Atmospheric Environment 156 (2017) 15–23

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Origins and trends in ethane and propane in the United Kingdom from 1993 to 2012

R.G. Derwent [a, *], R.A. Field [b], P. Dumitrean [c], T.P. Murrells [c], S.P. Telling [c]

[a] rdscientific, Newbury, UK
[b] Department of Atmospheric Science, University of Wyoming, Laramie, WY, USA
[c] Ricardo-AEA, Gemini Building, Harwell, Oxfordshire, UK

HIGHLIGHTS

- Ethane and propane have large urban sources from natural gas leakage.
- Urban ethane levels are rising whereas inventory emissions are declining.
- There is an additional urban source of propane from motor vehicle refuelling.
- Background levels of ethane associated with long range transport are rising.

ARTICLE INFO

Article history:
Received 29 November 2016
Received in revised form
15 February 2017
Accepted 16 February 2017
Available online 20 February 2017

Keywords:
Ethane
Propane
Natural gas leakage
NMVOC inventories

ABSTRACT

Continuous, high frequency in situ observations of ethane and propane 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. Whilst other monitored $C_2 - C_8$ hydrocarbons have shown dramatic declines in concentrations by close to or over an order of magnitude, ethane and propane levels have remained at or close to their 1993 values. Urban ethane sources appear to be dominated by natural gas leakage. Background levels of ethane associated with long range transport are rising. However, natural gas leakage is not the sole source of urban propane. Oil and gas operations lead to elevated propane levels in urban centres when important refinery operations are located nearby. Weekend versus weekday average diurnal curves for ethane and propane at an urban background site in London show the importance of natural gas leakage for both ethane and propane, and road traffic sources for propane. The road traffic source of propane was tentatively identified as arising from petrol-engined motor vehicle refuelling and showed a strong downwards trend at the long-running urban background and rural sites. The natural gas leakage source of ethane and propane in the observations exhibits an upwards trend whereas that in the UK emission inventory trends downwards. Also, inventory emissions for natural gas leakage appeared to be significantly underestimated compared with the observations. In addition, the observed ethane to propane ratio found here for natural gas leakage strongly disagreed with the inventory ratio.

1. Introduction

Ozone is widely regarded as a damaging air pollutant and has been the subject of much policy debate and action over the last several decades, particularly within Europe. 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. Since 2000, the EU has sought to unify VOC and NO_x policy

* Corresponding author.
E-mail address: r.derwent@btopenworld.com (R.G. Derwent).

http://dx.doi.org/10.1016/j.atmosenv.2017.02.030

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 PM set within the EU National Emission Ceilings (NEC) Directive (EU, 2001).

In our previous study, Derwent et al. (2014) showed how the installation of 3-way catalysts and evaporative canisters in petrol-engined motor vehicles has effectively reduced urban concentrations levels of 23 selected hydrocarbons by close to or more than an order of magnitude, over the 1993–2012 period, whereas the concentrations of ethane and propane have remained largely at, or close to their 1993 levels. Derwent et al. (2014) attributed this anomalous behaviour seen of ethane and propane to the relative importance of VOC emissions from natural gas leakage compared to those from road transport for the other 23 hydrocarbons. Our UK studies of ethane (Field et al., 1994; Derwent et al., 2000, 2014; Dollard et al., 2007) are consistent with other urban studies performed elsewhere in the world which reinforce the links between ethane and oil and gas emissions, see for example: Bilbao, Spain (Durana et al., 2006); Edmonton, (Cheng et al., 1997), Houston, USA (Leuchner and Rappengluck, 2010); Kaohsiung, Taiwan (Yang et al., 2005; Chang et al., 2009); Karachi, Pakistan (Barletta et al., 2002); Milan, Italy (Latella et al., 2005); Paris, Grenoble, Lyons, Marseille and Strasbourg, France (Boynard et al., 2014; Waked et al., 2016); San Francisco Bay (Fujita et al., 1995); Shanghai, China (Wang et al., 2013) and 43 other cities in China (Barletta et al., 2005).

In this study, we return to the ethane and propane observations in the UK and confirm the importance of natural gas leakage as their major source, attempt to quantify any other sources and reconcile the trends in the observations with those reported in VOC inventories.

2. Techniques

The monitoring locations for the Defra Hydrocarbons Monitoring Network, the instrumentation used and the period of operation for each of the network monitoring stations are summarized in Table S1 of the Supplementary Information. Further details of the network and its operation are provided elsewhere (Dollard et al., 1995, 2007; Derwent et al., 2000). Derwent et al. (2014) describe the instrumentation, network management and data management. Data from 13 monitoring stations have been employed in this assessment. Of the 13 stations, 7 were urban background stations sited away from the direct influence of road traffic (BEL, BIR, BRS, CAR2, EDMS, LDS, LVP and LON). There were 3 stations sited in urban population centres that were heavily influenced by local oil and gas industries (LVP, MID and SOUT). There was one urban kerbside station (LMY) which was sited on Marylebone Road, London, a heavily-trafficked arterial road. The remaining two stations were sited in rural locations (HAR and AUCH), both being classified as rural stations under the European Monitoring and Evaluation Program (EMEP).

Because of the significant changes made to the network during the 1993–2012 period in terms of number of sampling sites, instrumentation and site location, care has to be taken to ensure that consistent data have been used in the evaluation of trends. The eight urban background sites in Table S1 using VOCAIR analysers had different start dates but the same end dates with no changes in site location. Instrumental performance was satisfactory for the years 1995–2001 inclusive. At the London Marylebone Road kerbside site, measurements began during 1997 and are still ongoing without any changes in instrumentation and location. A composite series has been constructed for the rural Harwell site using the data from all three instruments and covering the period from 01/01/1995 through to 31/12/2012. This is also the case for the London Eltham site where VOCAIR and OPA instruments have provided a composite series from 08/10/1993 through to the present. The data from the Auchencorth Moss rural site began on 05/09/2006 and have continued to the present day without any change in location or instrumentation. There were some initialization problems with the analyser at this site which were crucial for ethane. As a result, the ethane data for the period up until 31/12/2007 were rejected.

Trend analysis has been performed through to the end of 2012 for all VOCs. Every effort has been made to ensure that any changes to locations or instrumentation have not materially influenced the evaluated trends. All of the data collected on the network have been archived at the UK National Air Quality Archive: https://uk-air.defra.gov.uk/. Periods of instrumental breakdown were represented as blanks in the archive and did not contribute to 90-day or annual averages.

Although VOC measurements began at the London Marylebone Road site in 1997, we have not reported any early data from this site until January 1st, 2000 because of a sizeable natural gas leak in the vicinity of the site. The leak was fixed on 1st April 1999 and so the records for 1997–1999 have not been used in the analyses reported below. A scatter plot was constructed for the observed ethane versus propane levels monitored at 05:00 h (the time of the ethane and propane maxima) in the period up until the leak was repaired. A linear regression through these paired observations gave:

$$\text{propane} = 0.395 \pm 0.008 \times \text{ethane} + 0.68 \pm 0.27; \quad R^2 = 0.97, \tag{1}$$

showing a high degree of correlation and an ethane vs propane ratio of 2.4: 1 for natural gas leakage in the distribution system of London during 1999. This observed ratio has been used to understand the extent of natural gas leakage sources in the analyses below.

3. Ethane and propane levels in the United Kingdom

3.1. Ethane

Ethane is a relatively unreactive alkane which is distributed globally. It is an important constituent of natural gas and because of leakage from the natural gas transmission and distribution systems, it is present in polluted urban atmospheres throughout the mainland UK. Ethane is also an important component of the vapours that arise from crude oil operations so elevated levels of ethane are observed close to oil refineries and other petroleum processing and handling activities.

It is not surprising therefore that significant ethane levels are found at all the UK Hydrocarbons monitoring network sites, as illustrated in Fig. 1. Levels are highest at the London Marylebone Road kerbside site, with a long-term average level of 9.9 $\mu g\ m^{-3}$, almost certainly because of the natural gas distribution pipes that are buried under the nearby road surface. The Cardiff, Leeds and Birmingham urban background sites showed only slightly lower annual mean ethane levels of about 8 $\mu g\ m^{-3}$ while those at the Middlesbrough, London Eltham, Southampton, Edinburgh and Bristol urban background sites were around 5 $\mu g\ m^{-3}$. Annual mean levels at the Liverpool site were the lowest of the urban sites on the mainland of Great Britain at 4.3 $\mu g\ m^{-3}$. Those at the Belfast urban background site were even lower, at about 2.4 $\mu g\ m^{-3}$ during the 1993–2001 period, well within the range of the rural levels, probably because the natural gas transmission and distribution system had not reached Northern Ireland at that time. Rural ethane concentrations were found to lie between 2.0 $\mu g\ m^{-3}$ at Auchencorth Moss and 2.6 $\mu g\ m^{-3}$ at Harwell. The annual mean northern