Fuel Processing Technology 92 (2011) 176–182

Contents lists available at ScienceDirect

Fuel Processing Technology

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

PAH in airborne particulate matter. Carcinogenic character of PM10 samples and assessment of the energy generation impact

M.S. Callén *, M.T. de la Cruz, J.M. López, A.M. Mastral

Instituto de Carboquímica (CSIC), C/Miguel Luesma Castán, 4, 50018 Zaragoza, Spain

ARTICLE INFO

Article history:
Received 17 November 2009
Received in revised form 14 May 2010
Accepted 20 May 2010

Keywords:
PM10
PAH
BaP
BaP equivalents
Diagnostic ratios
Long-range transport

ABSTRACT

One of the main anthropogenic sources producing Polycyclic Aromatic Hydrocarbons (PAH) is related to combustion processes especially transport, power generation processes and other industrial activities. Therefore, the main cities constitute one of the main pollution sources for population. Due to the carcinogenic character of some of these pollutants, Directive 2004/107/EC established a target value of 1.0 ng/m^3 with regard to Benzo(a) pyrene (BaP) for the total content in the particulate matter fraction averaged over a calendar year. Nevertheless, the consideration of only BaP can underestimate the carcinogenic character of the particulate matter.

In this work, the carcinogenic character of the airborne PM10 of Zaragoza was studied during 2003–2004 by determining the concentration of BaP equivalents (BaP-eq), using toxic equivalent factors provided by Larsen and Larsen. Diagnostic ratios were used to discern regarding the main pollution sources in Zaragoza city in which the prevailing emission sources were related to diesel emissions and combustion sources. As PAH can travel long distances around the world, the impact of local pollution sources and long-range atmospheric transport on those samples exceeding 1.0 ng/m^3 of BaP-eq that imply higher risk for human health were assessed by considering BaA/Chry and BaP/BeP ratios and by studying the origin of the air masses with the backward air trajectories according to the HYSPLIT model. Those samples were mainly produced during cold season. The local pollution sources were the dominant sources although one episode of long-range transport from European countries could be observed.

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAH) can be released to the atmosphere by natural and anthropogenic sources, being the human activity responsible of more than 90% of their atmospheric levels. One of the main anthropogenic sources producing PAH is related to combustion processes involving transport, power generation processes [1] and other industrial activities so that great cities can constitute one of the main pollution sources to which population is exposed. The main concern in knowing these pollutants is due to its carcinogenic and mutagenic character. In particular, BaP is one of the most studied PAH.

The concern by the carcinogenic effects of the products generated by combustion processes is coming from at least two centuries, when Sir Percival Pott watched higher incidence of scrotal cancer in soot workers in London [2]. The association between cancer and a specific chemical compound, the BaP, was reinforced in 1933 when this compound was isolated from chimney soot [3]. Several studies after this proved that other PAH, in addition to BaP, are also carcinogenic [4,5].

The United States Environmental Protection Agency [6] has classified PAH with BaP indicator species as a B-2 pollutant that means a probable human carcinogen with sufficient evidence from animal studies but inadequate evidence from human studies. According to the International Agency for Research on Cancer (IARC) classification, it is Group 2A [7], probably carcinogenic to humans. The World Health Organization (WHO) has already added PAH into the list of the priority pollutants in both air and water. France, Japan, Germany, Netherlands, Sweden and Switzerland prescribed emission standards for most of Hazardous Air Pollutants (HAPs) including PAH. WHO and the Netherlands [8,9] have even prescribed ambient air quality guidelines (AQG) for PAH (1.0 ng/m^3 and 0.5 ng/m^3 respectively).

These limits are not legally binding but it is common consensus that these pollutants require maximum emission reduction or 'zero levels'.

In fact, different European countries established, previous to the Directive 2004/107/EC [10], guideline values which allowed minimising harmful effects on human health. In this way, UK established a guideline value of 0.25 ng/m^3 for BaP.

Currently, BaP has been used as a marker for the carcinogenic risk of PAH in ambient air according to the Directive 2004/107/EC [10] by establishing a target value of 1.0 ng/m^3 for the total content in the particulate matter less than or equal to 10 μm (PM10) fraction averaged over a calendar year. This Directive, which will be reviewed in 2010, also

* Corresponding author. Tel.: +34 976 733977; fax: +34 976 733318.
E-mail address: marisol@icb.csic.es (M.S. Callén).

0378-3820/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.fuproc.2010.05.019

mentions the interest in knowing the concentrations in air of other carcinogenic Polycyclic Aromatic Hydrocarbons (PAH) as benzo(a) anthracene (BaA), benzo(b)fluoranthene (BbF), benzo(j)fluoranthene (BjF), benzo(k)fluoranthene (BkF), indeno(1,2,3-cd)pyrene (IcdP), and dibenz(a,h)anthracene (DahA) as markers for the carcinogenic risk of PAH. Nevertheless, only BaP is considered as guideline value. In locations strongly influenced by traffic, this source can provide 88% of the total of this compound [11].

Although these pollution sources are the main PAH emissions, PAH may be transported and deposited at other surface in very remote region at highly reduced concentration as a result of the effects of atmospheric dispersion and chemical reaction. The physical removal or transport of airborne particles is a function of the particle size and meteorological conditions. The occurrence of some PAH in remote areas such as Arctic and Marine atmospheres [12] was mainly explained by aerial transport from distant anthropogenic sources.

Air-mass back trajectories can provide useful information regarding the transport of pollutants from different regions of the world. Previous studies [13–15] have proved the influence of long-range transport of aerosol in addition to local pollution sources.

In this work, the carcinogenic character of the airborne PM10 of Zaragoza was studied during 2003–2004 by determining the concentration of BaP equivalents (BaP-eq), using toxic equivalent factors provided by Larsen and Larsen [16]. The impact of local pollution sources and long-range atmospheric transport on those samples exceeding 1.0 ng/m^3 of BaP-eq were assessed by considering BaA/Chry and BaP/BeP ratios and by studying the origin of the air masses with the backward air trajectories according to the HYSPLIT model. Finally, diagnostic ratios were capable to discern the main anthropogenic pollution sources in Zaragoza.

2. Experimental

2.1. Sampling area

The study was performed in an urban area of Zaragoza city (650,592 habitants) located in the Northeast of Spain (41°39′49.38″N; 0°53′16.68″W) and previously described in another article [17]. The main anthropogenic pollution sources include mobile sources related to city traffic and the presence of a highway and stationary sources related to several industrial parks: medium and small enterprises [13].

Airborne samples were collected every week throughout 15 months (2003–2004) on weekdays, collecting a total of 50 samples with a Graseby Andersen High-Volume air sampler with volumetric flow controlled system provided with a PM10 cut off inlet. A Teflon-coated, fibre-glass filter (0.6 μm pore size; 20.5×25.5 cm) and polyurethane foam (PUF) were used to collect respectively, PAH in particle and in the gas phases. More details regarding the sampling site can be obtained in previous publications [18,19].

2.2. PM10 determination

The concentration of PM10 was carried out by weighting the filter in an analytical balance at a precision of 0.1 mg, previous and after sampling, once the filter was conditioned in a desiccator for 24 h. PM10 concentration was calculated per unit volume of sampling air.

2.3. PAH determination

PAH were determined separately in both phases by GC–MS–MS with the internal standard method after Soxhlet extraction and fractionation through a silica gel column.

The compounds quantified during sampling by GC–MS–MS, according to their elution orders, were phenanthrene (Phe, *m/z* 152), anthracene (An, *m/z* 152), 2+2/4-methylphenanthrene (2+2/4MePhe, *m/z* 189), 9 methylphenanthrene (9MePhe, *m/z* 189), 1-methylphenanthrene (1MePhe, *m/z* 189), 2,5-/2,7-/4,5-dimethylphenanthrene (DiMePhe, *m/z* 191), fluoranthene (Fth, *m/z* 200), pyrene (Py, *m/z* 200), benzo(a) anthracene (BaA, *m/z* 226), chrysene (Chry, *m/z* 226), benzo(b) fluoranthene (BbF, *m/z* 250), benzo(k)fluoranthene (BkF, *m/z* 250), benzo(e)pyrene (BeP, *m/z* 250), benzo(a)pyrene (BaP, *m/z* 250), indeno (1,2,3-cd)pyrene (IcdP, *m/z* 274), dibenzo(a,h)anthracene (DahA, *m/z* 276), benzo(g,h,i)perylene (BghiP, *m/z* 274) and coronene (Cor, *m/z* 298) according to previous publications [19].

2.4. Statistical tools

All statistical analyses were conducted using SPSS for Windows version 12.0.

2.5. Origin sector of the backward air-mass trajectories

The HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory Model) version 4.8 (http://www.arl.noaa.gov/ready/hysplit4.html) was used in order to determine the backward air-mass trajectories. Isentropic backward air-mass trajectories were obtained for each sampling day at 9:00 h by taking into account the transport carried out the previous five days. The heights of the isentropic trajectories were 100, 500 and 1000 m, respectively. The meteorological data used to calculate these trajectories were provided by the FNL National Climatic Data (NCDC) Centre of the USA. The classification of the origin sector of the air-mass was performed according to Viana [20,21].

3. Results and discussion

3.1. PM10

Because the study of PAH was performed in the particulate matter PM10 and this pollutant is also legislated by the European Union according to Directive 2008/50/EC [22], it was interesting to know the concentrations of this other legislated pollutant along the sampling. The average concentration of PM10 in Zaragoza was 32.24±12.7 μg/m^3. Fig. 1 shows the daily concentrations as well as the daily and annual limit values established in the Directive 2008/50/EC [22]. Four percent of the samples exceeded the daily limit value of 50 μg/m^3. The fulfilling of this Directive cannot be predicted in Zaragoza because the sampling was not carried out every day of the year although by extrapolation, 29% of the samples exceeded this daily limit value. However, the Directive will subtract exceedances attributable to natural sources when they are demonstrated.

The average PM10 concentration is in the range found in other urban locations in Spain as Tarragona (37.4 μg/m^3), Huelva (37.5 μg/m^3), Alcobendas (32.2 μg/m^3), Llodio (31.7 μg/m^3) or the Canary Islands (44.4 μg/m^3). On the contrary, the concentration of PM10 in Zaragoza is lower than other sceneries with high traffic contribution such as Madrid (47.7 μg/m^3), L'Hospitalet (49.8 μg/m^3) or Barcelona (46.2 μg/m^3) [23].

Regarding the seasonal evolution of PM10 it is observed higher concentrations for the warm season (summer and spring) with an average of 34.6 μg/m^3 versus the cold season (autumn and winter) with an average value of 27.3 μg/m^3. This trend is different from other urban locations of Spain such as Segrera, Igualada or L'Hospitalet [20] and out of Spain (Thessalonika) [24] and was already found for previous samplings in Zaragoza [17]. These high PM10 concentrations are mainly produced during the warm period in which meteorological conditions favour episodes of regional recirculation as well as African intrusions.

3.2. Episodes of high BaP concentration

The average PAH concentration, both in gas and particle phases, for the samples taken in Zaragoza was 14.3 ng/m^3 ranging between 3.8 and 54.0 ng/m^3. Phe and Cor were the most abundant PAH found in the Zaragoza atmosphere. The first one due to its volatility was mainly