

Supplementary Information for:

**Diurnally Resolved Particulate and VOC Measurements at a Rural Site: Indication of
Significant Biogenic Secondary Organic Aerosol Formation**

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Supplementary Information from Coincident Aircraft Measurements

During BAQS, a number of flights were conducted by Environment Canada of the National Research Council Twin Otter over the southwestern Ontario region (Hayden et al., 2011). The aircraft was equipped with an Aerodyne C-ToF AMS and with an Aerolaser CO monitor. The average vertical profiles of OA/(CO-80 ppbv) as measured by the aircraft instruments over 12 flights over the region are plotted in Figure S1. It is seen that there is essentially no vertical structure to this quantity when plotted in aggregate, substantiating the use of CO as a tracer. Note that boundary layer heights were roughly between 400 and 2200m, as deduced from potential temperature and water vapour measurements.

Analysis of the only pre-dawn flight gives more specific information. In particular, from 4:15-7:15 on July 3rd, data indicate a strong inversion layer, with boundary layer height at ~ 400 m. The OA/(CO-80 ppbv) ratio was $0.026 \mu\text{g m}^{-3} \text{ ppbv}^{-1}$ in the boundary layer and $0.032 \mu\text{g m}^{-3} \text{ ppbv}^{-1}$ above to 1000 m, indicating a slight enhancement of OA/(CO-80 ppbv) in the nocturnal residual layer. Assuming air from this nocturnal residual layer is mixed down into the boundary layer later during the day, we note that the enhancement in OA/(CO-80 ppbv) that would arise is an order of magnitude smaller than the diurnal increase observed in this quantity at Harrow. Unfortunately the data set is limited, but this single case suggests that there is little mixing of excess OA from aloft.

Reference: Hayden, K.L., D.M.L. Sills, J.R. Brook, S.M. Li, P. Makar, M.Z. Markovic, P. Liu, K.G. Anlauf, J.M. O'Brien, Q. Li, and R. McLaren, Aircraft study of the impact of lake-breeze circulations on trace gases and particles during BAQS-Met 2007, *Atmos. Chem. Phys. Discuss.*, accepted, 2011.

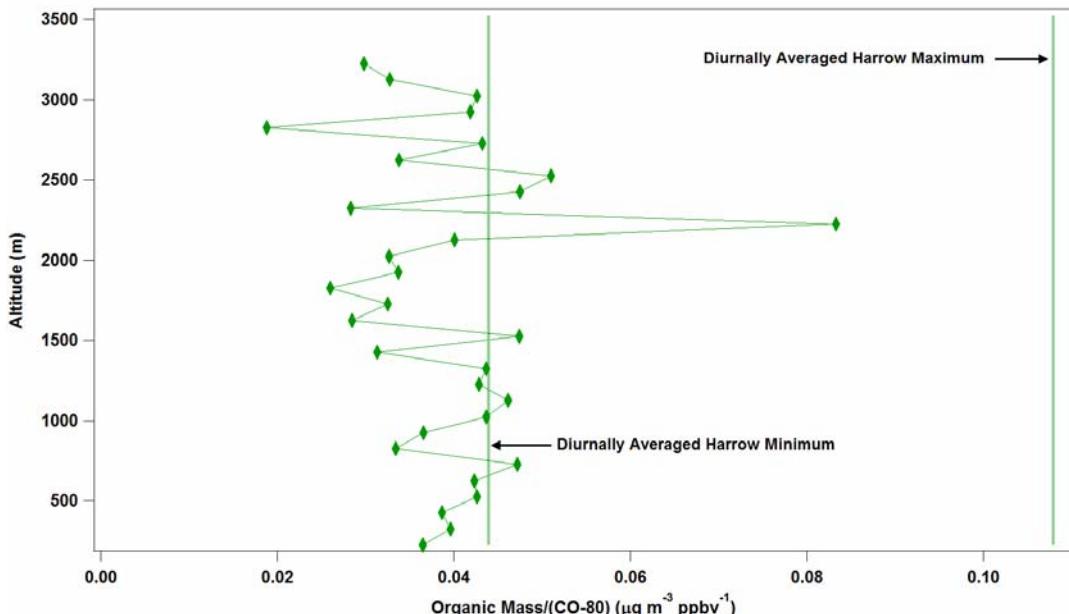


Figure S1: Plot of altitude vs. average levels of OA/(CO- 80 ppbv) for flights around Harrow during BAQS. The vertical lines indicate the indicated quantities as measured at the ground.

Supplementary Information for OH Concentration Diurnal Profile

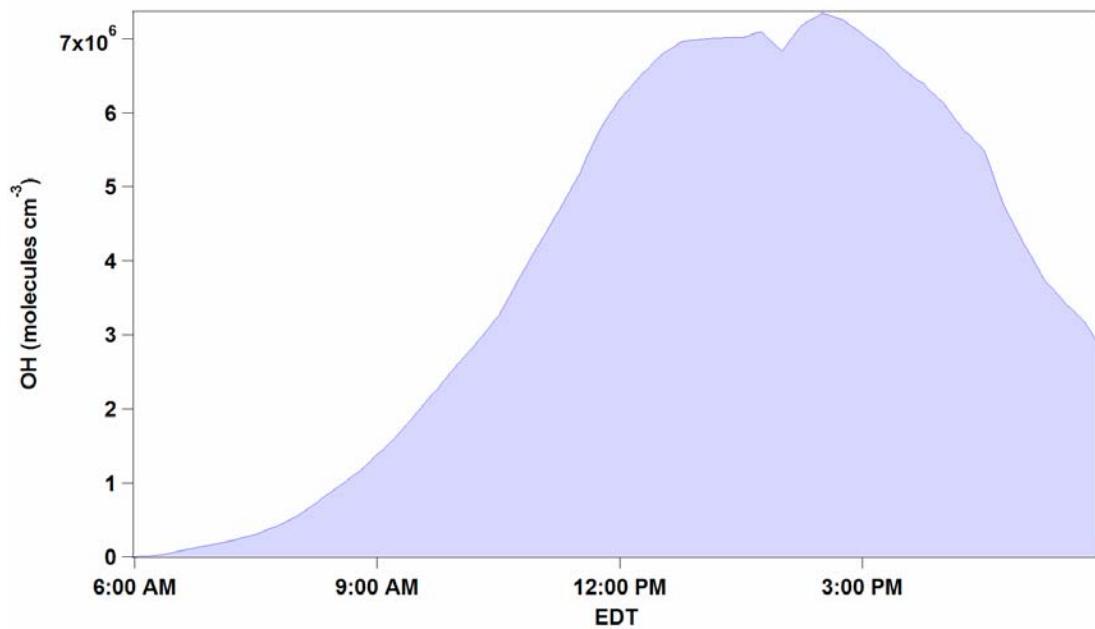


Figure S2. Diurnal profile of OH, as calculated using the approach described in the text.

Supplementary Information for Regional BTEX Values

Table S1: Mixing ratios of benzene as measured during BAQS by canister sampling at Windsor (24 hour samples) and Bear Creek (4 hour samples), and the corresponding mixing ratios for the same time periods at Harrow.

Benzene				
Date	Windsor (pptv)	Harrow (pptv)	Bear Creek (pptv)	Harrow (pptv)
6/23/2007				39
6/24/2007			46	140
6/25/2007			44	123
6/26/2007			41	103
6/27/2007			49	91
6/28/2007			54	43
6/29/2007	93	78		50
6/30/2007	286	143	33	151
7/1/2007			23	
7/2/2007	143		13	
7/3/2007	187	47	26	35
7/4/2007	312	80	93	61
7/5/2007	376	158	61	90
7/6/2007	434	227	47	299
7/7/2007			108	83
7/8/2007			63	82
7/9/2007	92	91	51	74
7/10/2007	178	107	40	89

Table S2: Mixing ratios of toluene as measured during BAQS by canister sampling at Windsor (24 hour samples) and Bear Creek (4 hour samples), and the corresponding mixing ratios for the same time periods at Harrow.

Toluene				
Date	Windsor (pptv)	Harrow (pptv)	Bear Creek (pptv)	Harrow (pptv)
6/23/2007				44
6/24/2007			41	101
6/25/2007			42	101
6/26/2007			29	135
6/27/2007			79	71
6/28/2007			73	129
6/29/2007	277	190		96
6/30/2007	1250	255	24	242
7/1/2007			16	
7/2/2007	751		12	
7/3/2007	1130	182	32	126
7/4/2007	1830	169	142	98
7/5/2007	1270	384	61	132
7/6/2007	1200	468	44	422
7/7/2007			107	51
7/8/2007			77	98
7/9/2007	263	111	62	57
7/10/2007	349	127	31	140

Table S3: Mixing ratios of C8 aromatics as measured during BAQS by canister sampling at Windsor (24 hour samples) and Bear Creek (4 hour samples), and the corresponding mixing ratios for the same time periods at Harrow.

C ₈ Aromatics				
Date	Windsor (pptv)	Harrow (pptv)	Bear Creek (pptv)	Harrow (pptv)
6/23/2007				43
6/24/2007			46	108
6/25/2007			23	76
6/26/2007			15	68
6/27/2007			46	87
6/28/2007			33	86
6/29/2007	184	149		89
6/30/2007	799	240	23	86
7/1/2007			12	
7/2/2007	341		12	
7/3/2007	252	66	15	54
7/4/2007	959	79	53	8
7/5/2007	781	283	34	40
7/6/2007	683	364	24	199
7/7/2007			35	9
7/8/2007			35	53
7/9/2007	159	130	24	67
7/10/2007	220	136	17	61

Supplementary Information for Calculations Performed Without CO Normalization

Table S4: Calculated Contributions to Secondary Organic Aerosol Formation for the Full Campaign, not normalized to CO.

	High NO _x		Low NO _x	
	Calculated ΔOrg ($\mu\text{g m}^{-3}$)	Fraction of Observed (%)	Calculated ΔOrg ($\mu\text{g m}^{-3}$)	Fraction of Observed (%)
Benzene-OH	8.2×10^{-3}	0.4	2.5×10^{-2}	1.3
Toluene-OH	3.7×10^{-2}	1.9	1.8×10^{-1}	9.0
C ₈ Aromatics-OH	4.3×10^{-2}	2.2	3.1×10^{-1}	15.8
Calculated Total Aromatic ΔOrg	8.8×10^{-2}	4.4	5.2×10^{-1}	26.0
Isoprene-OH	7.2×10^{-1}	36.0	6.1×10^{-1}	30.5
Monoterpenes-OH	5.0×10^{-1}	25.0	1.9	95.0
Monoterpenes-O ₃	7.3×10^{-1}	36.5	7.3×10^{-1}	36.5
Calculated Total Biogenic ΔOrg	2.0	100.0	3.2	160.0
Calculated Total ΔOrg	2.1	105.0	3.7	185.0
Measured ΔOrg	$2.0 \mu\text{g m}^{-3}$			

Table S5: Calculated Contributions to Secondary Organic Aerosol Formation for the Detroit Air period, not normalized to CO.

	High NO _x		Low NO _x	
	Calculated ΔOrg ($\mu\text{g m}^{-3}$)	Fraction of Observed (%)	Calculated ΔOrg ($\mu\text{g m}^{-3}$)	Fraction of Observed (%)
Benzene-OH	4.7×10^{-2}	0.7	9.5×10^{-2}	1.3
Toluene-OH	2.0×10^{-1}	2.8	7.4×10^{-1}	10.4
C ₈ Aromatics-OH	1.9×10^{-1}	2.7	9.9×10^{-1}	14.1
Calculated Total Aromatic ΔOrg	4.4×10^{-1}	6.2	1.8	25.4
Isoprene-OH	2.0	28.2	2.7	38.1
Monoterpenes-OH	8.7×10^{-1}	8.2	3.2	14.1
Monoterpenes-O ₃	7.7×10^{-1}	10.9	7.7×10^{-1}	10.9
Calculated Total Biogenic ΔOrg	3.6	50.7	6.7	94.4
Calculated Total ΔOrg	4.0	56.3	8.5	119.7
Measured ΔOrg	$7.1 \mu\text{g m}^{-3}$			

Table S6: Calculated Contributions to Secondary Organic Aerosol Formation for the Full Campaign less the Detroit Air period, not normalized to CO.

	High NO _x		Low NO _x	
	Calculated ΔOrg ($\mu\text{g m}^{-3}$)	Fraction of Observed (%)	Calculated ΔOrg ($\mu\text{g m}^{-3}$)	Fraction of Observed (%)
Benzene-OH	4.9×10^{-3}	0.2	1.5×10^{-2}	0.6
Toluene-OH	2.1×10^{-2}	0.9	1.1×10^{-1}	4.6
C ₈ Aromatics-OH	2.7×10^{-2}	1.1	2.0×10^{-1}	8.3
Calculated Total Aromatic ΔOrg	5.3×10^{-2}	2.2	3.3×10^{-1}	13.8
Isoprene-OH	4.1×10^{-1}	17.1	5.0×10^{-1}	20.8
Monoterpenes-OH	3.6×10^{-1}	15.0	1.7	70.9
Monoterpenes-O ₃	6.6×10^{-1}	27.5	6.6×10^{-1}	27.5
Calculated Total Biogenic ΔOrg	1.4	58.3	2.9	120.8
Calculated Total ΔOrg	1.5	62.5	3.2	133.3
Measured ΔOrg	$2.4 \mu\text{g m}^{-3}$			