



Concentrations of selected volatile organic compounds at kerbside and background sites in central London



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HIGHLIGHTS

- Volatile organic compound concentrations were measured in central London.
- Measurements were compared with the automatic hydrocarbon network.
- Vehicle emissions were the main source at both urban background and kerbside sites.
- Some effects of temperature on compound correlations were observed.
- Excellent qualitative agreement was seen between the measurement instruments.

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ABSTRACT

Ground-level concentrations of nine volatile organic compounds (VOCs) were measured using a proton transfer reaction-mass spectrometer (PTR-MS) in central London at an urban background (North Kensington, NK, during 16th–25th Jan 2012) and a kerbside site (Marylebone Rd, MRd, during 25th Jan–7th Feb 2012) as part of the winter intensive observation period of the ClearLo project. Site comparisons indicated that VOC concentrations at the urban background site were significantly lower than at the kerbside site (ratio MRd/NK of 2.3). At the kerbside site PTR-MS measurements of aromatics (benzene, toluene, C₂- and C₃-benzenes) were compared with the gas chromatography – flame ionization detector data from the UK Government's Automatic Hydrocarbon Network. Very good qualitative agreement was observed between the two methods ($r = 0.90\text{--}0.91$, $p < 0.001$, $N = 260$), although there was a significant offset between the instruments. This was partly due to issues with humidity dependent background measurements, but possibly also from isobaric interference of other compounds and their fragments, giving a positive bias to the PTR-MS data. Most compounds showed strong indications of traffic-related sources with double rush hour peaks in diurnal profiles and high correlations with known traffic-related compounds ($r = 0.68\text{--}0.97$ at NK, $0.48\text{--}0.87$ at MRd, $p < 0.001$, $N_{\text{NK}} = 2202\text{--}2227$, $N_{\text{MRd}} = 2705\text{--}2720$) and CO ($r = 0.80\text{--}0.96$ at NK, $0.65\text{--}0.84$ at MRd, $p < 0.001$, $N_{\text{NK}} = 223$, $N_{\text{MRd}} = 256\text{--}274$). Polar plots agreed with statistical analysis of wind direction dependency and identification of potential emission sources was attempted.

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1. Introduction

Anthropogenic sources of volatile organic compounds (VOCs) are of particular importance in urban areas due to the intensity of fossil fuel combustion and the relative paucity of biogenic sources

in cities. A wide range of VOCs are emitted directly by the evaporation of fuels and solvents, as unburnt fuel and as partially oxidized compounds from combustion processes, mostly vehicle emissions (Kansal, 2009). Some VOCs can directly affect human health (e.g. benzene, which is a known carcinogen) while others contribute to the formation of ozone and aerosol particles in the atmosphere (Derwent, 1995). Both have detrimental effects on human health and the environment (Kim et al., 2001). In winter elevated VOC concentrations are observed due to the shallow daytime boundary layer with limited dilution and mixing. In the

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UK, VOC emissions are subject to control under European Commission Directive 2008/50/EC. Monitoring networks such as the Automatic Hydrocarbon Network (AHN) provide a running annual mean concentration for a suite of pollutants. Emissions are estimated as part of the National Atmospheric Emission Inventory (NAEI) activity (Yardley et al., 2012).

A wide range of studies focus on VOC concentrations and air quality in cities around the world using diverse measuring techniques (Baker et al., 2008; Jobson et al., 2010). Due to the variety of emission sources, meteorological conditions, and often short atmospheric lifetimes of the compounds, VOC volume mixing ratios can be associated with large variability. Slow response instruments have identified seasonal and diurnal patterns of urban VOC concentrations (Kim et al., 2001), however only fast response instruments have been shown to record this short term variability.

The aim of this study was to:

- I. Quantify a suite of VOCs at an urban background and a kerbside site in winter and;
- II. Compare VOC volume mixing ratios from fast response PTR-MS measurements with the GC-FID measurements from the Automatic Hydrocarbon Network.

This study was part of the winter intensive observation period of the Clean Air for London project (ClearLo, www.clearflo.ac.uk), aimed to research boundary layer pollution over London in 2011–2012 (Bohnenstengel et al., submitted for publication). Here

we report measurements of nine VOC species measured at high temporal resolution at a kerbside and a background site in central London (16th January–7th February 2012).

2. Methods

2.1. Measurement sites and meteorology

Details of both the North Kensington (NK) background and Marylebone Rd (MRd) kerbside sites are compared (Supplementary content Table A1). Air was pumped through a PTFE inlet (and PTFE filter at MRd) attached to 1/4" OD PTFE tubing to a high sensitivity proton transfer reaction-mass spectrometer (PTR-MS; Ionicon Analytik GmbH, Innsbruck, Austria).

Meteorological measurements were co-located with the inlet at NK (Fig. 1 and Supplementary content Table A1). The mean UK temperature in January was 6.0 °C, i.e. 1.3 °C above the 1971–2000 average (UK Met Office, 2012), although February experienced low temperatures and snowfall, which is uncommon in London.

2.2. VOC sampling

VOC mixing ratios were measured on-line using a PTR-MS (de Gouw and Warneke, 2007; Lindinger et al., 1998). The instrument was operated in multiple ion detection (MID) and mass scan (SCAN) modes (Supplementary content A1). In MID mode the quadrupole mass spectrometer scanned through 11 pre-determined masses, to

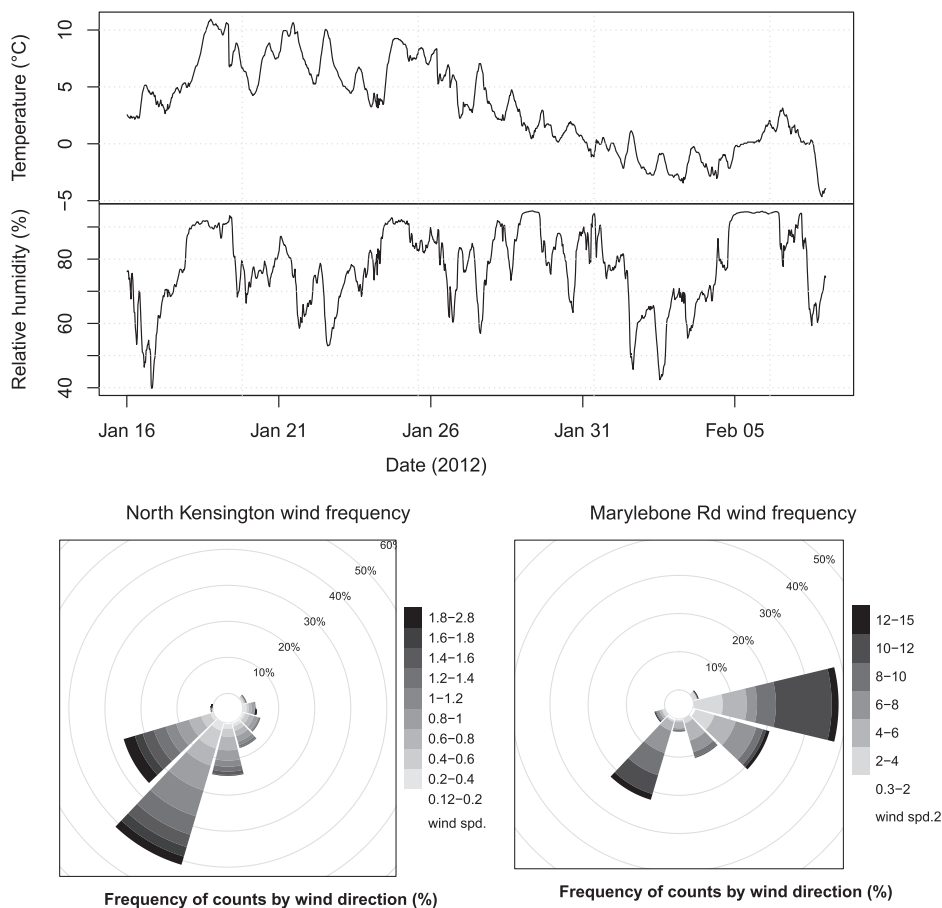


Fig. 1. Top: 5 min means of ambient air temperature (°C) and relative humidity (%) during the campaign 16th Jan–7th Feb 2012. Bottom: Frequency plots of mesoscale wind direction (%) with subcategories of wind speed (m s^{-1}) using 30 min mean data from the WXT520 (Vaisala Ltd) at 190 m on the BT tower at NK (16th–25th Jan 2012) (left) and MRd (25th Jan–7th Feb 2012) (right).

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