Geophysical Research Abstracts, Vol. 9, 00892, 2007
SRef-ID: 1607-7962/gra/EGU2007-A-00892

Eddy covariance measurements of trace gases and energy fluxes from a polluted megacity

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Direct measurements of emissions of trace gases that include all major and minor emission sources in urban areas are a missing requirement to improve and evaluate emission inventories, as well to understand better the atmospheric chemistry and the role that cities play in the global change, in particular megacities of developing countries. As part of the MCMA-2003 field campaign, we demonstrated the feasibility of using eddy covariance (EC) techniques coupled with fast-response sensors to measure urban fluxes of volatile organic compounds (VOC) and CO_2 from a residential district of Mexico City, where the spatial variability of surface cover, roughness and emission sources is high. With the objective to confirm the representativeness of the 2003 flux measurements in terms of the magnitude, composition, and overall distribution of urban emissions, a second flux system was deployed in a different district of Mexico City as part of the MILAGRO campaign in March 2006. For this second flux system a tall tower was erected in a busy district surrounded by congested avenues close to the center of the city.

In 2003 and 2006 olefins fluxes were measured using a Fast Olefin Sensor (FOS) by the EC technique. Fluxes of aromatic and oxygenated VOCs were analyzed by Proton Transfer Reaction-Mass Spectroscopy (PTR-MS) using the disjunct eddy covariance (DEC) technique. Fluxes of CO2 and H2O were measured using an open path Infrared Gas Analyzer (IRGA) and the EC technique. And fluxes of sensible and latent heat fluxes were also measured. In 2006 the number of VOC was extended using a disjunct eddy accumulation (DEA) system. This system collects whole air samples as function of the direction of the vertical wind component, and the samples are analyzed on

site using gas chromatography / flame ionization detection (GC-FID). Because a fast CO instrument could not be obtained, we employed a modified gradient method to estimate fluxes of CO.

In 2003 and 2006 we found that the urban surface is a net source of $CO_2$and VOCs. The diurnal patterns in both campaigns are similar, but the 2006 fluxes show higher values. This difference was due to the different characteristics of the monitored sites rather than an increment of the emissions over a 3-year period. In both campaigns the diurnal patterns show clear anthropogenic signatures, with important contribution from vehicular traffic. The 2006 DEA results for individual hydrocarbons, which were not measured in 2003, show that the alkane fluxes are considerably higher than alkene fluxes, which is consistent with ambient concentration measurements and with the emission inventory for Mexico City. CO fluxes, estimated from a modified gradient technique, were approximately 4% of the measured CO_2 fluxes which is generally consistent with expected combustion efficiencies for mobile and other sources. The energy balance distribution and radiative parameters observed are similar to distributions and parameters reported for other urban sites.