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Distribution, magnitudes, reactivities, ratios and diurnal patterns of volatile organic compounds in the Valley of Mexico during the MCMA 2002 & 2003 field campaigns

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Abstract. A wide array of volatile organic compound (VOC) measurements was conducted in the Valley of Mexico during the MCMA-2002 and 2003 field campaigns. Study sites included locations in the urban core, in a heavily industrial area and at boundary sites in rural landscapes. In addition, a novel mobile-laboratory-based conditional sampling method was used to collect samples dominated by fresh on-road vehicle exhaust to identify those VOCs whose ambient concentrations were primarily due to vehicle emissions. Four distinct analytical techniques were used: whole air canister samples with Gas Chromatography/Flame Ionization Detection (GC-FID), on-line chemical ionization using a Proton Transfer Reaction Mass Spectrometer (PTR-MS), continuous real-time detection of olefins using a Fast Olefin Sensor (FOS), and long path measurements using UV Differential Optical Absorption Spectrometers (DOAS). The simultaneous use of these techniques provided a wide range of individual VOC measurements with different spatial and temporal scales. The VOC data were analyzed to understand concentration and spatial distributions, diurnal patterns, origin and reactivity in the atmosphere of Mexico City. The VOC burden (in ppbC) was dominated by alkanes (60%), followed by aromatics (15%) and olefins (5%). The remaining 20% was a mix of alkynes, halogenated hydrocarbons, oxygenated species (esters, ethers,

etc.) and other unidentified VOCs. However, in terms of ozone production, olefins were the most relevant hydrocarbons. Elevated levels of toxic hydrocarbons, such as 1,3-butadiene, benzene, toluene and xylenes, were also observed. Results from these various analytical techniques showed that vehicle exhaust is the main source of VOCs in Mexico City and that diurnal patterns depend on vehicular traffic in addition to meteorological processes. Finally, examination of the VOC data in terms of lumped modeling VOC classes and its comparison to the VOC lumped emissions reported in other photochemical air quality modeling studies suggests that some alkanes are underestimated in the emissions inventory, while some olefins and aromatics are overestimated.

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