HUMAN EXPOSURE AND RISK ASSESSMENT OF PAHs BOUND TO THREE PM FRACTIONS (10, 2.5 AND 1) IN AN AREA INFLUENCED BY A CEMENT PLANT

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been recognized as a potential source of harmful effects on human health, being lung cancer one of the most worrying diseases. Although PAHs may have a natural origin (e.g., volcanic eruptions or wildfires), anthropogenic emission sources (e.g, road traffic, power production, house heating or waste incineration) are dominating[1]. High-energy demanding industries, such as cement plants[2], may be also important releasers of PAHs. In the cement industry, different amounts of fuel and raw materials are submitted to high temperatures, in order to yield cement. Nowadays, alternative fuels, such as sewage sludge or biomass waste, are also used in cement kilns to meet the energetic requirements of this industrial process. Unfortunately, this may possibly lead to a higher degree of heterogeneity in the amounts and profile of emitted PAHs[3]. Once in the air, PAHs can be present as gaseous and/or bounded to atmospheric particulate matter (PM), depending on the weather conditions and the physical-chemical properties of each individual hydrocarbon[4]. Currently, new efforts have been made to improve the understanding of PAH profiles within different PM fractions, and to assess their human health risks. However, only few studies have been developed regarding PM-bound PAHs in the surrounding of cement facilities[5,6], being focused in PM_{10}. Therefore, there is a clear lack of information concerning the PAH content, distribution, exposure and risk among different sizes of PM.

In the present study, we evaluated the concentrations of PAHs in 3 PM fractions (10, 2.5 and 1) collected in the surroundings of a cement plant located in Barcelona. PAH content and speciation were developed for the three fractions to elucidate their distribution among different sizes. Complementarily, the human health risks associated to the PAH exposure were risks by considering the daily activity pattern of an average adult living in of Barcelona (Spain).

Materials and methods

The site of study is placed in the outskirts of Barcelona. A cement plant has been operating in the area since 1917. Nowadays, sewage sludge, animal meal, refuse-derived fuel and biomass supply 35% of the total energy consumed in the cement kiln. Other sources of PM are present in the area, being among them an organic waste treatment plant and two highways with dense traffic close to the sampling point. Three PM fractions (PM_{10}, $PM_{2.5}$ and PM_1) were collected with high volume active samplers from 11/18/2014 to 12/07/2014 in the roof of a two-floor school located 300 m from the facility. PM was collected in quartz fiber filters (QFF) pre-heated at 200ºC for 2 hours. QFF were kept frozen at -20ºC, in aluminum foils, until analysis. PAH determination was performed by means of gas chromatography/mass spectrometry (GC/MS)[7]. Preliminary values of human exposure and carcinogenic risks derived from PAHs inhalation were calculated for an average adult individual, considering indoor and outdoor environments as well as the daily activity pattern, following a previously described model[8]. In order to calculate the overall exposure to PAHs and the associated carcinogenic risks, Toxicity Equivalency Factors (TEF) with respect to benzo[a]pyrene (BaP) and Inhalation Unit Risk (IUR) of this hydrocarbon were used[9]. ANOVA (parametric) or Kruskall Wallis (non parametric) tests were undergone for statistical treatment of the data, considering as a significant differences with a probability below 0.05 ($p < 0.05$).

Results and discussion

The airborne levels of PAHs in 3 different PM fractions are detailed in Table 1. No statistical significant differences ($p < 0.05$) were found in the content of PAHs among the different PM fractions, meaning that PM-bound PAHs in our study are mainly located in the PM_1 fraction, in agreement with previous studies[7].

Table 1. Air levels (µg/m³), organic carbon (µg/m³), and PAHs (ng/m³) in 3 different PM fraction around the cement plant.

		Rings	PM$_{10}$		PM$_{2.5}$		PM$_1$	
			average	SD	average	SD	average	SD
PM			32.1	11.8	15.2	3.37	9.12	3.30
Organic carbon			6.42	2.57	3.95	0.63	2.37	0.71
PAHs	phenanthrene	3	0.14	0.07	0.10	0.05	0.12	0.05
	retene	3	0.26	0.22	0.19	0.15	0.15	0.11
	fluoranthene	4	0.32	0.16	0.23	0.12	0.24	0.09
	pyrene	4	0.41	0.23	0.29	0.17	0.42	0.21
	benzo[a]anthracene	4	0.61	0.40	0.45	0.31	0.49	0.33
	chrysene	4	0.56	0.31	0.49	0.29	0.59	0.39
	benzo[b+j]fluoran.	5	1.31	0.82	0.93	0.50	1.08	0.51
	benzo[k]fluoran.	5	0.35	0.20	0.23	0.11	0.29	0.14
	benzo[e]pyrene	5	0.59	0.31	0.42	0.20	0.50	0.23
	benzo[a]pyrene	5	0.62	0.37	0.43	0.24	0.56	0.34
	inde[123cd]pyrene	6	0.90	0.47	0.72	0.40	0.91	0.51
	benzo[ghi]perylene	6	1.05	0.51	0.84	0.42	1.15	0.58
	coronene	6	0.16	0.08	0.14	0.08	0.20	0.12
	∑PAH		7.28		5.45		6.74	

SD: Standard deviation.

No statistical significant differences ($p<0.05$) were found when comparing distribution of PAHs according to the number of rings in the three analyzed fractions. Five- and six-ringed compounds were the most predominant PAHs in total PM mass, showing an increasing contribution when decreasing the particle size. More specifically, benzo[b+j]fluoranthene and benzo[ghi]perylene were the prevailing PAHs, having been recognized as predominant in urban-industrial environments[10]. According to previous studies[11], emissions from cement plants are characterized by a contribution of 3 rings compounds close to 30% of total PAHs mass. In the present study, only two 3-ringed PAHs were detected, reaching a mass contribution around 5% in every fraction.
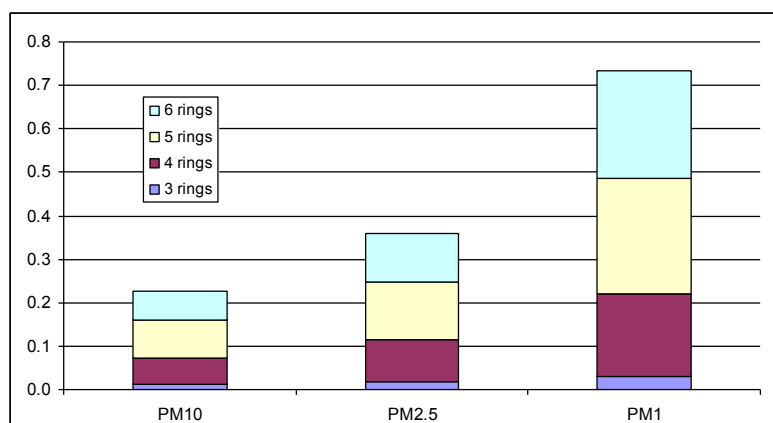

Figure 1. PAHs mass divided by PM mass (ng/µg) according to the number of rings.

Ambient PM$_{10}$ diagnostic ratios in the present study were more similar to those recorded previously[2] for incinerators or biomass burning than to cement plants (Table 2). Since the use of alternative fuels include the biomass and other residues, it seems plausible a contribution from the cement plant to ambient PAHs related with those sources. However, heating systems and burning of agricultural byproducts could be also sources of these compounds.

Table 2. PM_{10}-PAHs diagnostic ratios in present study and for different sources, as reported previously[2]

	Present study	Cement stack	Incinerator stack	Straw burning	Pine wood burning	Diesel vehicle	Gasoline vehicle
BaA/(BaA+BaP)	0.50	0.38	0.55	0.58	0.60	0.84	0.44
Chy/(BaP+Chy)	0.47	0.40	0.59	0.60	0.70	0.89	0.47
BaA/(BaA+Chy)	0.53	0.48	0.46	0.48	0.39	0.39	0.48
Flu/(Flu+Pyr)	0.44	0.68	0.56	0.55	0.54	0.52	0.49

BaA: benzo[a]anthracene; BaP: benzo[a]pyrene; Chy: chrysene; Flu: fluoranthene; Pyr: pyrene

In the present study, the PAH levels were higher than those recorded previously in the urban area of Barcelona[7]. In turn, they were similar to those previously found in other Mediterranean cities[12]. Comparing our study with those performed near other cement plants[6], a less predominance of PAHs with 3 rings was observed. Furthermore, the current levels or BaP (0.62 ng/m^3) and BaP-equivalents (0.90 ng/m^3) in PM_{10} were below the annual limit established by the European Commission in the directive 2004/107/EC. However, they were slighlty higher than the recommendations set in 0.12 ng/m^3 by the World Health Organization[13] (WHO). Regarding PM_{10} and $PM_{2.5}$, average levels of PAHs during the sampling period were also lower than the daily and annual limits established by European Commission.

The human exposure and the associated carcinogenic risks were evaluated for the PAHs compounds recognized as carcinogenic by the U.S. EPA. Since the total amount of carcinogenic PAHs content was located in the PM_1 fraction, this fraction accumulated the whole exposure and carcinogenic risk developed by PM. Exposure to carcinogenic PAHs in PM_1 accounted for $2.22 \cdot 10^{-7}$ mg BaP-eq/(kg·day), while the overall cancer risk in this fraction reached a value of $2.63 \cdot 10^{-7}$ (Figure 2). BaP was the compound that exhibited the highest exposure and carcinogenic activity, contributing close to 70% of the overall exposure and cancer risk values. Anyhow, the carcinogenic risk was below the threshold of acceptable risk established by the U.S. E.P.A.[9] in $1 \cdot 10^{-6}$ (one case of cancer for every 10^6 inhabitants).
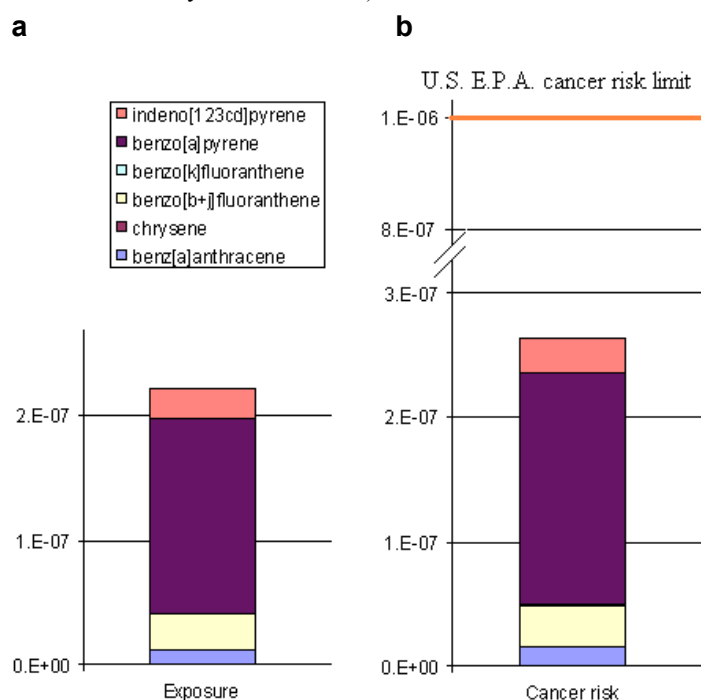

Figure 2. a) PM_1 exposure in mg BaP-eq/(kg·day), and b) and cancer risks (unitless), attributable to different carcinogenic PAHs.

Since most of the PAH content was located in the finest PM fraction, the PM_1 was the fraction registering the highest PAH exposure and the associated cancer risks. Although PAH levels and carcinogenic risks derived from PAH exposure were below the legal limits and recommendations established by the European Union and the U.S. EPA, they were above those recommended by the WHO. The contribution from the cement plant seems to show a very different PAH profile from previous studies, being in this case closer to that reported for waste incinerators or other biomass waste combustion processes. In order to better assess the health impacts of PM-bound PAHs, further investigation is needed. Upcoming research includes the use of a human respiratory tract model coupled to a physiologically based pharmacokinetic model. Results from these models will help to better understand not only the deposition of PAHs in the different regions of the respiratory tract but also the fate and health effects of these compounds within the human body.

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