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Twenty years of continuous high time resolution volatile organic compound monitoring in the United Kingdom from 1993 to 2012

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HIGHLIGHTS

- Observations were reported for $C_2 - C_8$ hydrocarbons for UK for 1994–2012.
- Dramatic declines in total VOCs were observed at kerbside, urban and rural sites.
- Similar declines were reported in UK road transport VOC emissions.

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ABSTRACT

Continuous, high frequency observations of $C_2 - C_8$ hydrocarbons began in the United Kingdom in 1993 and have continued through to the present day at a range of kerbside, urban background and rural locations. Most of the monitored hydrocarbons have shown dramatic declines in concentrations over the study period, with present levels close to an order of magnitude below their levels in the 1990s. The concentrations of 23 selected hydrocarbons have been aggregated up to give an estimate of the total VOC concentrations. These annual values have shown an exponential decline of $-18\%\ yr^{-1}$ at the London Marylebone Road kerbside site, $-11\%\ yr^{-1}$ at the London Eltham urban background site and $-22\%\ yr^{-1}$ at the rural Harwell site. Similar declines have been reported in UK road transport VOC emissions, demonstrating how the VOC emission inventories have apparently captured the salient features influencing real-world VOC emissions over the 1994–2012 period.

1. Introduction

Elevated ozone (O_3) levels have been the subject of much concern for European air quality policy-makers over the last 25 years. Early observations of O_3 episodes confirmed the importance of long-range trans-boundary transport (Cox et al., 1975). Policy actions to reduce O_3 levels began with the Nitrogen Oxides (NO_x) and volatile organic compounds (VOCs) Protocols to the United Nations Economic Commission for Europe (UN ECE) Convention on Long-Range Trans-boundary Air Pollution (CLRTAP) during the late 1980s (UN ECE, 2006). The reductions in O_3 precursor emissions required in these Protocols have been secured largely through mandatory vehicle emissions directives promulgated by the Commission of the European Communities (CEC, 1991), now the European Union (EU). During the 1990s, the UN ECE added the Gothenburg Protocol to abate acidification, eutrophication and ground-level O_3. The EU has implemented directives controlling emissions from large combustion plant, solvents and petrol evaporation. During the 2000s, the EU has sought to unify VOC and NO_x policy actions in its Clean Air for Europe (CAFÉ) Thematic Strategy on Air Pollution (EU, 2008). One of these policy actions was to renegotiate the national emission ceilings for SO_2, NO_x, VOCs and NH_3 set within the EU National Emission Ceilings (NEC) Directive (EU, 2001).

There is an important question concerning all of these policy actions to reduce O_3 precursor emissions and that addresses whether they have actually reduced real world emissions. To answer this question, twenty years of VOC monitoring data have been assembled for the United Kingdom (UK) for a range of monitoring site types and locations, whether urban roadside, urban background and rural, in a number of towns and cities across the UK. Trends are readily apparent in the VOC monitoring data and are

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Table 1
Volatile organic compound monitoring sites in the Defra Hydrocarbons Monitoring Network.

Site	Location	Start date	End date	Analyser
Auchencorth Moss ACTH R	NT248411	04/09/2006	Current	OPA
Belfast South BEL UB	IJ333726	01/08/1993	31/12/2000	VOCAIR
Birmingham East BIR UB	SP115888	04/08/1993	31/12/2000	VOCAIR
Bristol East BRS UB	ST599729	01/05/1994	31/12/2000	VOCAIR
Cardiff East CAR2 UB	ST193773	01/01/1994	31/12/2001	VOCAIR
	ST193773	01/01/2002	05/09/2002	VOC71M
Cardiff Centre UB	ST184765	05/09/2002	05/09/2007	VOC71M
Edinburgh Medical School EDMS UB	NT257730	13/05/1993	31/12/2001	VOCAIR
	NT257730	01/01/2002	31/07/2002	VOC71M
Glasgow Kerbside K	NS587652	01/08/2002	31/12/2010	VOC71M
Harwell HAR R	SU468860	01/01/1995	31/12/2001	VOCAIR
		01/01/2002	09/05/2007	VOC71M
		09/05/2007	Current	OPA
Leeds Potternewton LDS UB	SE307367	01/01/1995	31/12/2000	VOCAIR
Liverpool Speke LVP UI	SJ439836	24/11/1995	31/12/2000	VOCAIR
London Eltham LON UB	TQ440747	08/10/1993	31/12/2000	VOCAIR
		17/10/2003	Current	OPA
London Marylebone Road LMY1 K	TQ281820	01/09/1997	Current	OPA
London UCL UB	TQ299822	08/02/1993	31/12/2000	VOCAIR
Middlesbrough MID UI	NZ505196	01/01/1993	31/12/2000	VOCAIR
Southampton SOUT UI	SU426123	14/09/1995	31/12/2000	VOCAIR

Notes: i. site classifications: UB, urban background; UI, urban with industrial influence; K, kerbside; R, rural.

compared with VOC emission inventory data to see if the expected emissions reductions following the fitting of three-way catalysts and evaporative canisters have actually been realised in the real atmosphere. This study builds upon previous work (Dollard et al., 2007), by extending the time series of hourly hydrocarbon levels through to 2013 and by including a detailed comparison with the expectations built into the VOC emission inventories assuming complete compliance with the EU directives.

2. The network infrastructure and measurement methods

The monitoring locations, the instrumentation used and the period of operation for each of the network monitoring stations are summarized in Table 1 for the Defra Hydrocarbons Monitoring Network. Further details of the network, including a map showing site locations (Dollard et al., 1995), and its operation are provided elsewhere (Derwent et al., 2000; Dollard et al., 2007: online at http://uk-air.defra.gov.uk).

2.1. Instrumentation

Throughout the operation of the network, three different types of instrument have been used. Initially, the equipment used to monitor hydrocarbons was the Chrompack VOCAIR analyser. This instrument was used at the twelve original monitoring stations. The Chrompack VOCAIR allowed continuous gas chromatographic determinations at hourly intervals and consisted of an automatic thermo-desorption/cryogenic trapping system (Auto TCT), connected to a Chrompack gas chromatograph. These analysers were phased out and replacements installed in the period 2000 to 2001. From 2000 onwards the network has consisted of five sites, located at Cardiff, Glasgow, Harwell, Eltham and Marylebone Road (Table 1). Two types of instruments were employed at these sites. Three of the sites: Cardiff, Glasgow and Harwell, were fitted with Environnement VOC71M analysers, configured to measure and report the concentrations of 1,3-butadiene, benzene, toluene, ethylbenzene, (m + p)-xylene and o-xylene. The two other sites: London Marylebone Road and London Eltham, were fitted with automatic Perkin Elmer Ozone Precursor Analysers (OPA) which are capable of measuring and reporting at least 29 hydrocarbons. From 2005 onwards, monitoring has continued to the present day using OPA analysers at London Eltham LON, London Marylebone Road LMY1, Harwell HAR and Auchencorth Moss ACTH.

Comparative studies suggest that the three analyser types agree with each other to within ±10% of the measured value. The benzene and the 1,3-butadiene data are used for comparison with the UK Air Quality Standards. The benzene data are reported to the European Commission because of concerns about its toxicity and carcinogenicity. Benzene measurements are being made at around 35 additional sites using pumped sampling systems and these results will be reported separately in due course. The data for up to 29 hydrocarbons are reported to the European Commission to satisfy one of the monitoring requirements for ozone precursors under the EU Directives. All hourly data are available from http://uk-air.defra.gov.uk.

2.2. Network management

Since the Automatic Hydrocarbon Monitoring Network started, either Ricardo-AEA (formerly AEA Technology) or the National Physical Laboratory have undertaken the management and the quality assurance of the network. Currently, Ricardo-AEA, based at Harwell, Oxfordshire, manages and quality assures the network with local operator support for routine site operations. The National Physical Laboratory, Teddington, supplies calibration gas mixtures for use at the sites. The data quality of the hourly archived data is characterized by an uncertainty at 95% confidence of ±25% above 0.5 μg m^{-3} and ±0.1 μg m^{-3} below 0.5 μg m^{-3}.

2.3. Data management

Each analyser in the network has an associated PC operating several software packages: remote access software, modem control software, and equipment specific chromatographic acquisition and analysis software. The gas chromatographic software collects the raw chromatogram (binary file), integrates the peaks, and produces a report file. The site PC is either polled daily via modem or transmits files via internet connections on an hourly basis, with all files retrieved for storage on a workstation at Harwell in the network management centre. The sites are configured to complete a measurement for each VOC for each hour of the day. The routine operation of the network generates large numbers of hourly data,