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Emissions of volatile organic compounds inferred from airborne flux measurements over a megacity

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Abstract. Toluene and benzene are used for assessing the ability to measure disjunct eddy covariance (DEC) fluxes of Volatile Organic Compounds (VOC) using Proton Transfer Reaction Mass Spectrometry (PTR-MS) on aircraft. Statistically significant correlation between vertical wind speed and mixing ratios suggests that airborne VOC eddy covariance (EC) flux measurements using PTR-MS are feasible. City-median midday toluene and benzene fluxes are calculated to be on the order of 14.1±4.0 mg/m^2/h and 4.7±2.3 mg/m^2/h, respectively. For comparison the adjusted CAM2004 emission inventory estimates toluene fluxes of 10 mg/m^2/h along the footprint of the flight-track. Wavelet analysis of instantaneous toluene and benzene measurements during city overpasses is tested as a tool to assess surface emission heterogeneity. High toluene to benzene flux ratios above an industrial district (e.g. 10–15 g/g) including the International airport (e.g. 3–5 g/g) and a mean flux (concentration) ratio of 3.2±0.5 g/g (3.9±0.3 g/g) across Mexico City indicate that evaporative fuel and industrial emissions play an important role for the prevalence of aromatic compounds. Based on a tracer model, which was constrained by BTEX (BTEX– Benzene/Toluene/Ethylbenzene/m, p, o-Xylenes) compound concentration ratios, the fuel marker methyl-tertiary-butyl-ether (MTBE) and the biomass burning marker acetonitrile (CH_3CN), we show that a combination of industrial, evaporative fuel, and exhaust emissions account for >87% of all BTEX sources. Our observations suggest that biomass burning emissions play a minor role for the abundance of BTEX compounds in the MCMA (2–13%).

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