
20
25
ethylbenzene
(delta values)
17 - 18
18 - 19
21 - 22
22 - 23
23 - 24
24 - 25
25 - 26
26 - 27
27+

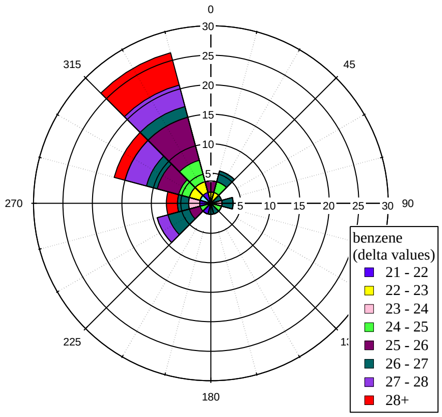

0
45
180
225
270
315
5
10
15
20
25
p,m-xylene
(delta values)
17 - 18
19 - 20
20 - 21
21 - 22
22 - 23
23 - 24
24 - 25
25 - 26
26 - 27
27 - 28
28+

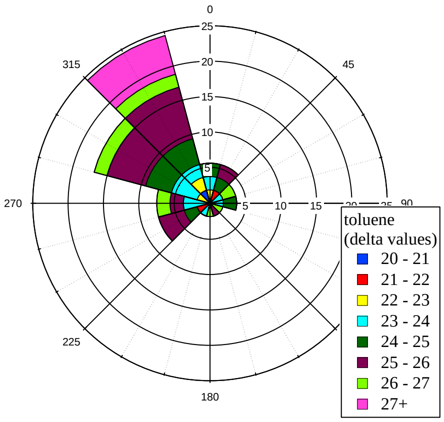

0
45
180
225
270
315
5
10
15
20
25
o-xylene
(delta values)
18 - 19
20 - 21
21 - 22
22 - 23
23 - 24
24 - 25
25 - 26
26 - 27
27+

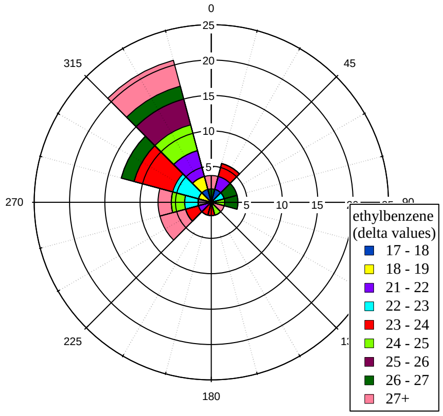
# M2: Toronto Samples

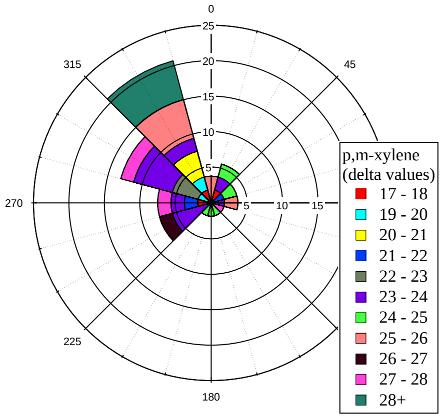


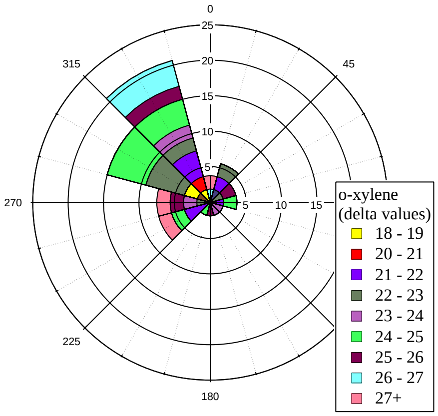











0
25
20
15
10
5
45
315
270
5
10
15
225
180
o-xylene
(delta values)
18 - 19
20 - 21
21 - 22
22 - 23
23 - 24
24 - 25
25 - 26
26 - 27
27+

## Appendix N: Number of the sample occurrences per different air origin range (sectors)

### N1: Egbert

| Sector (°)[a] | # of samples per sector | hexane | benzene | heptane | toluene | ethyl-benzene | p,m-xylene | o-xylene |
|---|---|---|---|---|---|---|---|---|
| 0-45 | 4 | 1 | 4 | 3 | 3 | 3 | 3 | 3 |
| 45-90 | 5 | 1 | 3 | 3 | 3 | 2 | 3 | 3 |
| 90-135 | 2 | 0 | 2 | 2 | 2 | 2 | 2 | 2 |
| 135-180 | 2 | 0 | 1 | 2 | 1 | 2 | 2 | 2 |
| 180-225 | 3 | 1 | 2 | 1 | 2 | 2 | 2 | 2 |
| 225-270 | 6 | 4 | 5 | 5 | 4 | 4 | 4 | 4 |
| 270-315 | 14 | 9 | 14 | 13 | 15 | 14 | 14 | 14 |
| 315-360 | 17 | 10 | 15 | 13 | 14 | 11 | 11 | 11 |

### N2: Toronto

| Sector (°) | # of samples per sector | hexane | benzene | heptane | toluene | ethyl-benzene | p,m-xylene | o-xylene |
|---|---|---|---|---|---|---|---|---|
| 0-45 | 14 | 4 | 12 | 3 | 14 | 13 | 13 | 12 |
| 45-90 | 15 | 3 | 6 | 5 | 8 | 7 | 6 | 6 |
| 90-135 | 16 | 1 | 4 | 1 | 4 | 4 | 4 | 3 |
| 135-180 | 17 | 0 | 2 | 1 | 2 | 2 | 2 | 2 |
| 180-225 | 18 | 1 | 1 | 1 | 2 | 2 | 2 | 1 |
| 225-270 | 19 | 4 | 8 | 5 | 8 | 8 | 10 | 7 |
| 270-315 | 20 | 9 | 13 | 7 | 14 | 12 | 13 | 14 |
| 315-360 | 21 | 19 | 16 | 9 | 18 | 19 | 19 | 19 |

(a) Air origins: 0° – North, 90° – East, 180°- South, 270° – West, 360° – North.

# Appendix O: Statistical analysis of VOC concentrations when separated by the air origin.

## O1: Egbert

| hexane | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sector (°)[a] | # of observations per sector | Max | Min | Average | 25pct[b] | 50pct | 75pct |
| 0-45 | 1 | 4.02 | | | | | |
| 45-90 | 1 | 1.89 | | | | | |
| 90-135 | 0 | | | | | | |
| 135-180 | 0 | | | | | | |
| 180-225 | 1 | 1.96 | | | | | |
| 225-270 | 4 | 5.30 | 0.18 | 1.89 | 0.54 | 1.04 | 2.39 |
| 270-315 | 9 | 15.88 | 0.44 | 3.34 | 1.00 | 1.84 | 2.70 |
| 315-360 | 10 | 5.12 | 0.59 | 1.59 | 0.90 | 1.28 | 1.56 |
| | | | | | | | |
| benzene | | | | | | | |
| Sector (°) | # of observations per sector | Max | Min | Average | 25pct | 50pct | 75pct |
| 0-45 | 4 | 0.26 | 0.07 | 0.18 | 0.14 | 0.20 | 0.24 |
| 45-90 | 3 | 0.18 | 0.11 | 0.14 | 0.13 | 0.15 | 0.16 |
| 90-135 | 2 | 0.14 | 0.13 | | | | |
| 135-180 | 1 | 0.10 | | | | | |
| 180-225 | 2 | 0.37 | 0.05 | | | | |
| 225-270 | 5 | 0.88 | 0.06 | 0.34 | 0.08 | 0.14 | 0.53 |
| 270-315 | 14 | 0.24 | 0.05 | 0.12 | 0.07 | 0.12 | 0.15 |
| 315-360 | 15 | 0.18 | 0.03 | 0.08 | 0.06 | 0.08 | 0.09 |
| | | | | | | | |
| heptane | | | | | | | |
| Sector (°) | # of observations per sector | Max | Min | Average | 25pct | 50pct | 75pct |
| 0-45 | 3 | 0.90 | 0.12 | 0.45 | 0.22 | 0.31 | 0.61 |
| 45-90 | 3 | 4.86 | 0.44 | 2.21 | 0.88 | 1.32 | 3.09 |
| 90-135 | 2 | 1.80 | 1.76 | | | | |
| 135-180 | 2 | 0.81 | 0.19 | | | | |
| 180-225 | 1 | 0.47 | | | | | |
| 225-270 | 5 | 4.83 | 0.19 | 1.37 | 0.32 | 0.40 | 1.11 |

| Sector (°) | # of observations per sector | Max | Min | Average | 25pct | 50pct | 75pct |
|---|---|---|---|---|---|---|---|
| 270-315 | 13 | 3.06 | 0.10 | 0.94 | 0.25 | 0.42 | 1.38 |
| 315-360 | 13 | 1.50 | 0.11 | 0.39 | 0.16 | 0.23 | 0.37 |
| | | | | | | | |
| toluene | | | | | | | |
| Sector (°) | # of observations per sector | Max | Min | Average | 25pct | 50pct | 75pct |
| 0-45 | 3 | 0.39 | 0.18 | 0.31 | 0.27 | 0.36 | 0.38 |
| 45-90 | 3 | 0.20 | 0.06 | 0.11 | 0.07 | 0.07 | 0.13 |
| 90-135 | 2 | 0.17 | 0.17 | | | | |
| 135-180 | 1 | 0.25 | | | | | |
| 180-225 | 2 | 0.16 | 0.08 | | | | |
| 225-270 | 4 | 1.15 | 0.14 | 0.43 | 0.18 | 0.21 | 0.45 |
| 270-315 | 15 | 0.36 | 0.06 | 0.14 | 0.10 | 0.13 | 0.15 |
| 315-360 | 14 | 0.23 | 0.04 | 0.10 | 0.06 | 0.09 | 0.14 |
| | | | | | | | |
| ethylbenzene | | | | | | | |
| Sector (°) | # of observations per sector | Max | Min | Average | 25pct | 50pct | 75pct |
| 0-45 | 3 | 0.06 | 0.02 | 0.04 | 0.03 | 0.05 | 0.05 |
| 45-90 | 3 | 0.06 | 0.01 | 0.03 | 0.01 | 0.02 | 0.04 |
| 90-135 | 2 | 0.02 | 0.01 | | | | |
| 135-180 | 2 | 0.04 | 0.03 | | | | |
| 180-225 | 2 | 0.02 | 0.03 | | | | |
| 225-270 | 4 | 0.19 | 0.01 | 0.06 | 0.01 | 0.02 | 0.06 |
| 270-315 | 14 | 0.06 | 0.01 | 0.02 | 0.01 | 0.02 | 0.03 |
| 315-360 | 11 | 0.03 | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 |
| | | | | | | | |
| p,m-xylene | | | | | | | |
| Sector (°) | # of observations per sector | Max | Min | Average | 25pct | 50pct | 75pct |
| 0-45 | 3 | 0.15 | 0.03 | 0.09 | 0.06 | 0.08 | 0.12 |
| 45-90 | 3 | 0.14 | 0.01 | 0.06 | 0.03 | 0.04 | 0.09 |
| 90-135 | 2 | 0.05 | 0.02 | | | | |
| 135-180 | 2 | 0.11 | 0.07 | | | | |
| 180-225 | 2 | 0.02 | 0.07 | | | | |

| Sector (°) | # of observations per sector | Max | Min | Average | 25pct | 50pct | 75pct |
|---|---|---|---|---|---|---|---|
| 225-270 | 4 | 0.47 | 0.01 | 0.14 | 0.02 | 0.04 | 0.16 |
| 270-315 | 14 | 0.15 | 0.01 | 0.04 | 0.02 | 0.04 | 0.04 |
| 315-360 | 11 | 0.07 | 0.01 | 0.03 | 0.01 | 0.03 | 0.03 |
| | | | | | | | |
| o-xylene | | | | | | | |
| Sector (°) | # of observations per sector | Max | Min | Average | 25pct | 50pct | 75pct |
| 0-45 | 3 | 0.05 | 0.01 | 0.03 | 0.02 | 0.03 | 0.04 |
| 45-90 | 3 | 0.04 | 0.003 | 0.02 | 0.01 | 0.02 | 0.03 |
| 90-135 | 2 | 0.013 | 0.008 | | | | |
| 135-180 | 2 | 0.03 | 0.02 | | | | |
| 180-225 | 2 | 0.01 | 0.02 | | | | |
| 225-270 | 4 | 0.14 | 0.01 | 0.05 | 0.01 | 0.01 | 0.05 |
| 270-315 | 14 | 0.05 | 0.003 | 0.02 | 0.01 | 0.02 | 0.02 |
| 315-360 | 11 | 0.02 | 0.001 | 0.01 | 0.004 | 0.01 | 0.01 |

**O2:Toronto**

| hexane | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sector (°) | # of observations per sector | Max | Min | Average | 25pct | 50pct | 75pct |
| 0-45 | 4 | 1.61 | 0.07 | 0.56 | 0.10 | 0.27 | 0.74 |
| 45-90 | 3 | 1.29 | 0.09 | 0.61 | 0.26 | 0.44 | 0.86 |
| 90-135 | 1 | 1.13 | | | | | |
| 135-180 | 0 | | | | | | |
| 180-225 | 1 | 1.00 | | | | | |
| 225-270 | 4 | 0.98 | 0.88 | 0.93 | 0.91 | 0.95 | 0.96 |
| 270-315 | 9 | 1.66 | 0.14 | 0.82 | 0.44 | 0.91 | 1.09 |
| 315-360 | 19 | 1.50 | 0.06 | 0.51 | 0.22 | 0.46 | 0.68 |
| benzene | | | | | | | |
| Sector (°) | # of observations per sector | Max | Min | Average | 25pct | 50pct | 75pct |
| 0-45 | 12 | 0.33 | 0.02 | 0.12 | 0.07 | 0.09 | 0.14 |
| 45-90 | 6 | 0.16 | 0.02 | 0.11 | 0.08 | 0.11 | 0.14 |
| 90-135 | 4 | 0.20 | 0.04 | | | | |
| 135-180 | 2 | 0.10 | 0.09 | | | | |
| 180-225 | 1 | 0.14 | | | | | |
| 225-270 | 8 | 0.30 | 0.05 | 0.18 | 0.10 | 0.17 | 0.26 |
| 270-315 | 13 | 0.74 | 0.02 | 0.10 | 0.07 | 0.11 | 0.12 |
| 315-360 | 16 | 0.47 | 0.02 | 0.11 | 0.06 | 0.08 | 0.12 |

| heptane | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sector (°) | # of observations per sector | Max | Min | Average | 25pct | 50pct | 75pct |
| 0-45 | 3 | 0.07 | 0.02 | 0.04 | 0.02 | 0.02 | 0.05 |
| 45-90 | 5 | 0.25 | 0.01 | 0.13 | 0.02 | 0.12 | 0.23 |
| 90-135 | 1 | 0.18 | | | | | |
| 135-180 | 1 | 0.17 | | | | | |
| 180-225 | 1 | 0.19 | | | | | |
| 225-270 | 5 | 0.29 | 0.02 | 0.21 | 0.16 | 0.28 | 0.29 |
| 270-315 | 7 | 0.29 | 0.05 | 0.14 | 0.07 | 0.11 | 0.20 |
| 315-360 | 9 | 0.18 | 0.04 | 0.09 | 0.04 | 0.08 | 0.11 |

toluene

| Sector (°) | # of observations per sector | Max | Min | Average | 25pct | 50pct | 75pct |
|---|---|---|---|---|---|---|---|
| 0-45 | 14 | 1.54 | 0.15 | 0.49 | 0.23 | 0.38 | 0.56 |
| 45-90 | 8 | 0.85 | 0.12 | 0.55 | 0.42 | 0.60 | 0.77 |
| 90-135 | 4 | 0.86 | 0.11 | 0.58 | 0.50 | 0.68 | 0.76 |
| 135-180 | 2 | 0.68 | 0.54 | | | | |
| 180-225 | 2 | 2.11 | 0.56 | | | | |
| 225-270 | 8 | 1.57 | 0.32 | 0.94 | 0.44 | 0.91 | 1.47 |
| 270-315 | 14 | 1.50 | 0.22 | 0.66 | 0.38 | 0.54 | 0.91 |
| 315-360 | 18 | 1.39 | 0.09 | 0.62 | 0.38 | 0.59 | 0.85 |

ethylbenzene

| Sector (°) | # of observations per sector | Max | Min | Average | 25pct | 50pct | 75pct |
|---|---|---|---|---|---|---|---|
| 0-45 | 13 | 0.16 | 0.01 | 0.04 | 0.02 | 0.03 | 0.03 |
| 45-90 | 7 | 0.06 | 0.01 | 0.05 | 0.05 | 0.05 | 0.05 |
| 90-135 | 4 | 0.09 | 0.01 | 0.06 | 0.05 | 0.07 | 0.08 |
| 135-180 | 2 | 0.07 | 0.05 | | | | |
| 180-225 | 2 | 0.15 | 0.03 | | | | |
| 225-270 | 8 | 0.15 | 0.03 | 0.08 | 0.05 | 0.08 | 0.10 |
| 270-315 | 12 | 0.18 | 0.03 | 0.08 | 0.05 | 0.06 | 0.11 |
| 315-360 | 19 | 0.20 | 0.02 | 0.07 | 0.04 | 0.06 | 0.08 |

p,m-xylene

| Sector (°) | # of observations per sector | Max | Min | Average | 25pct | 50pct | 75pct |
|---|---|---|---|---|---|---|---|
| 0-45 | 13 | 0.41 | 0.03 | 0.10 | 0.04 | 0.07 | 0.10 |
| 45-90 | 6 | 0.15 | 0.03 | 0.12 | 0.11 | 0.14 | 0.14 |
| 90-135 | 4 | 0.24 | 0.01 | 0.15 | 0.13 | 0.17 | 0.19 |
| 135-180 | 2 | 0.14 | 0.06 | | | | |
| 180-225 | 2 | 0.39 | 0.06 | | | | |
| 225-270 | 10 | 0.35 | 0.07 | 0.18 | 0.11 | 0.15 | 0.23 |
| 270-315 | 13 | 0.48 | 0.04 | 0.21 | 0.08 | 0.18 | 0.31 |
| 315-360 | 19 | 0.56 | 0.05 | 0.18 | 0.10 | 0.16 | 0.21 |

| o-xylene | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sector (°) | # of observations per sector | Max | Min | Average | 25pct | 50pct | 75pct |
| 0-45 | 12 | 0.09 | 0.01 | 0.03 | 0.01 | 0.02 | 0.04 |
| 45-90 | 6 | 0.05 | 0.01 | 0.04 | 0.03 | 0.04 | 0.05 |
| 90-135 | 3 | 0.08 | 0.05 | 0.06 | 0.05 | 0.06 | 0.07 |
| 135-180 | 2 | 0.08 | 0.05 | | | | |
| 180-225 | 1 | 0.02 | | | | | |
| 225-270 | 7 | 0.10 | 0.02 | 0.05 | 0.03 | 0.04 | 0.07 |
| 270-315 | 14 | 0.13 | 0.01 | 0.06 | 0.02 | 0.04 | 0.09 |
| 315-360 | 19 | 0.13 | 0.01 | 0.05 | 0.03 | 0.04 | 0.06 |

(a) Air origins: 0° – North, 90° – East, 180°- South, 270° – West, 360° – North.

(b) percentile