Measurement of air pollutants in the troposphere

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ABSTRACT This article describes the principles, applications and performances of methods to measure gas-phase air pollutants that either utilise passive or active sampling with subsequent laboratory analysis or involve automated *in situ* sampling and analysis. It focuses on air pollutants that have adverse impacts on human health (nitrogen dioxide, carbon monoxide, sulfur dioxide and benzene), vegetation (ozone) or climate change (ozone, carbon dioxide, methane and nitrous oxide). It begins with an explanation of why air pollutants are measured and concludes with prospects for the future and an illustration of recent trends in air pollutants derived from road traffic recorded in central London.

Measurements of ozone (O_3) in the troposphere (the lowest region of the atmosphere) have been made throughout Europe since 1850. Initially, Schönbein papers covered in a paste of starch and potassium iodide, which turns a darker shade of blue in the presence of increasing concentrations of O_3, were exposed to ambient air in a network of more than 300 sites in the mistaken belief of beneficial health effects of O_3. From 1876 to 1886, a more refined method using iodine-catalysed oxidation of aqueous arsenite was deployed at the Montsouris Observatory near Paris. Comparison of O_3 measurements at Montsouris using both methods led to revision of data from many other sites. More recent validation of the Montsouris method against modern instrumentation based on ultraviolet (UV) photometry and comparison with contemporary data from Arkona on the Baltic coast has confirmed that present-day O_3 concentrations in the background troposphere are not only a factor of 2 or so greater than in the pre-industrial late nineteenth century but also exhibit a seasonal dependence with a spring maximum (Clemitshaw, 2004). Similar conclusions can be drawn from historical O_3 monitoring data from Athens (Greece), Arosa (Switzerland), Bavaria (Germany) and Moncalieri (Italy) (Vingarzen, 2004).

Since these quite modest beginnings, a wide range of increasingly sophisticated measurement methods have been developed, not only for O_3 but also for the primary air pollutants, such as carbon monoxide (CO), volatile organic compounds (VOCs) and oxides of nitrogen, that react via complex mechanisms to produce O_3 and other secondary air pollutants in the troposphere. This article describes the principles, applications and performances of selected methods to measure gas-phase air pollutants that utilise passive or active sampling with subsequent laboratory analysis or involve automated *in situ* sampling and analysis. It focuses on air pollutants that have adverse impacts on:

● human health – nitrogen dioxide (NO_2), CO, sulfur dioxide (SO_2) and benzene (C_6H_6);
● vegetation – O_3;
● climate change – O_3, carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O).

Why measure gas-phase air pollutants?

There are several reasons why gas-phase air pollutants are measured. Research is essential to understand natural and artificial sources of gas-phase air pollutants, their dispersion and chemical conversion, and their impacts on health, vegetation, ecosystems and climate. Research is also essential to understand how air quality changes on timescales of days, weeks, seasons and years at contrasting urban, rural and remote geographic locations. This understanding is vital to formulate national and international

strategies and policies to reduce emissions and manage air quality on local, regional and global scales. Also, by understanding the key processes involved, numerical modelling of air pollution and meteorological data can be used to forecast seasonal episodes of poor air quality. Preliminary data from air pollution monitoring networks can be quickly ratified and relayed to the public via a range of media to inform individuals with health problems and concerns about their personal exposure to poor air quality. Finally, member states of the European Union (EU) are legally obliged to comply with Framework (and Daughter) Directives on air quality assessment and management. Within the UK, local authorities use methods recommended by the EU to monitor and assess air quality to demonstrate that EU and UK Air Quality Strategy objectives to reduce levels of pollutants by certain dates are being met (Defra, 2007). If not, air quality management areas are declared, with action plans implemented to reduce local emissions of offending pollutants. Table 1 summarises the UK and EU air quality objectives for the air pollutants discussed below, and also includes information for particulate matter (PM). The series of reports by the UK Air Quality Expert Group (AQEG) addresses many of these issues in some detail (AQEG, 2004; 2005; 2007a; 2007b; 2009).

Passive diffusion tube sampling for NO_2 and benzene

Nitric oxide (NO) and NO_2, known collectively as NO_x, are formed during high-temperature combustion processes. Global production of NO_x by volcanic action and lightning far exceeds that generated by combustion of fossil fuels for heating, power and transport. Human health impacts of NO_2 include irritation of the eyes and respiratory system, and shortness of breath. Benzene is a VOC with major sources from the combustion, refining, distribution and evaporation of petrol. Long-term exposure to benzene (and to 1,3-butadiene, $CH_2(CH)_2CH_2$) can lead to cancer and thus both compounds are subject to air quality objectives and widespread monitoring. For benzene, cumulative exposure and health risks continue to reduce in the UK as ambient concentrations have decreased over the last 10 years, largely in response to changes in fuel formulations and technology.

Passive diffusion tube samplers provide an inexpensive and effective maintenance-free means of conducting wide-scale spatial surveys of NO_2 and benzene averaged over time periods of several weeks. For NO_2, Palmes tubes that comprise 7.1 cm long acrylic tubes of internal diameter 1.08 cm are generally used. Two stainless steel meshes impregnated with triethanolamine (TEA; $N(CH_3CH_2OH)_3$) are fixed with a red polythene cap at one end; following vertical suspension of the tube, a white cap at the other end is removed for a measured exposure time. A diffusion flux F of NO_2 in ambient air at a concentration of C and with a diffusion coefficient of D is created along the tube length L, according to Fick's law, $F = -D(dC/dL)$, with the NO_2 absorbed by the TEA in the form of NO_2^- (nitrite ion). After extraction into water, aqueous NO_2^-, which is related to gas-phase NO_2, may be quantified directly using ion chromatography or indirectly via measurement of a coloured diazo dye derivative. A bias correction, calculated from measurements of NO_2 using chemiluminescence, is often applied. Note that the samplers described by Ferm and Svanberg (1998) are only 1 cm long, which lessens the production of NO_2 within the tube via reaction between ambient NO and O_3. Furthermore, a porous membrane protected by a stainless steel mesh minimises turbulence along the tube, which impairs the performance of the Palmes tubes. The relative merits of diffusion tubes to monitor NO_2 have been reviewed recently (Cape, 2009).

For benzene, 9 cm long and 0.5 cm internal diameter stainless steel tubes filled with a solid polymer adsorbent (Chromosorb 106) and fitted with two brass caps are used. The tubes are mounted vertically and during exposure to ambient air the lower cap is replaced by an aluminium diffuser. Benzene concentrations are determined by thermal desorption followed by gas chromatography with mass spectrometric or flame ionisation detection. Diffusion tube analyses are typically subcontracted to accredited analytical and testing laboratories that use approved standard operating procedures and certified reference materials.

Active sampling and automated measurements of O_3, NO, NO_2, CO, SO_2 and hydrocarbons

In contrast with passive sampling, active sampling involves chemical and/or physical collection of air pollutants by pumping a measured volume of air through a solution, cartridge or filter, etc., for

Table 1 UK and EU air quality objectives; all are based on human health impacts except those for O_3, which are based on protection of vegetation and ecosystems

Pollutant	Measure	UK		EU	
		Objective	Date	Objective	Date
NO_2	1 hour mean	$200\,\mu g\,m^{-3}$ not to be exceeded more than 18 times a year	31 Dec 2005	$200\,\mu g\,m^{-3}$ not to be exceeded more than 18 times a year	1 Jan 2010
	Annual mean	$40\,\mu g\,m^{-3}$	31 Dec 2005	$40\,\mu g\,m^{-3}$	1 Jan 2010
NO_x	Annual mean	$30\,\mu g\,m^{-3}$	31 Dec 2000	$30\,\mu g\,m^{-3}$	19 Jul 2001
SO_2	15 minute mean	$266\,\mu g\,m^{-3}$ not to be exceeded more than 35 times a year	31 Dec 2005		
	1 hour mean	$350\,\mu g\,m^{-3}$ not to be exceeded more than 24 times a year	31 Dec 2004	$350\,\mu g\,m^{-3}$ not to be exceeded more than 24 times a year	1 Jan 2005
	24 hour mean	$125\,\mu g\,m^{-3}$ not to be exceeded more than 3 times a year	31 Dec 2004	$125\,\mu g\,m^{-3}$ not to be exceeded more than 3 times a year	1 Jan 2005
	Annual mean and winter mean	$20\,\mu g\,m^{-3}$	31 Dec 2000	$20\,\mu g\,m^{-3}$	19 Jul 2001
O_3	8 hour mean	$100\,\mu g\,m^{-3}$ not to be exceeded more than 10 times a year	31 Dec 2005	$120\,\mu g\,m^{-3}$ not to be exceeded more than 25 times a year over 3 years	31 Dec 2010
	5 year mean from 1 hour values during May–July	$18\,000\,\mu g\,m^{-3}$ based on AOT40	1 Jan 2010		
CO	Maximum daily running 8 hour mean	$10\,mg\,m^{-3}$	31 Dec 2003	$10\,mg\,m^{-3}$	1 Jan 2005
PAHs	Annual mean	$0.25\,ng\,m^{-3}$ B[*a*]P	31 Dec 2010	$1\,ng\,m^{-3}$ B[*a*]P	31 Dec 2012
Benzene	Running annual mean	$16.25\,\mu g\,m^{-3}$	31 Dec 2003		
	Annual mean	$5\,\mu g\,m^{-3}$ (England and Wales)	31 Dec 2010	$5\,\mu g\,m^{-3}$	1 Jan 2010
	Running annual mean	$3.25\,\mu g\,m^{-3}$ (Scotland and Northern Ireland)	31 Dec 2010		1 Jan 2010
1,3-butadiene	Running annual mean	$2.25\,\mu g\,m^{-3}$	31 Dec 2003		
PM_{10}	24 hour mean	$50\,\mu g\,m^{-3}$ not to be exceeded more than 35 times a year	31 Dec 2004	$50\,\mu g\,m^{-3}$ not to be exceeded more than 35 times a year	1 Jan 2005
	Annual mean	$40\,\mu g\,m^{-3}$	31 Dec 2004	$40\,\mu g\,m^{-3}$	1 Jan 2010
	24 hour mean	$50\,\mu g\,m^{-3}$ not to be exceeded more than 7 times a year (Scotland)	31 Dec 2010		
	Annual mean	$18\,\mu g\,m^{-3}$ (England and Wales)	31 Dec 2010		
$PM_{2.5}$	Annual mean	$25\,\mu g\,m^{-3}$	2020	Target value $25\,\mu g\,m^{-3}$	2010
	Annual mean	$12\,\mu g\,m^{-3}$	2020	Limit value $25\,\mu g\,m^{-3}$	2015
	Annual mean	15% reduction in urban background concentrations	2010–2020	20% reduction in urban background concentrations	2010–2020

AOT40 = accumulated ozone exposure over a threshold of 40 parts per billion; B[*a*]P = benzo[*a*]pyrene; PAH = polyaromatic hydrocarbon; PM_{10} = particulate matter with aerodynamic diameter of $10\,\mu m$ or less; $PM_{2.5}$ = particulate matter with aerodynamic diameter of $2.5\,\mu m$ or less.

a measured time period. This approach provides relatively low-cost data, especially if subsequent laboratory analyses are not labour intensive.

Although generally quite expensive, automated *in situ* monitoring produces real-time data for a wide range of air pollutants, including NO,

NO_2, CO, O_3, SO_2 and VOCs, at typical time intervals of 1 minute to 1 hour. This approach requires high standards of instrument maintenance and operation. It also requires documented and audited quality assurance to assess and improve data collection and quality, with rigorous quality control of sampling and multi-point calibration procedures and operational specifications.

Ozone

O_3 is produced in the troposphere via the oxidation of VOCs and CO in the presence of NO_x, a process that is initiated by hydroxyl radicals (OH) and propagated by peroxy radicals (HO_2 and RO_2). The observed trends of increasing O_3 throughout much of the troposphere are of concern because O_3 acts as a greenhouse gas in the troposphere and contributes to global warming, and also has adverse impacts on health, vegetation and materials. Measurements of O_3 are therefore essential to evaluate the effectiveness of policies to reduce O_3 based on strategies to abate emissions of VOCs and NO_x, and to monitor compliance with air quality objectives set primarily to decrease adverse impacts on vegetation and ecosystems.

There is a wide range of commercially available instruments that utilise the absorption of 254 nm UV radiation from a low-pressure mercury lamp to monitor O_3. Sample (O_3) and reference (O_3-free) signals are determined sequentially with a single optical cell equipped with a bypassable O_3 fore-trap, or are obtained simultaneously using twin cells in parallel, each with a bypassable O_3 fore-trap. For a measured optical path length (L), O_3 concentrations (C) are related to the sample (S) and reference (R) signals by application of the Beer–Lambert Law, $C = \ln(R/S)/(LX)$, where X is the absorption cross section of O_3 at 254 nm. Response times are typically 5–10 seconds, accuracy and precision are less than 5%, and detection limits are approximately 1 ppbv (parts per billion by volume) O_3. Despite non-negligible positive interferences in highly polluted atmospheres from aromatic VOCs that also absorb 254 nm radiation, this relatively simple but highly reliable method remains in widespread use for routine and research measurements of O_3.

Nitric oxide and nitrogen dioxide

Detection of NO and NO_2 generally exploits the chemiluminescent gas-phase reaction of NO with excess O_3 during which light of wavelength

590–875 nm is emitted from the electronically excited NO_2 product NO_2^*:

$$NO + O_3 \rightarrow NO_2^* + O_2$$
$$NO_2^* \rightarrow NO_2 + light$$
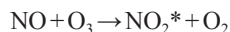
The intensity of emitted light is generally measured with a red-filtered, temperature-controlled photomultiplier tube (PMT) and is directly proportional to the concentrations of calibration gas mixtures of NO/N_2 blended with air, and therefore to ambient NO (Figure 1). Measurements of NO_2 require its modulated conversion to NO, with NO_2 derived by subtracting NO from the ($NO + NO_2$) NO_x signal. Almost exclusively, commercial instruments for NO and NO_2 use molybdenum heated to 300–400 °C to convert NO_2 into NO with typical efficiencies of 95–100%. However, it has long been recognised that nitrous acid (HNO_2 or HONO), nitric acid (HNO_3), peroxyacetylnitrate (PAN; $CH_3C(O)O_2NO_2$) and organic nitrates ($RONO_2$) are also converted to NO with high efficiency and measured as NO_2 (Clemitshaw, 2004). Elevated levels of these compounds formed during photochemical air pollution episodes may contribute to erroneous breaches of EU air quality objectives.

Research instrumentation mainly employs high-pressure xenon arc lamps (or more selective laser systems) to photo-dissociate NO_2 to NO:
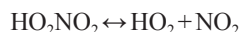
$$NO_2 + hf \rightarrow NO + O$$
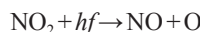
where *hf* represents the photon energy. Conversion efficiencies of up to 70% can be achieved. However, positive interference from photo-dissociation of HONO to NO,

$$HONO + hf \rightarrow HO + NO$$
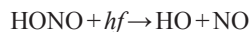
may be significant, with temperature control required to minimise thermal decomposition to NO_2 of PAN,

$$CH_3C(O)O_2NO_2 \leftrightarrow CH_3C(O)O_2 + NO_2$$
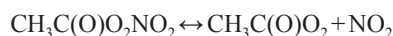
and peroxynitric acid (PNA; HO_2NO_2),

$$HO_2NO_2 \leftrightarrow HO_2 + NO_2$$

Sequential or simultaneous measurements of NO and NO_2 may be made with instruments equipped with single or dual detectors. In each case, a sequence of zero (obtained by pre-reacting the sample air with O_3 upstream of the reaction vessel to remove NO), NO or NO_x, zero, … is usually adopted. For integration time periods of 10 seconds,
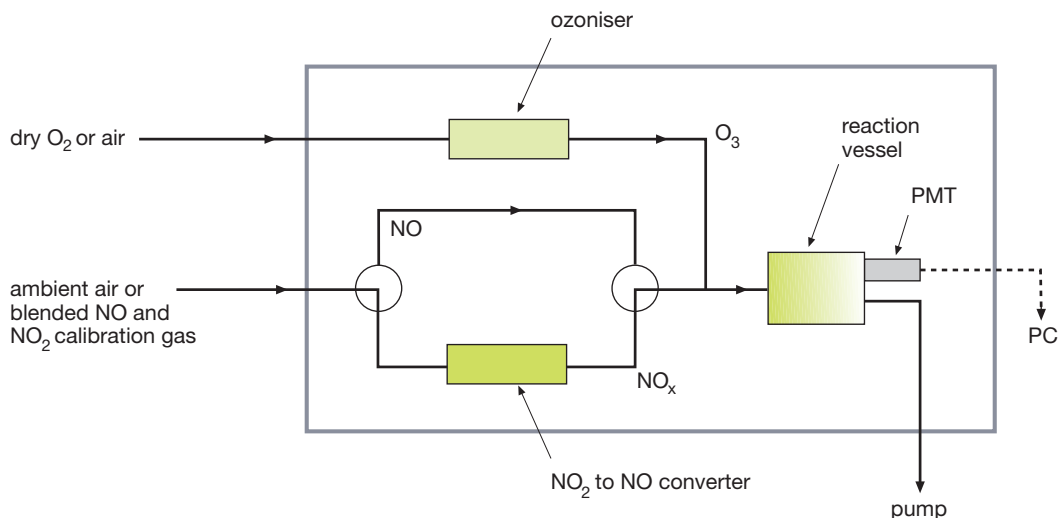
Figure 1 Simplified schematic diagram of a chemiluminescent analyser for measurements of NO and NO_x. Ambient air (or NO and NO_2 calibration gases) either flows directly to the reaction vessel where it reacts with O_3 and thus NO is measured, or flows through the NO_2 to NO convertor in which case NO_x is measured. NO_2 is obtained from the difference between NO_x and NO. PMT = photomultiplier tube.

sensitivities of 10 counts per second and detection limits of 1 pptv (parts per trillion by volume) NO are achievable with estimated uncertainties of 10%.

Carbon monoxide

Combustion of fossil fuels for transport, biomass burning, and the oxidation of VOCs provide important sources of CO, which plays a central role in the troposphere as a major sink for OH. Ground-based measurements of CO may be made with gas filter correlation (GFC) and gas chromatography (GC) with HgO reaction/UV detection (GC-HgO/UV). Analysis of air samples by gas chromatography with flame ionisation detectors (GC-FID) is also widely used. However, tunable diode laser absorption spectroscopy (TDLAS) and resonance-fluorescence spectroscopy provide higher frequency and more precise and sensitive measurements suitable for airborne studies of CO.

Gas filter correlation (GFC) is a modified version of non-dispersive infrared (NDIR) radiometry in which radiation from a stable broadband infrared source is filtered and focused before passing through an optical cell containing the sample gas. A reference signal is recorded by passing the radiation through a cell containing a calibration gas mixture. The difference in sample and reference signals detected quantifies the gas present in the sample. In GFC, a chopper wheel

is used to modulate the reference cell into and out of the optical path of a multi-pass sample cell. Although individual measurements are short, long averaging times of 10–60 minutes are required to achieve acceptable detection limits of 20–70 ppbv CO and precisions of 5–10%.

Commercial GC-HgO/UV instruments switch between sampling ambient air and a calibration gas mixture, and allow air sample pressure to equilibrate before analysis. Pre-columns of silica gel allow back-flushing of potential detector contaminants such as CO_2, non-methane hydrocarbons (NMHCs) and H_2O vapour, which elute after H_2 and CO. CO is separated from H_2 in a molecular sieve column at about 105 °C and then oxidised on a bed of solid HgO at 265 °C to produce Hg vapour, which is measured by UV absorption at 254 nm. Detection limits of approximately 1 ppbv are typical. Frequent multi-point calibrations using air as a carrier gas are required to characterise non-linear responses.

Sulfur dioxide

Although natural sources of SO_2 are significant globally, the highest levels of SO_2 derive from combustion of fossil fuels for power, heating and industry. In the UK, impacts of SO_2 on health, such as bronchitis and asthma, and within the EU on vegetation and ecosystems via precipitation of

its oxidation product, sulfuric acid (H_2SO_4), have reduced considerably as a consequence of greatly reduced UK emissions of SO_2 from power stations and a decline in the burning of coal for domestic heating. Air quality monitoring networks typically use instrumentation based on the detection of UV fluorescence: after adsorption of interfering fluorescent hydrocarbons from ambient air, SO_2 is excited from its ground state to a higher electronic state via the absorption of laser or filtered UV light in an optical cell. The intensity of light emitted during the return to the ground state is measured with a PMT perpendicular to the light source. This method is limited to chemical species with bound upper electronic states because of the need to reduce competing processes of dissociation, physical deactivation and fluorescence quenching. With enhanced light collection optics, detection limits of 80–100 pptv SO_2 with a precision of 10–20 pptv can be achieved for measurement integration times of 5–10 minutes.

Hydrocarbons

Biogenic emissions and industrial and vehicle combustion of fossil fuels provide major sources of hydrocarbons in the troposphere. Sampling methods for hydrocarbons include the collection of ambient air, either at high pressure in passivated stainless steel canisters or by trapping on a wide variety of solid organic polymeric, inorganic and carbon-based adsorbents. Sample analyses can be carried out in the laboratory, or in near real time following automated sample collection. A widely applied quantitative analytical technique for C_2 to C_9 NMHCs is GC-FID, which is often combined with mass spectrometry (GC-MS) to identify compounds unambiguously from their retention times and mass spectra. However, the closely related methods of chemical ionisation mass spectrometry (CIMS) and proton transfer reaction mass spectrometry (PTR-MS) are being used increasingly for specific hydrocarbons. Differential optical absorption spectroscopy (DOAS) and, to lesser extent, LIDAR (light detection and ranging) are used particularly for spatially integrated measurement of monocyclic aromatic hydrocarbons in air pollutant plumes.

Prospects for the future

A versatile measurement method that is finding increasingly widespread application is cavity ring-down spectroscopy (CaRDS), which was first described in the late 1980s. CaRDS is based on measurement of the rate of loss of intensity as a pulse of laser light is multiply reflected between a set of highly reflective mirrors that comprises an optical resonator or ring-down cavity. Light intensity decreases during reflection and scattering, and via absorption by a gas-phase species, X. The rate of loss of intensity is measured by abruptly stopping the injection of light into the cavity, thereby allowing it to 'ring down'. The resulting decay transient is exponential and is characterised by a typical ring-down time, τ, of approximately 40–60 μs, which corresponds to an optical path of 12–18 km. The rate of loss of light intensity per unit distance in the cavity, r, is given by $(c\tau)^{-1}$, where c is the speed of light, and is equivalent to the sum of the baseline cavity losses per distance, L_B, and molecular absorption or the CaRDS signal, α. The dominant baseline loss process is failure of the mirrors to reflect light but, because reflectivity is largely independent of wavelength, L_B is essentially a baseline offset. After subtraction of L_B, α represents the product of the absorption cross section at the laser wavelength, α_X, and the absolute concentration of the gas-phase species, [X].

CaRDs systems are commercially available for the quantitative detection of many air pollutants, such as CO and ammonia (NH_3), and greenhouse gases, such as CO_2, CH_4 and N_2O, which is formed by bacterial denitrification of soils. They provide high sensitivity, precision and accuracy with negligible drift, and fast, continuous, interference-free data over a large dynamic range.

Illustrative air pollutant monitoring data

Finally, some recent trends in air pollutants derived from road traffic recorded at a kerbside site on Marylebone Road in central London are illustrated in Figure 2. The road traffic data show similar mean daily profiles each year, with a gradual decline in the period 1999–2002, levelling off thereafter. Congestion charging was introduced in 2003, which increased the proportion of taxis and heavy goods vehicles such as buses passing the monitoring site. Largely in response to changes in fuel formulations, benzene concentrations declined rapidly throughout the period 1999–2008 to below the EU objective of an annual mean of 5 mg m^{-3} to be achieved by 2010. In contrast, ethane (C_2H_6), which does not have road traffic sources, has declined far less rapidly.

CO and NO showed similar steady declines throughout the period 1999–2008 in fairly good agreement with traffic volume. CO has health
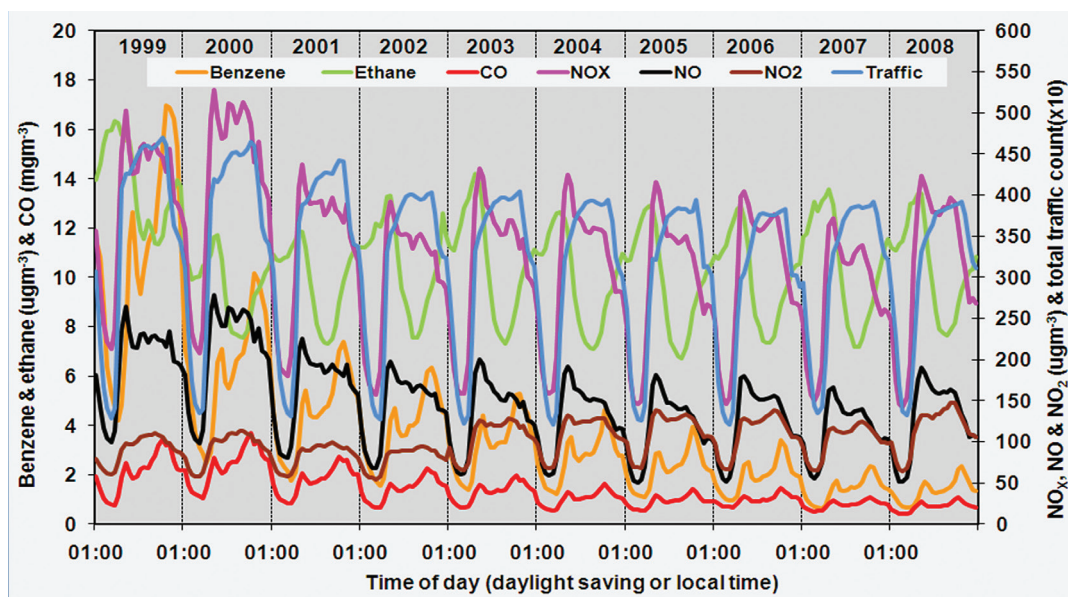
Figure 2 Average diurnal profiles of air pollutants and traffic volume recorded by Dr David Green (King's College London) at the London Air Quality Network (LAQN) Marylebone Road kerbside site in central London during the period 1999–2008. Validated quality-assured data were downloaded from the LAQN website data archive (www.londonair.org.uk/london/asp/datadownload.asp) and worked up by Ms Lynette Clapp.

impacts but, even at this polluted kerbside site in central London, concentrations are well below the EU objective of an annual mean of less than $10 \, mg \, m^{-3}$ by 2005. NO_2 also has health impacts, and slowly increased after 2003 to well above the EU objective of an annual mean of $40 \, mg \, m^{-3}$ by 2010. This increase is probably due to fitting HGVs with diesel particulate filters that emit higher ratios of NO_2 to NO_x ($NO + NO_2$) than previous exhaust systems.

References

AQEG (2004) *Nitrogen Dioxide in the United Kingdom*. London: Defra. Available from: www.defra.gov.uk/ environment/quality/air/air-quality/committees/aqeg/ publish/.

AQEG (2005) *Particulate Matter in the United Kingdom*. London: Defra. Available from: www.defra.gov.uk/ environment/quality/air/air-quality/committees/aqeg/ publish/.

AQEG (2007a) *Air Quality And Climate Change: a UK Perspective*. London: Defra. Available from: www.defra. gov.uk/environment/quality/air/air-quality/committees/ aqeg/publish/.

AQEG (2007b) *Trends in Primary Nitrogen Dioxide in the UK*. London: Defra. Available from: www.defra.gov.uk/ environment/quality/air/air-quality/committees/aqeg/ publish/.

AQEG (2009) *Ozone in the United Kingdom*. London: Defra. Available from: www.defra.gov.uk/environment/ quality/air/air-quality/committees/aqeg/publish/.

Cape, J. N. (2009) The use of passive diffusion tubes for measuring concentrations of nitrogen dioxide in air. *Critical Reviews in Analytical Chemistry*, **39**, 289–310.

Clemitshaw, K. C. (2004) A review of instrumentation and measurement techniques for ground-based and airborne field studies of gas-phase tropospheric chemistry. *Critical Reviews in Environmental Science and Technology*, **34**, 1–108.

Defra (2007) *The Air Quality Strategy for England, Scotland, Wales and Northern Ireland (Volume 1)*. Department for Environment, Food and Rural Affairs in partnership with the Scottish Executive, Welsh Assembly Government and Department of the Environment Northern Ireland. Norwich: TSO.

Ferm, M. and Svanberg, P.-A. (1998) Cost-efficient techniques for urban and background measurements of SO_2 and NO_2. *Atmospheric Environment*, **32**(8), 1377–1381.

Vingarzan, R. (2004) A review of surface ozone background levels and trends. *Atmospheric Environment*, **38**, 3431–3442.

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