MILAGRO Meeting, May 2007, Mexico City, MX

Spatial Variability of VOC Measurements at T0 During MILAGRO

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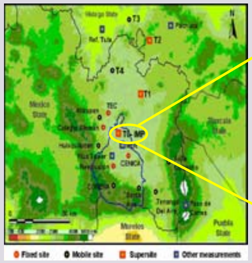
Abstract:
Open-path and point sampling hydrocarbon measurements from the T0 urban site during MCMA-2006 are compared. Co-located VOC measurements via Long-Path Differential Optical Absorption Spectroscopy (**DOAS**), Proton Transfer Mass Spectrometery (**PTR-MS**), and **canister** samples analyzed by Gas Chromatography (GC) provide a unique library of hydrocarbons at T0. Characterizing VOC speciation at T0 is an important first step towards constructing a detailed chemical box model to assess the oxidative capacity of the atmosphere during MILAGRO-2006.



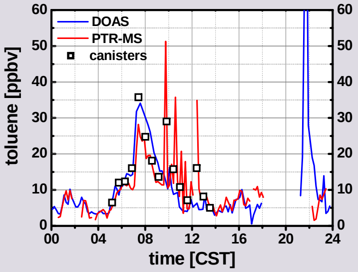
Long-Path DOAS:
2 light-paths measuring aromatic VOC
a) PEMEX building – 250 m
b) COMEX water tower – 1026 m

Point-sampling:
1) PTR-MS situated in shed on roof of IMP
2) Coordinated and intensive canister sampling
March 16, 19-23, 27-30

Table 1. Select VOC measured by DOAS and PTR-MS at T0

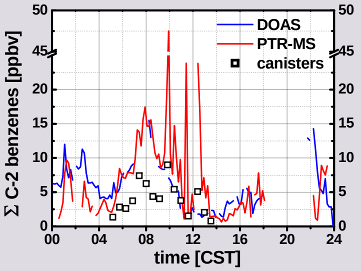
DOAS	PTR-MS
benzene	benzene
toluene	toluene
styrene	styrene
phenol	phenol
xylenes	C2-benzenes
ethyl benzene	C3-benzenes
benzaldehyde	methanol
naphthalenes	acetic acid
p-cresol	acetaldehyde
tolualdehydes	isoprene

VOC measurements on March 28



Toluene

- mobile sources *and* solvent sources
- good agreement: timing and magnitude
- noticeable plumes in point-sampling techniques; not always observed in open-path DOAS (see Merten *et al* poster for more information on plumes observed by PTR-MS and DOAS)

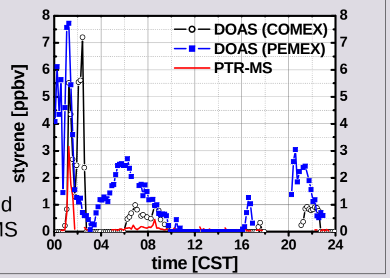


C-2 Benzenes

- almost exclusively mobile/combustion sources
- C2-benzenes defined:
  - DOAS sum of xylenes, benzaldehyde
  - PTR-MS: generic signal (+ fragments)
  - canisters: sum of xylenes (expected to be under-estimated in comparison
- excellent agreement between DOAS and PTR-MS; plumes/peaks in early morning not observed via DOAS; qualitatively, canisters look good, and, as expected, concentrations are low

Styrene

- non-combustion related sources; point industrial sources
- heterogeneity of airmass is observed:
  - both DOAS lightpaths and PTRMS show peak around 1 a.m.
  - only longer DOAS lightpath observes peak at 3 a.m; whereas other stronger peaks are observed over the shorter lightpath, and only very weakly on the longer lightpath, and not at all via PTRMS



References: [1]Volkamer et al, ACPD,7, 2007 [2]Sheehy et al, to be submitted, 2007

Determining VOC-speciation ratios from canister sampling

Table 2 (A-C). VOC-acetylene (ppbv/ppbv) ratios on a 24-hr average basis, averaged over rush-hour traffic (4-7 a.m.), and averaged over rising boundary layer conditions (8 a.m.-3 p.m). Values are listed as x10^2

A

alkanes	24-hr (±σ)	04-07 avg	08-15 avg
ethane	88 (43)	118	65
propane	469 (232)	636	363
i-butane	61 (26)	78	49
n-butane	186 (81)	238	151
i-pentane	50 (13)	44	51
n-pentane	35 (9)	34	35
n-hexane	23 (13)	20	24
2-methyl pentane	21 (5)	21	19
3-methyl pentane	15 (4)	15	13
2,2-dimethyl butane	5.4 (0.9)	5.1	5.3
2,3-dimethyl butane	28 (5)	27	27
n-heptane	5.1 (1.5)	5.0	4.6
n-octane	1.6 (0.7)	1.6	1.4
n-nonane	1.4 (0.8)	1.6	1.1
n-decane	2.7 (2.0)	3.2	1.8
cyclohexane	2.6 (0.5)	2.4	2.6

B

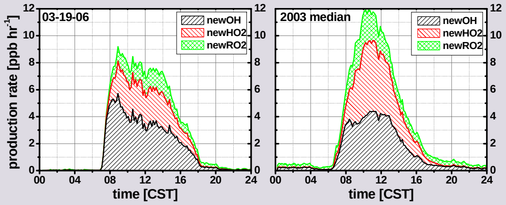
alkenes	24-hr (±σ)	04-07 avg	08-15 avg
ethene	81 (12)	92	74
propene	23 (9)	30	17
c-2-butene	1.9 (1.1)	2.4	1.3
t-2-butene	2.4 (1.2)	3.3	1.6
1-pentene	1.3 (0.5)	1.5	1.0
c-2-pentene	1.2 (0.5)	1.5	0.9
t-2-pentene	2.5 (1.2)	3.0	1.9
3-methyl-1-butene	0.7 (0.2)	0.7	0.5
2-methyl-2-butene	3.2 (1.8)	4.2	2.2
1,3-butadiene	1.8 (0.9)	2.6	1.2
isoprene	1.6 (0.8)	1.5	1.6

C

aromatics	24-hr (±σ)	04-07 avg	08-15 avg
benzene	13 (2)	11	13
toluene	117 (75)	115	84
o-xylene	8.5 (7.7)	11	6.4
m-xylene	13 (13)	18	9.8
p-xylene	6.9 (6.9)	8.8	5.5
ethyl benzene	11 (10)	16	8.6
isopropyl benzene	0.7 (0.4)	0.8	0.5
n-propyl benzene	2.6 (1.4)	3.3	1.9
o-ethyl toluene	2.5 (1.6)	3.3	1.6
m-ethyl toluene	6.2 (4.2)	8.3	4.1
p-ethyl toluene	3.6 (2.2)	4.7	2.5
1,3,5-trimethyl benzene	3.3 (2.7)	5.1	1.8
1,2,4-trimethyl benzene	11 (8.0)	11	8.0

In some cases e.g., propane, propene, and toluene, we observe a significant decrease in the VOC-acetylene ratio after rush hour. In other cases, however, e.g., n-hexane, isoprene, and benzene, we observe only small changes in the VOC-acetylene ratios before and after rush hour traffic. In building a model for MCMA-2006, we must take these variations into account when predicting radical source strength, radical cycling, and radical concentrations.

Preliminary Modeling using Master Chemical Mechanism (MCMv3.1) – March 19, 2006

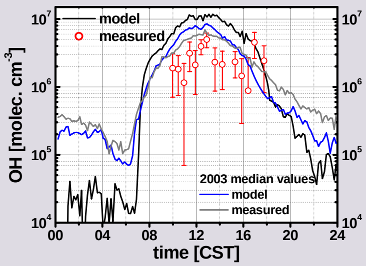


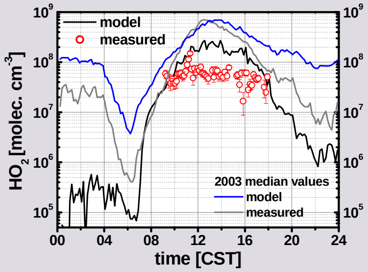
HO$_x$ sources well-constrained for Mexico City using DOAS measurements: O$_3$, HCHO, HONO

Model used extensively for MCMA-2003[1,2]

Radical sources for 03-19-06 are weaker than the median case for 2003; however, dataset is still improving

Large difference between night-time radical production via reactions of O$_3$ with alkenes





Outlook
A complete dataset for all measurements at T0 (i.e., radical sources and sinks) will allow us to begin modeling on a median and an individual day basis. Furthermore, a more detailed analysis of HO$_x$ sources is necessary, as well as a final determination of the VOC speciation.

Acknowledgments: This research was supported by funds from the NSF, DoE, and MIT/AGS. P. Sheehy acknowledges JI Steinfeld for his financial (via MIT/AGS) and advisory support. R. Volkamer acknowledges the Alexander von Humboldt Foundation for a Feodor Lynen Fellowship. PS and RV are both grateful to Ulrich Platt for the use of the DOAS instruments during MILAGRO.