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Traffic Emissions of Semi-Volatile Organic Compounds Analysed by GC×GC ToF MS

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Epidemiological studies have consistently shown links between adverse health outcomes and airborne particle exposure. Within the urban environment, road traffic, particularly diesel vehicles, is one of the most significant emission sources of particles. Many uncertainties exist regarding the semi-volatile organic component of the particles, which partitions directly between gas and particulate phase under ambient conditions. Detailed knowledge of the identities and chemical composition of SVOC is elusive, as traditional gas chromatographic methods are unable to separate and characterise complex mixtures adequately. There are few studies on the abundance of gaseous longer chain hydrocarbons emitted from traffic in the atmosphere. This study identifies and quantifies SVOC in both gas and particle phases from C12 to C31, providing a more comprehensive understanding of the semi-volatile organic compounds emitted from traffic.

Ambient air samples were collected by an in-house autosampler during the winter period 24 Jan to 18 April 2017 in central London (UK) on heavily trafficked Marylebone Road and adjacent Regent's Park, about 380m north of Marylebone Road. Twin-site measurements were applied to quantify the change in composition of SVOC during advection from the traffic to the cleaner atmosphere of the park. Samples were collected simultaneously on the roof of University of Westminster (WM) above Marylebone Road and a roof of Regent's University (RU) located in Regent's Park. Samples were also collected over different time periods in a kerbside cabin on the south side of Marylebone Road (M Road) below the WM monitoring site and an urban background site, Eltham. The air was drawn through a PTFE filter to collect the particulate phase and then through an adsorbent tube to collect the gas phase. Samples were analysed using thermal desorption coupled to comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (TD-GC×GC-ToF-MS). Complementary data were also collected including black carbon, particle size distributions and various meteorological parameters.

Groups of compounds identified and quantified in vapour and particles include total alkanes (n-alkanes and branched alkanes), cyclic alkanes, bicyclic alkanes, monocyclic aromatics, ketones, aldehydes, decalins, tetralins, PAH, and oxygenated-PAH. The low molecular weight n-C12 to n-C18 alkanes were the most abundant homologues in the gas phase, while the n-C14 to n-C17 and n-C21 to n-C22 alkanes were the most abundant homologues in the particulate phase. The peaks present in alkanes in C15-C20 derive from diesel fuel, and C18-C33 from engine oil, based upon their volatility profile and mass spectra. The concentrations of hydrocarbons at WM were higher than RU. Expectedly M Road concentrations were the highest of all sites as it is a heavily trafficked site. The large SVOC concentrations in the gas phase could contribute to secondary organic aerosol (SOA) generation following reaction with atmospheric oxidants. These compounds may also contribute to increased OH reactivity. Gas-particle phase partitioning is discussed and compared between sites. Pearson correlations between SVOCs and black carbon, and SVOCs and NO_x in multiple locations were compared to investigate the influence of traffic sources.