Micrometeorological Measurements of Anthropogenic VOC Emissions from Urban Areas

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 1

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Summary

Emission fluxes of anthropogenic volatile organic compounds were measured above several European cities to quantify the emissions, assess the quality of emissions inventories, derive emission factors and to study the controls of the emissions.

Introduction

Emissions of anthropogenic volatile organic compounds (VOC) from area sources in the urban environment are currently highly uncertain, with most official national atmospheric emission inventories not providing a spatial breakdown of the VOCs. Even less is known about the emission of oxygenated compounds as these are difficult to measure reliably with gas chromatography. With the advent of the commercially available Ionicon Proton Transfer Reaction Mass Spectrometer (PTR-MS), several groups have recently reported direct micrometeorological measurements of VOC fluxes above vegetation. However, this technique has rarely been applied above urban areas, during two studies in Mexico City [Velasco *et al.*, 2005; Tom Jobson, 2006, unpublished data].

Scientific activities

We have recently measured VOC fluxes above several European cities, including Gothenburg, Sweden (February 2005) [Nemitz, *et al.*, 2005], Edinburgh, U.K. (November 2005), Manchester, U.K. (May 2006) and London, U.K. (October 2006) and report here preliminary results of the latest measurement campaign: measurements were made from 29th September to 2nd November 2006 at a height of 200 m from the Telecom Tower in central London (51°31'17" N; 0°08'20" W). The tower has a typical diameter of 16 m. A 12 m tall lattice tower structure was erected on its flat top (Level 40), with the ultrasonic anemometer (Model R3-50, Gill Instruments, U.K.) and gas inlet mounted 3 m above the top of the lattice tower. Air for the PTR-MS analysis was sampled down a 45 m Teflon tube (3/8" OD) to the instrument on Level-35 of the building, at a flow rate of about 60 *l* pm. Simultaneous measurements included fluxes of H_2O, CO_2, CO and O_3, aerosol fluxes (total number fluxes, size-segregated fluxes and chemically resolved). The PTR-MS was set up to scan through 10 masses at 50 ms dwell time, taking just over 1 s for each scan. Each concentration measurement was paired up with the associated wind data, in a virtual disjunct eddy covariance approach [Karl *et al.*, 2002], where the time lag of approximately 5 s was obtained as the maximum in the cross correlation function. For preliminary data analysis, concentrations were calculated using reaction rate constant (k) values from Zhao and

Zhang [2004] and reaction time (t) values were calculated as $t = L/v_d$, where L is the length of the reaction chamber and v_d is the drift velocity [Lindinger, 1998].

Scientific results and highlights

This section presents some of the highlights of the preliminary data analysis. An example time-series of the concentrations and fluxes of acetone and ethylbenzene are shown in Figure 1. Fluxes show a clear diurnal pattern and are reduced at the weekend (21st and 22nd October) and largest on the Monday (23rd October). The ratio in the fluxes of these two compounds is variable.

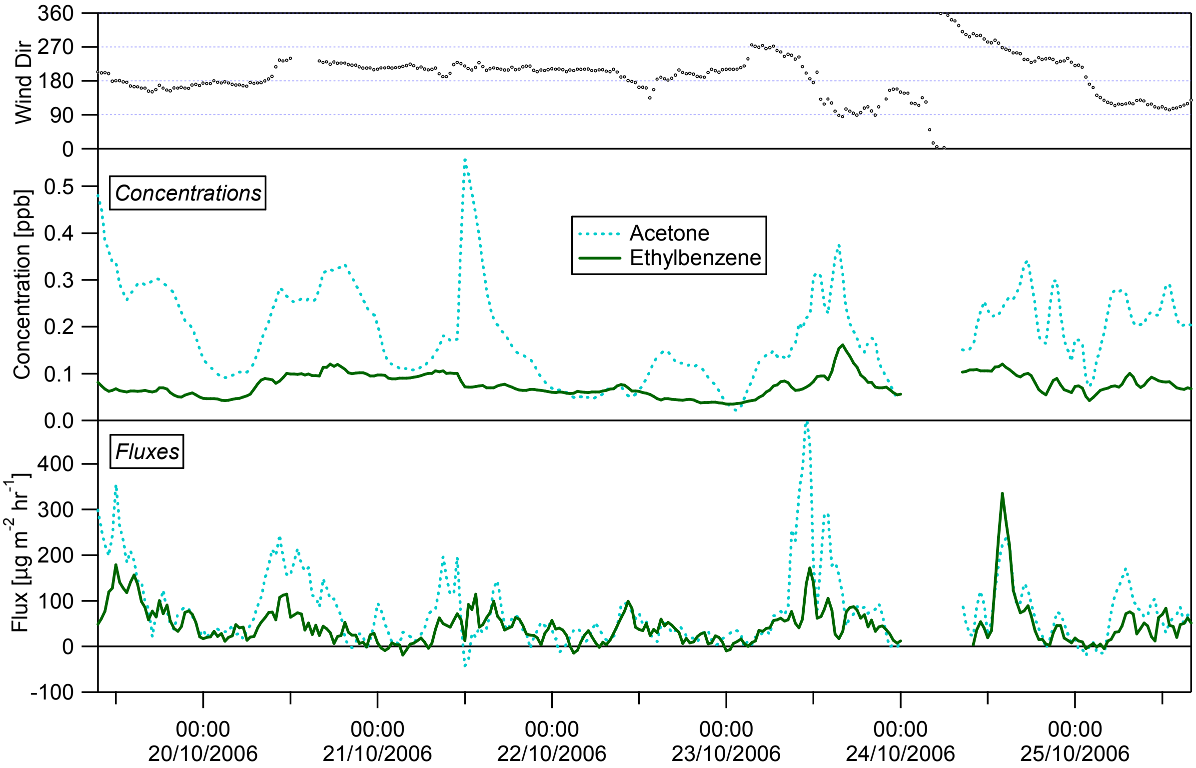

Figure 1. Example time series of acetone (derived from *m/z* 59) and ethylbenzene (derived from *m/z* 107) in relation to wind speed.

Averaged diurnal cycles for the third measurement week (19th – 26th October) are presented in Figure 2. The average diurnal patterns of the fluxes of the different compounds is roughly similar and follows the expected pattern of traffic activity in the city. The absence of a clear two-peak rush-hour pattern is consistent with earlier CO_2 flux measurements made above a city centre [Nemitz *et al.,* 2002]; rush-hour behaviour tends to be more pronounced on commuter roads. However, while traffic starts to rise around 6 am local time, as measured at the nearby Marylebone Road [AQEG, 2004], the observed emissions rise at 10 GMT (8 am local time). It is probable, that at night, due to the high measurement height, the site is de-coupled from the street-canyon activity and that fluxes are only observed as the nocturnal boundary layer breaks up in the morning.

Despite the fluxes following a similar pattern, there are also differences. For example, isoprene emissions rise later in the day, indicating that a biological control may be contributing to the emissions. Some emissions remain relatively large into the late evening hours (benzene, acetaldehyde, acetonitrile), while others decrease more rapidly (isoprene, ethylbenzene, acetone, methanol). This may be due to a change in the sources in the evening (*e.g.* larger contribution of residential heating sources, shift of the traffic composition away from HGV, larger fraction of taxi journeys) or a change in the meteorological drivers (such as surface temperature for biological and fugitive sources).

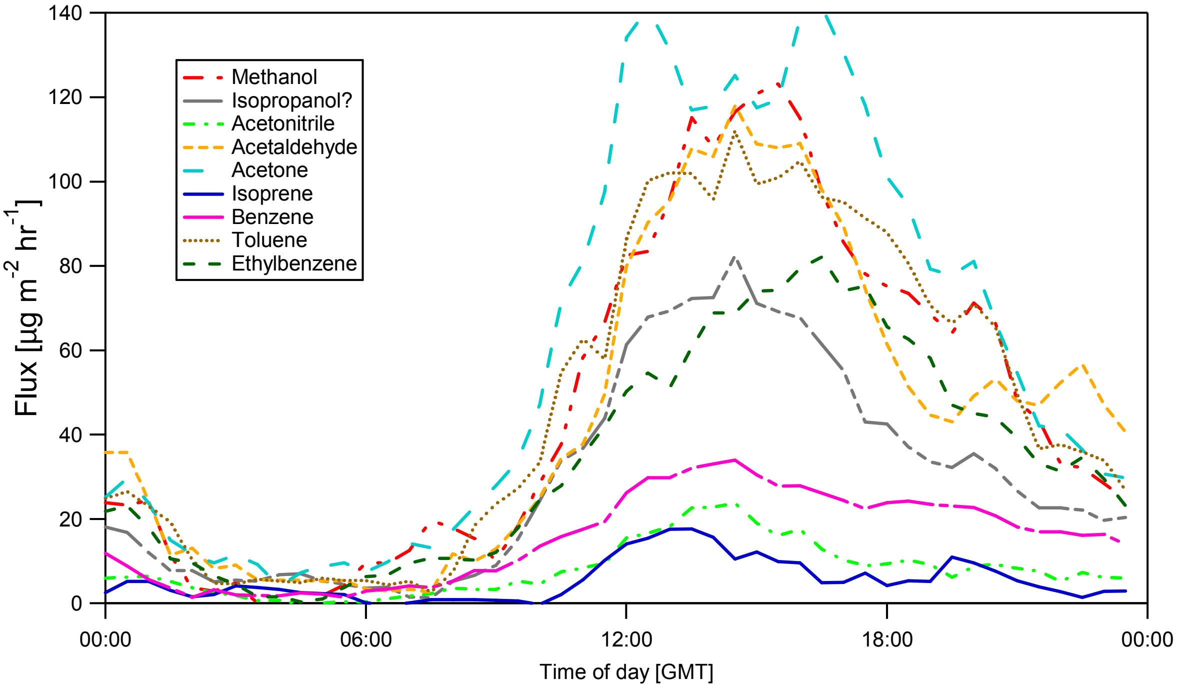

Figure 2. Averaged diurnal cycles of the flux for measurement week 19th-26th October 2006.

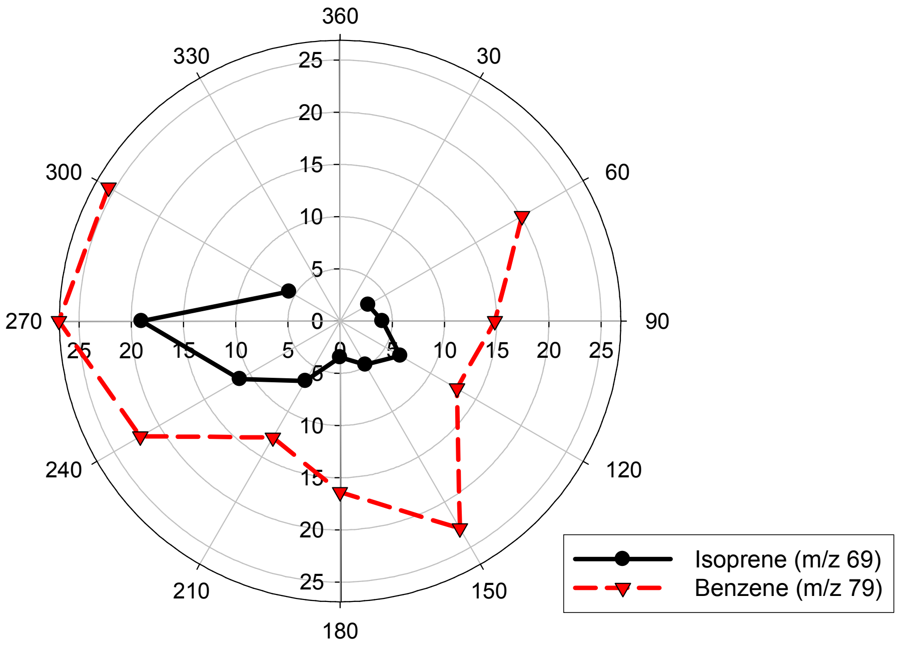

Figure 3. Wind sector dependence of the flux of isoprene and benzene (in μg m^{-2} hr^{-1}).

The different compounds also differ in their wind sector dependence. For example, isoprene shows a distinct increase under westerly conditions, possibly linked to urban park land in this direction, while many compounds, such as benzene, show a more homogeneous wind sector distribution (Figure 3). Isoprene has been reported to be emitted both from vehicle sources and from humans. However, the different behaviour of isoprene observed in this study (both in terms of temporal and spatial pattern), compared with the clearly anthropogenic gases, indicates that biogenic sources may contribute to the emission of this compound, even in autumn in a UK city.

Future outlook

The data presented here constitute only a very preliminary analysis and will need to be analysed in the context of the ancillary measurements (such as fluxes of CO_2 and CO). In addition, comparison with GC analysis of flask samples and adsorption cartridges will need to confirm the interpretation of the m/z measured with the ptr-ms. However, the data already look extremely promising and show that direct flux measurements in the urban environment by ptr-ms and eddy-covariance and possible, provide an independent assessment of emission inventories and provide information on the control of the emissions of a range of anthropogenic VOCs.

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