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Mixing ratios and eddy covariance flux measurements of volatile organic compounds from an urban canopy (Manchester, UK)

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Abstract. Mixing ratios and fluxes of six selected volatile organic compounds (VOCs) were measured above the city of Manchester (UK) during the summer of 2006. A proton transfer reaction-mass spectrometer was used for the measurement of mixing ratios, and fluxes were calculated from these using both the disjunct and the virtual disjunct eddy covariance techniques. The two flux systems, which operated in alternate half hours, showed good agreement, with R^2 values ranging between 0.74 and 0.9 for the individual analytes. On average, fluxes measured in the disjunct mode were approximately 20% lower than those measured in the virtual mode. This difference is due to both the dampening of the VOC signal by the disjunct flux sampler and carry over from one sample to the next. Correcting for these effects reduced the difference to less than 7%. Observed fluxes are thought to be largely controlled by anthropogenic sources, with vehicle emissions the major contributor. However, both evaporative and biogenic emissions may account for some of the VOCs present. Concentrations and fluxes of the oxygenated compounds were highest on average, ranging between 0.15 to 1 mg m^{-2} h^{-1}; the fluxes of aromatic compounds were lower, between 0.12 to 0.28 mg m^{-2} h^{-1}. The observed fluxes were up-scaled to give city wide emission estimates for each compound and the results compared to estimates made by the National Atmospheric Emission Inventory (NAEI) for the same flux footprint. Fluxes of toluene and benzene compared most closely differing by approximately 50%, while in contrast the oxygenated fluxes were found to be between 3.6–6.3 times larger than the annual average predicted by the NAEI.

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