Stable carbon isotope ratio and its use in determination of photochemical processing of ambient volatile organic compounds

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INTRODUCTION

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

Stable Carbon Isotope Composition (δ)

$\delta^{13}C$ is defined as a ratio of number of ^{13}C atoms over that of ^{12}C ($^{13}C/^{12}C$) and typically expressed in delta notation ($\delta^{13}C$) as per mille values (‰) relative to a standard:

$$\delta^{13}C\ (‰) = \frac{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{VPDB}}{(^{13}C/^{12}C)_{VPDB}} \times 1000‰$$

Kinetic Isotope Effect (KIE, ε)

KIE is defined as a ratio of the rate constants for ^{12}C and ^{13}C containing compounds and is presented as the relative difference between the rate constants in epsilon notation (ε) as per mille values:

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

Photochemical Age (PCA)

PCA is used to quantitatively determine photochemical processing of VOC and usually is defined as the time integral of the OH radical concentration for an air mass.

In the **isotope hydrocarbon clock** (IHC) approach, if KIE and isotopic composition of VOC are known, PCA can be determined as:

$$t[OH] = \frac{\delta^{13}{}_RC - \delta^{13}{}_SC}{k_{OH}\varepsilon_{OH}}$$

where δ is stable carbon isotope composition of VOC at the source (S) and the receptor site (R).

It has been shown that the PCA derived by the IHC approach is for all practical purposes the VOC's average PCA (Rudolph and Czuba, 2000).

MATERIALS AND METHODS

In the field, VOC were sampled using adsorbent-filled cartridges

In the laboratory VOC were desorbed from the cartridge in the temperature controlled furnace and collected at cryo traps. The VOC then were separated using gas chromatography and individually combusted in the oxidation interface. The resulting CO_2 was analyzed on-line by IRMS for the stable carbon isotope ratio.
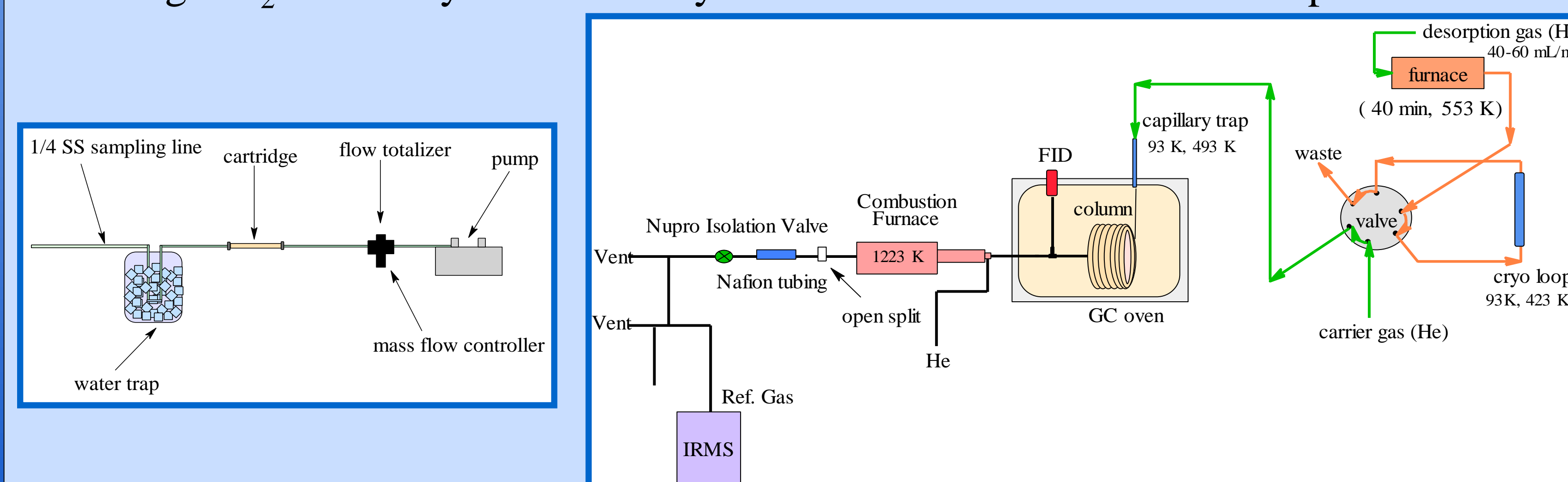

Sampling Sites

Two sampling sites were used in this study. The first sampling site was in Egbert, Ontario and was considered to be a semi-rural location since it was surrounded by agricultural fields and some forested regions with no major anthropogenic sources nearby.
The second sampling was at a suburban location on the outskirts of metropolitan Toronto.
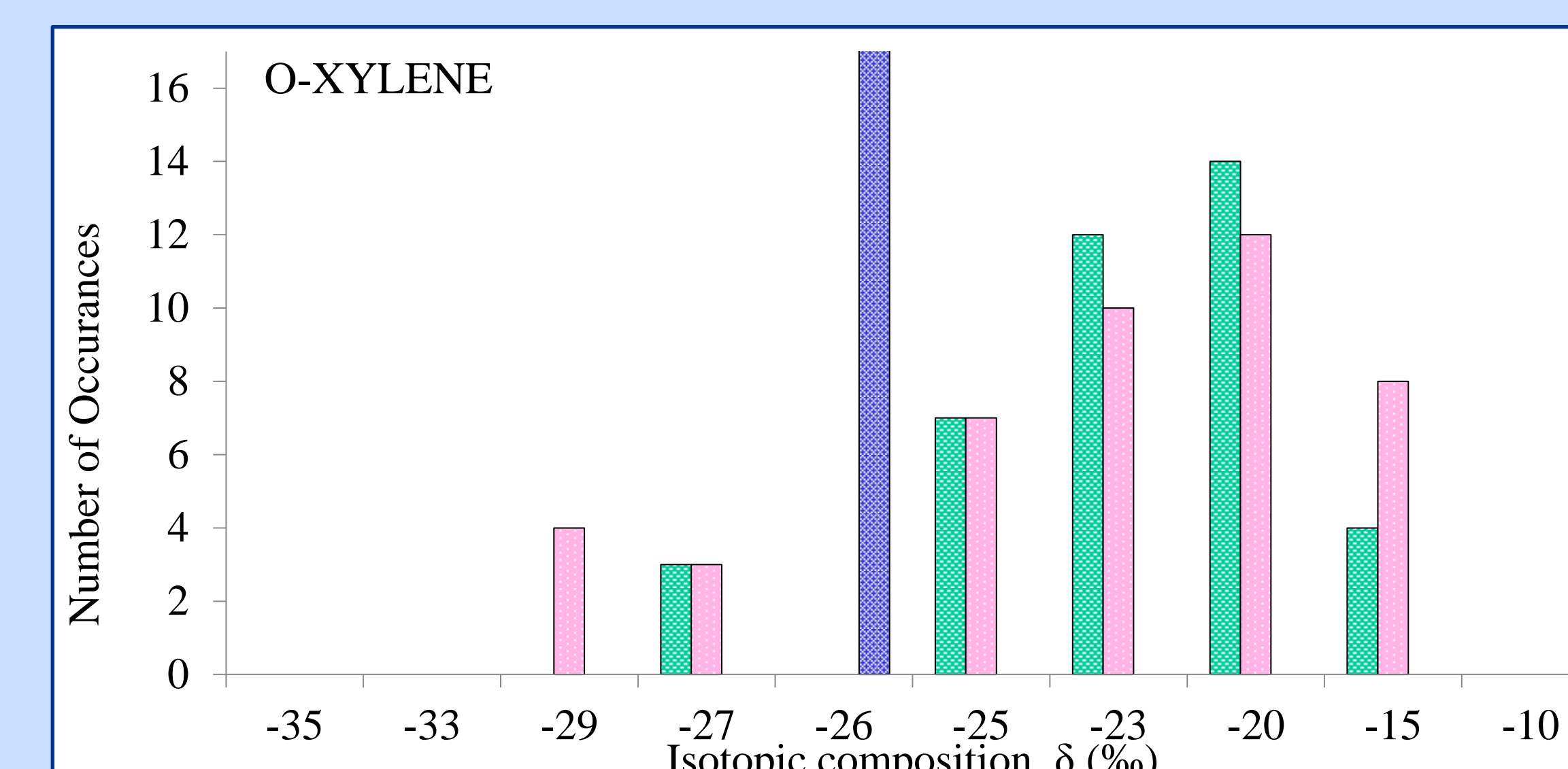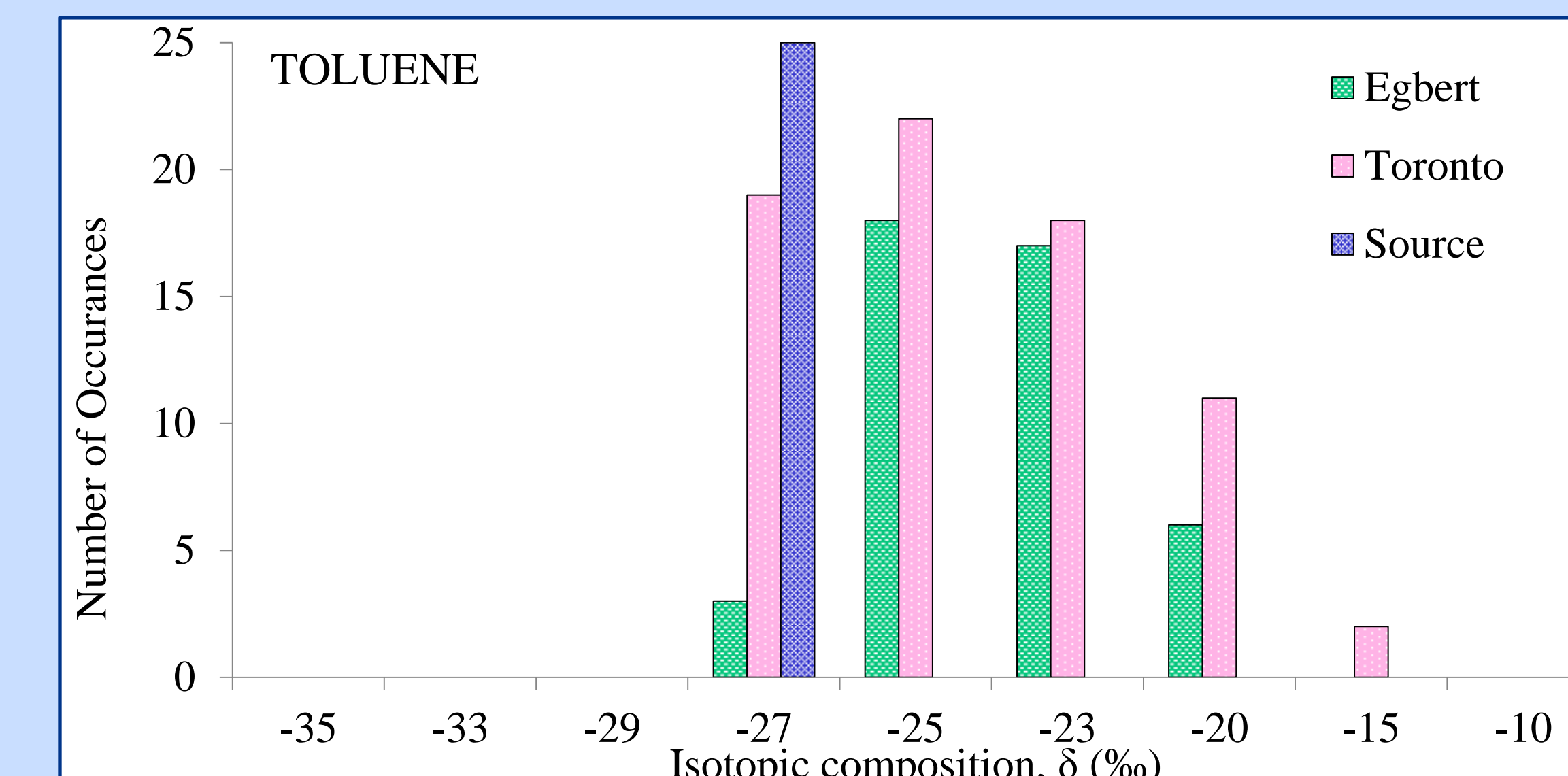
RESULTS AND DISCUSSION

PCA determined by HC and IHC cover a wide range, with IHC values differing for individual VOC:
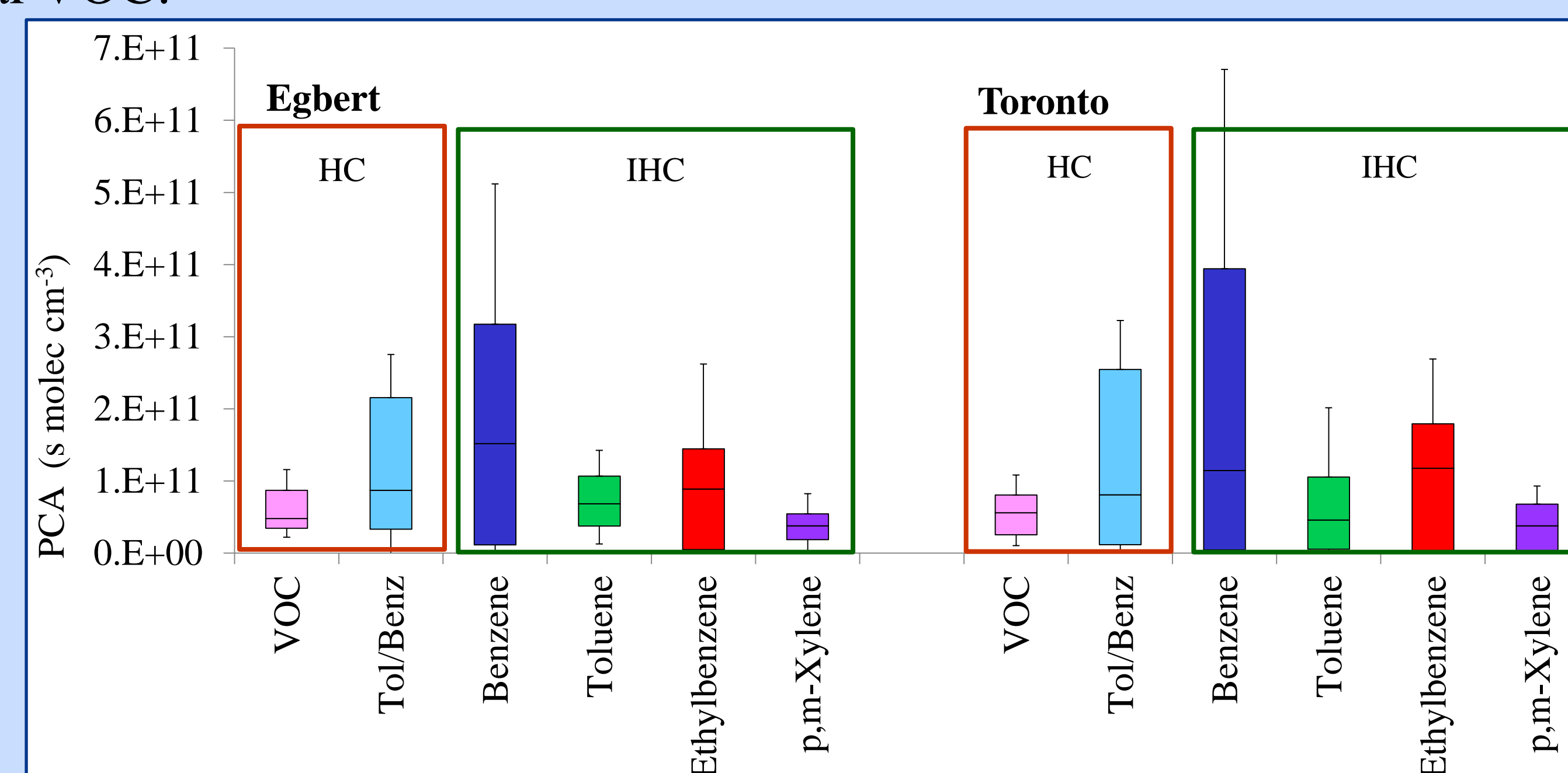

Compound	Concentration (ppbv)					
	TORONTO			EGBERT		
	Average	Min	Max	Average	Min	Max
Benzene	0.13	0.02	0.74	0.14	0.03	0.88
Toluene	0.63	LDL	2.11	0.17	0.04	1.15
Ethylbenzene	0.06	LDL	0.26	0.03	0.01	0.19
p,m-Xylene	0.17	LDL	0.74	0.05	0.01	0.47

RESULTS AND DISCUSSION

Delta values were determined for ambient VOC collected at two locations in southern Ontario: Egbert (rural) and the north of Toronto (urban). The results show VOC aged to varying extent resulting in VOC enriched in ^{13}C compared to their source with reactive VOC being more enriched in ^{13}C.
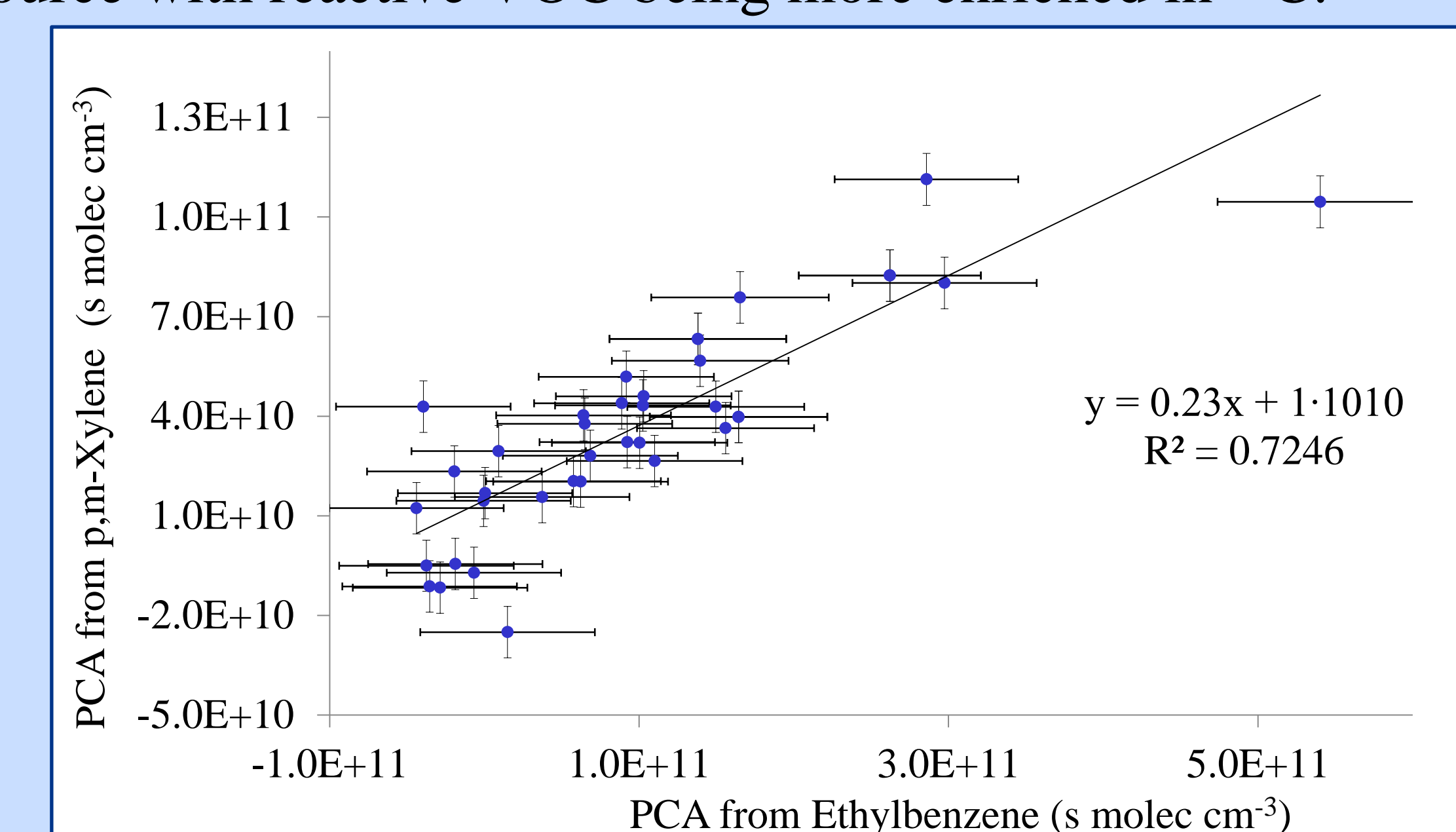
The correlation between PCA determined by IHC for different VOC indicates similar photochemical history, however more reactive compounds are removed faster and therefore have lower PCA

ACKNOWELDGEMENTS

References: 1. Rudolph and Czuba, *Geophysical Research Letters*, 3865-3868 (2000)   2. Kleinmen *et al.*, *Journal of Geophysical Research*, 108(D3) (2003)   3. Gelencsér *et al.*, *Environmental Science & Technology*, 2869-2872 (1997)