Atmospheric Environment 122 (2015) 427–438

Contents lists available at ScienceDirect

Atmospheric Environment

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

Diurnal variability of polycyclic aromatic compound (PAC) concentrations: Relationship with meteorological conditions and inferred sources

Mohammed S. Alam, Ian J. Keyte, Jianxin Yin, Christopher Stark, Alan M. Jones, Roy M. Harrison*

Division of Environmental Health and Risk Management, School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

HIGHLIGHTS

- A wide range of PAH, oxy-PAH and nitro-PAH are analysed.
- Roadside and urban background are measured.
- Eight 3-h samples are collected each day.
- Diurnal profiles reveal compounds generated from traffic and domestic combustion.
- Isomer ratios show some influence of atmospheric chemistry.

ARTICLE INFO

Article history:
Received 27 July 2015
Received in revised form
17 September 2015
Accepted 18 September 2015
Available online 9 October 2015

Keywords:
Polycyclic aromatic hydrocarbons
Polycyclic aromatic compounds
Nitro-PAH
Quinones
Diurnal variations
Source processes

ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) and their nitro and oxy derivatives have been sampled every three hours over one week in winter at two sites in Birmingham UK. One site is heavily influenced by road traffic and is close to residential dwellings, while the other site is a background urban location at some distance from both sources of emission. The time series of concentrations has been examined along with the ratio of concentrations between the two sampling sites. A comparison of averaged diurnal profiles has shown different patterns of behaviour which has been investigated through calculating ratios of concentration at 18:00–21:00 h relative to that at 06:00–09:00 h. This allows identification of those compounds with a strong contribution to a traffic-related maximum at 06:00–09:00 h which are predominantly the low molecular weight PAHs, together with a substantial group of quinones and nitro-PAHs. Changes in partitioning between vapour and particulate forms are unlikely to influence the ratio as the mean temperature at both times was almost identical. Most compounds show an appreciable increase in concentrations in the evening which is attributed to residential heating emissions. Compounds dominated by this source show high ratios of 18:00–21:00 concentrations relative to 06:00–09:00 concentrations and include higher molecular weight PAH and a substantial group of both quinones and nitro-PAH. The behaviour of retene, normally taken as an indicator of biomass burning, is suggestive of wood smoke only being one contributor to the evening peak in PAH and their derivatives, with coal combustion presumably being the other main contributor. Variations of PAH concentrations with wind speed show a dilution behaviour consistent with other primary pollutants, and high concentrations of a range of air pollutants were observed in an episode of low temperatures and low wind speeds towards the end of the overall sampling period consistent with poor local dispersion processes. Results from a short summer campaign give indications of the formation of some nitro-PAH by atmospheric chemical reactions.

---

* Corresponding author. Also at: Department of Environmental Sciences, Center of Excellence in Environmental Studies, King Abdulaziz University, PO Box 80203, Jeddah, 21589, Saudi Arabia.
E-mail address: r.m.harrison@bham.ac.uk (R.M. Harrison).

http://dx.doi.org/10.1016/j.atmosenv.2015.09.050
1352-2310/

1. Introduction

A number of the polycyclic aromatic hydrocarbons (PAHs) which are present in the atmosphere have been identified as being carcinogenic, and the exposure to PAHs may also have other adverse health effects (WHO, 2013). One of these PAH congeners - benzo(a)pyrene – is widely used as a marker for PAHs in the atmosphere, and an EU target value of an annual average of 1 ng m^{-3} is currently in force. In the United Kingdom (UK), an air quality standard of an annual average of 0.25 ng m^{-3} for benzo(a)pyrene is included in the National Air Quality Strategy. Within the UK, a network of 34 monitoring sites collects daily samples of PM_{10} which are analysed to determine the concentration of 39 PAH congeners at each site. PAHs may be present in the atmosphere in both gaseous and particulate form, with the lower molecular weight PAH congeners being predominantly gaseous, while congeners with higher molecular weight are predominantly particulate. This partitioning is influenced by both the ambient temperature and ambient PM concentration (Yamasaki et al., 1982). PAHs are chemically reactive with atmospheric lifetimes of hours to days (Keyte et al., 2013). Consequently, while there is a long-range transport component, urban concentrations are influenced predominantly by urban emissions and processes.

Airborne PAHs are mainly combustion products or arise from the evaporation of volatile fuels. Jang et al. (2013) used Positive Matrix Factorization (PMF) and spatial distribution analysis on seven datasets to apportion PAHs measured in the UK between four source types – diesel exhausts, evaporation of vehicle fuels (although in some cases these two sources were combined), coal burning (for either domestic or industrial purposes) and wood burning. While individual PAH congeners may come from a number of source types, these authors associated low molecular weight species, especially phenanthrene, with vehicle exhaust, benz(a) anthracene and benzo(a)pyrene with coal burning, and retene and anthracene with wood burning.

Most assessments of atmospheric PAH concentrations have involved individual measurements over periods of 24 h or longer. The consequence is that information that can be extracted from diurnal changes in PAH concentrations is unavailable. Concentrations of PAH and their derivatives in the atmosphere may be subject to diurnal variations due to changes over the course of the day in source strengths, dispersion of material due to diurnal changes in meteorological factors (particularly atmospheric stability) (Williams, 2014), atmospheric reactivity (Alam et al., 2014; Keyte et al., 2013), and in the case of the particle phase, changes in temperature of the atmosphere (Yamasaki et al., 1982).

The complex nature of sample collection and analysis has limited the number and length of studies of the diurnal variability of PAH concentrations. Particulate matter has been collected by filter, over periods of less than a day, and analysed for a variety of PAH congeners and their derivatives by Souza et al. (2014) (day and night samples); Morville et al. (2011) and Delhomme and Millet (2012) (morning, midday and evening samples); Fine et al. (2004) and Reisen and Arey (2005) (four periods during day); and by Sklorz et al. (2007); Ohura et al. (2013); Tsapakis and Stephanou (2007); Pongpiachan (2013) (six periods during day). These sampling campaigns have been restricted to a limited number of days. More extensive measurement campaigns have been carried out using photo-electric aerosol sensors in which particulate matter is photo-ionised by UV radiation to which PAHs are sensitive (Chetwittayachan et al., 2002; Han et al., 2011; Cheng et al., 2012), or Aerodyne Aerosol Mass Spectrometers (Poulain et al., 2011). These instruments are limited to accessing the total PAH concentration, but are able to report concentrations on an hourly time scale.

At a site heavily influenced by road traffic (Cheng et al., 2012) concentrations of total PAH were highest throughout the working day and were correlated with the numbers of goods vehicles and buses, while Tsapakis and Stephanou (2007) found no diurnal pattern for particulate PAHs at a coastal site. The more usual diurnal pattern in urban and rural sites is for a peak in PAH concentrations in the morning, lower concentrations at midday, and a second peak in concentrations in the evening (e.g. Chetwittayachan et al., 2002; Han et al., 2011; Poulain et al., 2011; Fine et al., 2004), with these peaks generally attributed to traffic and heating respectively, in conjunction with greater atmospheric stability at these times of day.

In studies of individual congeners, Morville et al. (2011) report that in winter fluorene, phenanthrene and pyrene have similar concentrations throughout the day, while benzo(a)pyrene, benz(a) anthracene and benzo(ghi)perylene have a midday minimum concentration, with similar concentrations in the morning and evening periods. In the summer these authors found that all six congeners had a midday minimum and that the concentration was higher in the morning than in the evening. Sklorz et al. (2007) found that in summer the concentrations of benzo(ghi)perylene and coronene were greatest during the day, while those of benzo(k) fluoranthene and indeno(1,2,3-cd)pyrene were greatest at night. During the winter there was little diurnal variability of these congeners. While benzo(a)pyrene and benzo(e)pyrene concentrations did not show clear periodic variation during the summer, in winter they were higher at night (Sklorz et al., 2007).

Few studies have investigated the diurnal variation of nitro-PAH and quinone congeners. Ringuet et al. (2012) collected 12 h samples representing both diurnal and nocturnal variations at traffic and suburban sites in Paris. Although concentrations of PAH and oxy-PAH were approximately 10 times larger at the traffic site, only a small increase was observed at nighttime relative to that of daytime. 1-Nitropyrene was found to be the most abundant nitro-PAH at the traffic site suggesting a diesel source, while 2+3-nitrofluoranthene was predominantly measured at the suburban site indicative of secondary formation. Souza et al. (2014) reported significantly larger PAH, nitro-PAH and oxy-PAH concentrations during the night which was attributed to biomass burning (which occurred during night), while daytime measurements were dominated by vehicular emissions.

While a number of the studies described above were conducted in Europe, it is expected that considerable variations will be seen across the continent, reflecting the different sources and climate factors which predominate. To date, there have been many studies of PAH in the UK (e.g. Mari et al., 2010; Alam et al., 2013, 2014; Jang et al., 2013; Katsoyiannis et al., 2011), studies of PAH quinones are far fewer (Delgado-Saborit et al., 2013; Alam et al., 2013), and those of nitro-PAH are very few in number, and are now somewhat outdated (Dimashki et al., 2000). Although for PAH both airborne concentrations and source apportionment are fairly well understood, knowledge of the quinones and nitro-PAH is far less adequate.

During a one week period in January 2014, three-hourly mean concentrations of a number of particle phase PAH, quinone and nitro-PAH congeners were measured simultaneously at a roadside site and a nearby background site in southwest Birmingham. In a further short study, both particulate and vapour forms were collected during summer. We report the results and an interpretation of the influences of meteorology and sources on the measured concentrations.

2. Experimental

2.1. Measurement sites and period of measurements

The locations of the sites are presented in Table S1. The roadside