Compound Specific Measurement of Stable Carbon Isotope Ratios of Atmospheric Secondary POM

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INTRODUCTION

The photochemical formation of atmospheric secondary particulate organic matter (POM) from volatile organic compounds (VOC) is not well understood. POM is of interest due to its adverse health effects and environmental impact. It is proposed that isotope ratio measurements of secondary pollutants formed specifically by VOC reactions can be used as tracers and assist in understanding their relation precursors and differentiate between various atmospheric processes.
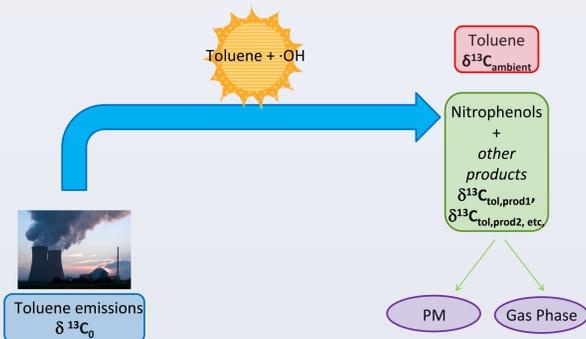

Figure 1 – VOC processing in the atmosphere

Nitrophenols, which are secondary pollutants, are proposed to be formed specifically through the photo oxidation of aromatic VOC (Atkinson, 2000 and Forstner, 1997) but primary sources in vehicle exhaust have also been found (Tremp, 1993). They are semi-volatile compounds, therefore existing in both gas phase and particulate matter (PM). 2-methyl-4-nitrophenol (2-me-4-NP) is consistently the most abundant methyl nitrophenol detected, and therefore will be the main target compound in this study. The sampling of both gas phase and PM was conducted at York University, which is a mixed industrial and residential area in the outskirts of metropolitan Toronto. Samples were then analyzed to obtain both concentration data and carbon isotopic composition.

METHODOLOGY

Uncoated quartz filters (for sampling PM) and XAD coated filters (for gas + PM sampling) were used for sampling on high volume air samplers at a standard flow rate of 1.13 m^3 min^{-1} for a period of 1 to 3 days.

Filters were extracted based on the procedure described by Moukhtar, et al. Filters were extracted with acetonitrile and after several evaporation and rinsing steps, HPLC separation combined with solid phase extraction was used as a "clean-up" step. The phenols were derivatized before analysis by GC-MS for concentration measurements and GC-IRMS for isotopic composition.
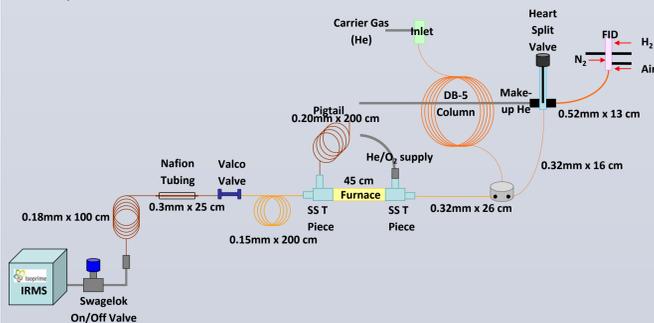

Figure 2 – Schematic of GC-C-IRMS set-up
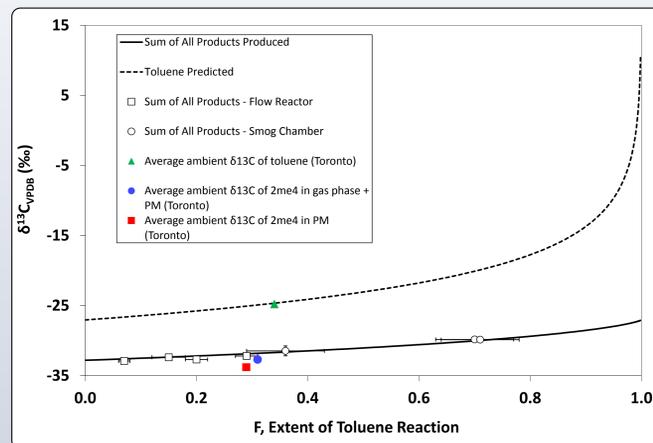
KINETIC ISOTOPE EFFECT (KIE)

Figure 3– Plot of $\delta^{13}C$ of secondary POM observed in smog chamber and flow reactor experiments (adapted from Irei et al. (2011))

The kinetic isotope effect occurs when rates of reactions of reacting species are sensitive to atomic mass. Since these differences are small, they are represented in per mille notations. This effect has been measured and observed in laboratory studies (Figure 3) and has been applied to ambient measurements.

By knowing the average ambient mixing ratios of precursors and applying the extent of the reaction (F), the amount of precursor (χ) that has been processed can be predicted and hence, yields can be derived. The extent of reaction can be derived from the change in isotope ratios of the precursor (Equation 1) or the isotope ratios of products and reactants (Equation 2).
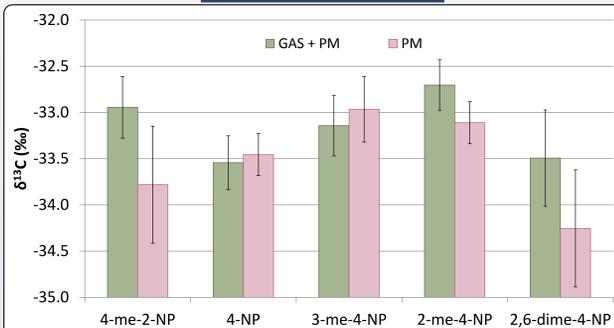
AMBIENT RESULTS

Figure 4 – Mean isotope ratios of select target nitrophenol compounds; error bars represent the error of the mean
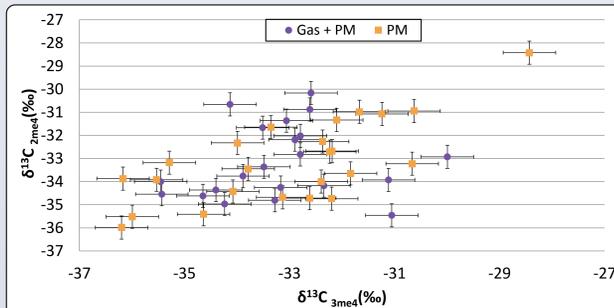

Figure 5 – Comparison of isotopic composition of isomers 2-methyl-4-nitrophenol and 3-methyl-4-nitrophenol in gas phase + PM and in PM
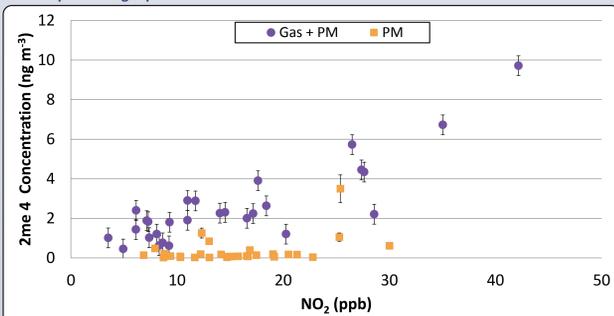

Figure6– Dependence of 2-me-4 concentration on NO_2 mixing ratios (NO_2 data were acquired from the Ministry of the Environment Toronto North location and were averaged over the sampling time)

RESULTS & DISCUSSION

Table1– Predicted values for the extent of the toluene + OH reaction using ambient isotopic composition data in Toronto. For details of the concentrations and isotope ratios of the precursor VOC see poster by Kornilova et al.

Precursor	Product	F (Eqn 1)	F (Eqn 2) for Gas + PM	F (Eqn 2) for PM
toluene	4-me-2-NP	0.34	0.30	0.27
	3-me-4-NP		0.29	0.30
	2-me-4-NP		0.31	0.29
p,m-xylene	2,6-dime-4-NP	0.48	0.34	0.31
benzene	4-NP	0.23	0.24	0.25

- Each of the nitrophenols have average isotopic compositions that are less than -32‰ (Figure 4) which is substantially below the isotope ratio of the precursors

- Consistent with predictions from laboratory experiments and mass balance considerations (Figure 3)

- Possible reason for variability of the nitrophenol isotope ratios is differences in the extent of precursor processing (Figure 3)

- Figure 5 shows a the dependence of isotopic composition between different isomers; this suggests a correlation between isotope ratios as expected however the scatter is significant and does not justify firm conclusions

- Dependence between nitrophenol concentration and NO_2 mixing ratio is consistent with the assumption that nitrophenols are primarily from reactions of precursors

- Nitrophenols in PM do not show this dependence, most likely because the distribution between gas and particle phase will depend on many factors such as temperature, PM concentration and PM composition

RESULTS & DISCUSSION

Table 2 – Comparison of nitrophenol yields from the photooxidation of aromatic VOC in laboratory studies and ambient measurements (*Measured by Forstner, et al, 1997, [†]measured by Irei, 2008)

Target Compound	Laboratory Yield (%)	Gas + PM		PM	
		Ambient Yield (%)	Average Ambient Isotope Ratio (‰)	Ambient Yield (%)	Average Ambient Isotope Ratio (‰)
4-me-2-NP	4.4*	0.09	-32.9	0.004	-33.8
3-me-4-NP	0.096[†]/6.8*	0.03	-33.1	0.004	-33.0
2-me-4-NP	16.3[†]/10*	0.12	-32.7	0.02	-33.1
2,6-dime-4-NP	3.3*	0.06	-33.5	0.006	-34.2

- Absence of a systematic dependence between NO_2 mixing ratio and nitrophenol carbon isotope ratio (Figure 7) suggests that the nitrophenol formation mechanism is independent of precursor concentration

- Precursor for 2-,6-dime-4-NP is p-xylene, but measurements are only available for the sum of p- and m-xylene. For 2,6-dime-4-NP the assumption that its isotope ratio is identical to that derived from a mass balance has not been confirmed by laboratory studies
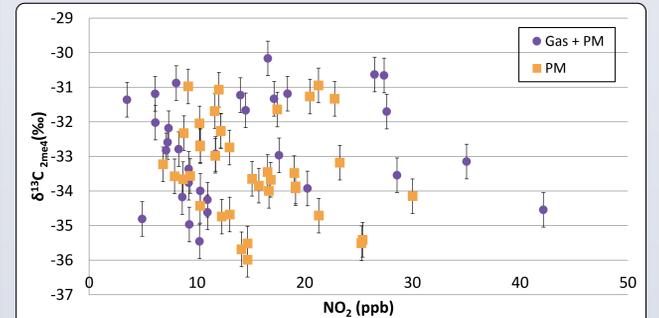

Figure7– Dependence of 2-me-4 isotopic composition on NO_2 mixing ratios (NO_2 data were acquired from the Ministry of the Environment Toronto North location and were averaged over the sampling time)

CONCLUSION

- Results strongly support the assumption that for the studied conditions, nitrophenols are primarily secondary pollutants formed by reaction of precursor VOC in the presence of NO_2

- Measurement of carbon isotope ratios allows determination of the extent of precursor processing

- Different approaches (Equations 1 and 2) result in consistent values for precursor processing

- Yields of nitrophenols for atmospheric conditions are substantially lower than those from laboratory studies, most likely the consequence of the unrealistically high precursor concentrations used in most laboratory experiments

- Presented results are based on averages from several measurement series, data sets that would allow analysis of individual episodes are not yet available.

ACKNOWLEDGEMENTS

References: 1. Atkinson, R. Atmos. Enviro, 2063-2101 (2000).   2, Forstner, H. et al, Enviro Sci & Tech, 1345-1358 (1997)   3.Irei, S., et al. Atmos. Enviro, 856-862.(2011)   4. Irei, S. Dissertation (2008)   5. Moukhtar, S., et al. Atmos. Meas. Tech, 2453-2464 (2011)   6.Tremp, J., et al. Water, Air & Soil Poll, 113-123 (1993)