Atmospheric Chemistry and Physics
An Interactive Open Access Journal of the European Geosciences Union

Atmos. Chem. Phys., 10, 1989-2005, 2010
www.atmos-chem-phys.net/10/1989/2010/

Comparison of aromatic hydrocarbon measurements made by PTR-MS, DOAS and GC-FID during the MCMA 2003 Field Experiment

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Abstract. A comparison of aromatic hydrocarbon measurements is reported for the CENICA supersite in the district of Iztapalapa during the Mexico City Metropolitan Area field experiment in April 2003 (MCMA 2003). Data from three different measurement methods were compared: a Proton Transfer Reaction Mass Spectrometer (PTR-MS), long path measurements using a UV Differential Optical Absorption Spectrometer (DOAS), and Gas Chromatography-Flame Ionization analysis (GC-FID) of canister samples. The principle focus was on the comparison between PTR-MS and DOAS data. Lab tests established that the PTR-MS and DOAS calibrations were consistent for a suite of aromatic compounds including benzene, toluene, p-xylene, ethylbenzene, 1,2,4-trimethylbenzene, phenol and styrene. The point sampling measurements by the PTR-MS and GC-FID showed good correlations (r=0.6), and were in reasonable agreement for toluene, C_2-alkylbenzenes and C_3-alkylbenzenes. The PTR-MS benzene data were consistently high, indicating interference from ethylbenzene fragmentation for the 145 Td drift field intensity used in the experiment. Correlations between the open-path data measured at 16-m height over a 860-m path length (retroreflector in 430 m distance), and the point measurements collected at 37-m sampling height were best for benzene (r=0.61), and reasonably good for toluene, C_2-alkylbenzenes, naphthalene, styrene, cresols and phenol (r>0.5). There was good agreement between DOAS and PTR-MS measurements of benzene after correction for the PTR-MS ethylbenzene interference. Mixing ratios measured by DOAS were on average a factor of 1.7 times greater than the PTR-MS data for toluene, C_2-alkylbenzenes, naphthalene and styrene. The level of agreement for the toluene data displayed a modest dependence on wind direction, establishing that spatial gradients – horizontal, vertical, or both – in toluene mixing ratios were significant, and up to a factor of 2 despite the fact that all measurements were conducted above roof level. Our analysis highlights a potential problem in defining a VOC sampling strategy that is meaningful for the comparison with photochemical transport models: meaningful measurements require a spatial fetch that is comparable to the

grid cell size of models, which is typically a few 10 km^2. Long-path DOAS measurements inherently average over a larger spatial scale than point measurements. The spatial representativeness can be further increased if observations are conducted outside the surface roughness sublayer, which might require measurements at altitudes as high as 10 s of metres above roof level.

Final Revised Paper (PDF, 5527 KB) Discussion Paper (ACPD)

Citation: Jobson, B. T., Volkamer, R. A., Velasco, E., Allwine, G., Westberg, H., Lamb, B. K., Alexander, M. L., Berkowitz, C. M., and Molina, L. T.: Comparison of aromatic hydrocarbon measurements made by PTR-MS, DOAS and GC-FID during the MCMA 2003 Field Experiment, Atmos. Chem. Phys., 10, 1989-2005, 2010. Bibtex EndNote Reference Manager