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ScienceDirect

Food Chemistry 108 (2008) 347–353

Food Chemistry

www.elsevier.com/locate/foodchem

Analytical Methods

Effects of a chemical company fire on the occurrence of polycyclic aromatic hydrocarbons in plant foods

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Received 3 September 2007; received in revised form 9 October 2007; accepted 11 October 2007

Abstract

On Friday, September 1, 2006, the facilities of a chemicals distributor in the Spanish town of Caldas de Reis, were almost completely destroyed as a result of a fire. Comprehensive liquid chromatography-fluorescence detection (LC-FD) analyses were performed on plant foods to determine the toxic impact of this kind of accident on population. PAHs from a polluted atmosphere are generally transferred to plants by particle-phase deposition on the waxy leaf cuticle or by uptake in the gas phase through stomata. PAH levels in all samples were not alarming (total PAHs were below 4.240 ng/g) and the PAH profiles were similar, with the exception of peppers, in all vegetal materials (5-to-4 rings ratio of 1–2), suggesting the similarity in source type (the fire). PAH concentrations in plants were related to their surface exposed to air, indicating that the contribution of soil/water PAHs to plants (aerial part) accumulation was insignificant.

Keywords: PAHs; Firing; Pollution; Residues in plants

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of chemicals that are formed during the incomplete burning of chemical products and pyrolysis process by a series of complex chemical reactions (Dhammapala, Claiborn, Simpson, & Jimenez, 2007; Ergut et al., 2006; Lafleur, Taghizadeh, Howard, Anacleto, & Quilliam, 1996; Voutsa, Terzi, Muller, Samara, & Kouimtzis, 2004; Wang, Li, Lambert, & Yang, 2007). PAHs have been included in several priority pollutant lists of the Agency of Toxic Substances and Disease Register (ATSDR), of the International Agency for Research on Cancer (IARC), of the European Community (EC) and of the Environmental Protection Agency (EPA), due to their mutagenic and carcinogenic properties. In 1984 the United States Environmental Protection Agency (USEPA) listed 16 PAHs as compounds of interest under a suggested procedure for reporting test measurement results (USEPA (U.S. Environmental Protection Agency), 1984). In the International Programme on Chemical Safety (IPCS, 1998), other 17 PAHs were added to the 16 PAHs designed by USEPA. Of all the 33 risk assessed PAHs, 15 PAHs (benzo[*a*]anthracene, cyclopenta [*cd*]pyrene, chrysene, 5-methylchrysene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]-pyrene, indeno[1,2,3-*cd*]pyrene, dibenzo[*ah*]anthracene, benzo[*g,h,i*]perylene, dibenzo[*a,l*]pyrene, dibenzo[*a,e*]pyrene, dibenzo[*a,i*]pyrene, dibenzo[*a,h*]pyrene) were recognized as clearly mutagenic and carcinogenic (Commission Regulation (EC) No. 208/, 2005). Bay and fjord regions in their structure make them highly reactive (Codex Alimentarius Commission (CX/FAC05/37/34), 2004).

Human exposure to PAHs is 88–98% connected with food (Kluska, 2003). PAH can penetrate food indirectly (from air or water) and directly, e.g. during smoking. Once these compounds released into the atmosphere they can be

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doi:10.1016/j.foodchem.2007.10.042

transported away from their emission sources over long distances and/or deposited to the terrestrial and aquatic environment through dry and wet deposition. A major issue associated with the emission of these compounds is the zone of influence, which determines whether the possible source has predominately local impacts or contributes to regional or global background levels (Voutsa et al., 2004). In fact, uptake of gaseous chemicals by plants is one of the major pathways of many semi-volatile contaminants including PAHs into the agricultural food chain and is a key process in determining human exposure (McLachlan, 1996). This pathway is particularly important for chemicals with $\log K_{\mathrm{oa}} > 6$ (octanol-air partition coefficient) and $\log K_{\mathrm{aw}} > -6$ (air–water partition coefficient), for example PAHs (Cousins & Mackay, 2001). This is very important in Mediterranean countries given the fact that vegetables are basic foods in the diet. It has been reported that plant uptake of PAHs is primarily from atmosphere through gas and particle-bound depositions and the relative importance of these two mechanisms is driven by the gas/particle partitioning of the compound (Simonich & Hites, 1995). It was demonstrated by using two-photon excitation microscopy that anthracene was identifiable as a thin diffuse layer in the upper surface of the epicuticular wax and as thick diffuse bands extending through the cuticle (Wild, Dent, Barber, Thomas, & Jones, 2004). However, knowledge gap still remains for relationship between the level in the air and the plant accumulation with the intention to determine the contributions of local fires to contaminant loadings. Vegetation plays an important role in the global cycling of PAHs (Collins, Fryer, & Grosso, 2006), but heretofore the various processes of accumulation, migration, and transformation of PAHs within plants have not been well understood. The majority of hydrocarbons are situated on the skin of fruits and vegetables (Kluska, 2003).

Although some works have been done to obtain information on whether high molecular weight PAHs are generated during combustion (tire, coal, chemical and petrochemical industries) (Nadal, Schuhmacher, & Domingo, 2004; Voutsa et al., 2004; Wang et al., 2007), to our knowledge, no studies have been performed to quantify impacts of regional fires on PAHs deposition in Galician vegetation. Therefore, to study this subject is sure to be of considerable interest to researchers working in this field now and in future. Furthermore, characterization of the complete suit of the PAHs produced by a fire is extremely important for understanding the fate and behaviour and predicting the potential long-term impact of the fire products on the human health. Farms of O Salnés supply of food for the cities of NW Spain, which has a population of about 2.8 million people. Among various crops grown in the area, vineyards cover approximately 6200 ha with an annual production of 31,000 tons (Consellería de Medio Rural., 2005).

In this paper, we report comprehensive qualitative and quantitative results of 11 of the 15 PAHs selected by the Scientific Committee on Food as carcinogens (benzo[*a*]anthracene, chrysene, 5-methylchrysene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenzo[*ah*]anthracene, benzo [*ghi*]perylene, dibenzo[*al*]pyrene) in food plant samples collected after a fire of a chemical company. Quantification of target PAHs was performed on a LC-FD.

2. Experimental

2.1. Chemicals, solutions and materials

The eleven PAHs studied (benzo[*b*]fluoranthene (B[*b*]F, 98%), benzo[*k*]fluoranthene (B[*k*]F, 98%), benzo[*a*]pyrene (B[*a*]P, 97%), benzo[*ghi*]perylene (B[*ghi*]P, 98%), indeno[1,2,3-*cd*]pyrene (I[1,2,3-*cd*]P, 98%), benzo[*a*]anthracene (B[*a*]A, 98%), dibenzo[*ah*]anthracene (DB[*ah*]A, 97%), chrysene (Chr, 99%), 5-methylchrysene (5-Mch, 99%), dibenzo[*al*]pyrene (DB[*al*]P, 99%) and benzo[*j*]fluoranthene (B[*j*]FA, 100%)) were purchased from Aldrich, Supelco or Isostandards (Madrid, Spain). HPLC grade acetonitrile and water, and analytical grade *n*-hexane and toluene were all supplied by Panreac (Madrid, Spain). Individual 100 mg/L stock solutions of PAHs were prepared by dissolving about 0.01 g of product in a small amount of acetonitrile, hexane or acetonitrile:toluene (2:3) and diluting to 100 mL with the same solvent, which was selected depending on the solubility of the PAH. From these solutions, solutions containing 10 and 0.1 mg/L concentrations of the different PAHs in *n*-hexane were prepared separately. From these diluted individual solutions, mixed solutions with PAHs ranging from 10 to 700 μg/L we prepared in acetonitrile following evaporation of the hexane. Working standard solutions used to construct the calibration line were prepared in acetonitrile by dilution to reach concentrations between 0.02 and 40 μg/L. These solutions were stored in amber flasks at 4 °C, where they were stable for at least 6 months. Waters Sep-Pak silica (690 mg) cartridges (Santiago de Compostela, Spain) were used as solid-phase extraction (SPE) mini-columns for purification and concentration. Analytical grade C-45 nitrogen was supplied by Carburos Metálicos (Vigo, Spain). Additional equipment included a rotary evaporator (Heidolph, Barcelona, Spain), an ultrasonic bath (P-Selecta, Barcelona, Spain), an analytical precision scale (Sartorius, Madrid, Spain) and a vortex shaker (Heidolph, Barcelona, Spain). Disposables used were nylon filters (0.45 μm), micropipettes (200–1000 μL) and injection vials (2 mL) furnished with screw caps and PTFE-lined butyl rubber septa and inserts (0.35 mL).

2.2. Chromatographic conditions

The liquid chromatographic system used was a Thermo Separation Products (TSP) P2000 binary pump equipped with a TSP AS1000 autosampler, a TSP SCM1000 vacuum membrane degasser and a Jasco FP-1520 fluorescence detector. Separations were performed with a 25 cm × 4.6 mm (length × i.d.), 5 μm particle, Supelcosil LC-PAH obtained from Supelco (Madrid, Spain). The temperature of the HPLC column was kept constant at 33 °C to obtain reproducible PAHs retention times, what is of paramount importance when using a defined wavelength programme, which allows the optimization of sensitivity for each PAH. The used mobile phases were acetonitrile (ACN) and water. The gradient was: 80:20 ACN/H_2O change to 95:5 ACN/H_2O in 40 min change again to 80:20 ACN/H_2O in 1 min and hold for 10 min giving an analysis time of 51 min. The injection volume was set to 50 μL by LC flow rate of 1 mL/min. Detection was performed at selected excitation and emission wavelengths as Table 1 shows. Dibenzo[*al*]pyrene and dibenzo[*ah*]anthracene were almost co-eluting what made necessary the use of, respectively, 393/453 nm and 296/406 nm wavelengths for their quantification.

2.3. Description of study sites and samples

The Ría de Arousa (Fig. 1) is the most extensive estuary of the Rías Baixas. Its mouth opens between the Covasa point in the north and San Vicente point in the south. To the north it clearly borders on Serra do Barbanza and to the south it seems surrounded by the gentle flatlands of O Salnés. The profile of Arousa gives rise to a large number of coves and peninsulas that favour the settlement of inner towns such as Caldas de Reis but also numerous marine towns such as Carril, Vilagarcía, Vilaxoán, Vilanova, Cambados and O Grove to the south. The lower sections of the rivers that give on to the estuary are the As Pedras, the Ulla and the Umia.

Table 1
Fluorescence detection conditions for the quantification of PAHs at a gain of 1000

PAH	Time window (min)	λ_{exc} (nm)	λ_{em} (nm)	Retention time (min)
B[*a*]A	10–16	274	414	12.0
Chr				13.3
5-Mch				14.0
B[*j*]F	16–22	300	446	16.5
B[*b*]F				18.0
B[*k*]F				20.7
B[*a*]P	22–30	296	406	24.0
D[*al*]P		393	453	27.9
D[*ah*]A				28.5
B[*ghi*]P	30–40	300	470	32.5
I[1,2,3-*cd*]P				34.7

From the economic viewpoint, it must be stressed that the wealth of Arousa does not come down simply to the shellfish sector, fishing, agriculture or the preserve industry. Of great importance too is the wine sector, where we have the Albariño white wines. Vilagarcía de Arousa is an important commercial and fishing port with extraordinary economic activity at the centre of the region of O Salnés, famous for its Rías Baixas Appellation Controlée wines.

On September 1, at around 14:30 pm local time, a fire broke out on at chemical distributor of a chemical company's site in Caldas de Reis, Pontevedra province, Spain, during the unloading of a tank truck filled with toluene. With the aim of the evaluation of the pollution by PAHs in the area to the South-West of Caldas de Reis, a 64 km^2-triangle formed by Caldas de Reis-Vilanova de Arousa-Cambados was monitored. The area of sampling was chosen based on the following reasons: (a) because it is on the direction of the dominant winds at the end on the Summer under anticyclone conditions (from North-East to South-West), and (b) because it is one of the most intensive agricultural areas in O Salnés. Vegetable samples of 5 types (cabbage, maize, grape, "Padron-type" pepper and tomato) with lipid contents between 0.16% and 0.20% were collected in triplicate in the sampling area (Fig. 1) the week after the chemical company fire. Lipid contents in the tissues were so similar that it was not necessary to normalize PAH concentrations to lipids. Following the incident the samples were immediately taken back to University of Vigo and stored in a temperature-controlled room at 0–4 °C.

2.4. Sample treatment

The pre-analytical treatment used in this work was based on a procedure for the determination of PAHs in smoked foods or instant coffee previously reported by the present authors (García-Falcón, Cancho Grande, & Simal-Gándara,

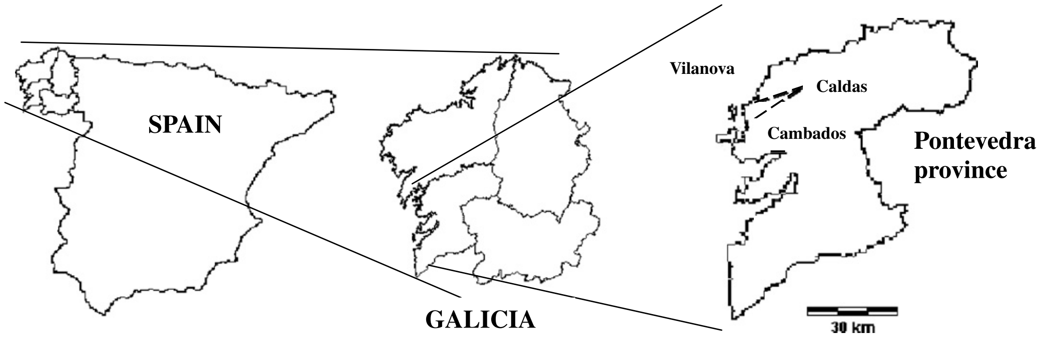


Fig. 1. Area (Caldas de Reis-Vilanova de Arousa-Cambados) where the samples of plant foods were collected (Caldas de Reis at 42°36′11″N and 8°38′26″W).

2005a, 2005b; García-Falcón, & Simal-Gándara, 2005c; García Falcón, López de Alda Villaizán, González Amigo, Simal Lozano, & Lage Yusty 1996). A piece of sample (which external surface and weight was measured) was immersed in *n*-hexane (20–100 mL depending on the size of the whole piece) and subjected to ultrasound-assisted solvent extraction for 20 min. The extract obtained was separated and cleaned up directly with sep-pack silica plus cartridges (Waters, Spain), adding 10 mL *n*-hexane to avoid losses. Finally, the extract was evaporated till dryness under a stream of nitrogen in a TurboVap LV Concentration Workstation (Caliper Life Sciences, Spain) and filled up to a final volume of 0.5 mL with ACN.

3. Results and discussion

3.1. HPLC procedure performance

Chromatographic conditions were based on the method developed by García-Falcón et al. (2005b, 2005c). Thought 15 PAHs have been selected by the Scientific Committee on Food as carcinogens, cyclopenta[*cd*]pyrene was not determined due its lack of fluorescence, and dibenzo[*al*]pyrene was selected as representative of the 4 isomers dibenzo[*al*]-pyrene, dibenzo[*ae*]pyrene, dibenzo[*ai*]pyrene and dibenzo[*ah*]pyrene because of its toxicity (Devanesan et al., 1999). In order to select the most appropriate detection wavelengths for the news selected analytes such as chrysene, 5-methylchryse, benzo[*j*]fluoranthene and dibenzo[*al*]-pyrene, excitation and emission fluorescence spectra were recorded. Though different gradient elution programs were applied in order to obtain a good resolution of chromatographic peaks, retention times of dibenzo[*al*]pyrene and dibenzo[*ah*]anthracene were very similar (Table 1). To solve the close coelution problem that pose these two PAHs, an alternative λ_{ex} and λ_{em} were selected at their elution retention time window between 22 and 30 min that are selective for dibenzo[*al*]pyrene 393/453 nm. No selective excitation and emission wavelengths for dibenzo[*ah*]anthracene was found and λ_{ex} at 296 nm and λ_{em} at 406 nm were used to its quantification.

3.2. PAH extraction procedure performance

In the present work PAH recoveries were determined by spiking the surface of PAH-blank materials. After spiking, samples were stored at refrigeration in the dark for 24 h to facilitate equilibration with the sample matrix. The set of samples analyzed was processed together with a reagent blank to test for contamination in the extraction process. Spiking levels were selected in accordance with the PAH levels typically found in this type of samples. As Table 2 shows recoveries obtained were between 82% and 103% with RSD (%) about 8.0%. Therefore, the selected method was robust enough to quantify PAHs in plant food samples. Detection and quantification limits (LODs and LOQs) were evaluated on the basis of the noise obtained with the analysis of unfortified blank samples ($n = 4$). LOD and LOQ were defined as the concentration of the analyte the produced a signal-to-noise ratio of 3 and 10, respectively (American Chemical Society (ACS), 1980) and were then tested experimentally by spiking blank samples at such levels. External standard calibration was used to quantify the samples by LC-FD technique using multicomponent standards (Table 2). Good precision of the curves (RSD $\leqslant$ 6%) was obtained. Linear calibration plots – verified by the Mandel fitting test ($P = 99\%$) (Mandel, 1964) – were obtained over a concentration range of two or three orders of magnitude, depending on the compound.

3.3. Occurrence of PAHs in plant foods after the fire

The degradation of the environment quality by PAHs pollution is a cause of concern. The occurrence and distribution of PAHs in the area Caldas de Reis-Vilanova de Arousa-Cambados was monitored after a fire of a chemical company in an industrial area. The main reason of investigations in this area is strong carcinogenic and mutagenic

Table 2
Recoveries ± repeatabilities, instrument linear dynamic ranges, determination coefficients (r^2) and limits of detection (LOD) and quantification (LOQ) in μg/L ($n = 6$)

PAH	LOD	LOQ	Instrument linearity		Added (μg/L)	Recovery[b] ± RSD
			Standards[a] concentration range	r^2		
B[*a*]A	0.08	0.20	0.020–3.4	0.999	0.80	82 ± 3.0
Chr	0.50	1.5	0.12–20	0.999	5.0	85 ± 2.0
MCh	0.25	0.70	0.12–20	0.999	5.0	102 ± 2.0
B[*j*]F	1.3	3.5	0.30–60	0.999	7.0	95 ± 4.0
B[*b*]F	0.17	0.50	0.040–6.0	0.999	1.5	92 ± 6.0
B[*k*]F	0.020	0.050	0.010–1.0	0.999	0.20	102 ± 7.0
B[*a*]P	0.050	0.15	0.010–2.0	0.993	0.50	103 ± 5.0
DB[*al*]P	0.33	1.0	0.15–25	0.999	6.0	90 ± 3.0
DB[*ah*]A	0.17	0.50	0.040–7.0	0.999	2.0	97 ± 4.0
B[*ghi*]P	1.4	3.5	0.30–60	0.999	7.0	98 ± 3.0
I[1,2,3-*cd*]P	0.67	2.0	0.20–30	0.999	7.0	89 ± 3.0

[a] $n = 12$; 6 levels in μg/L in duplicate.
[b] ($n = 4$) determinations.

activity of PAHs. Generally, the most injurious for human organisms are compounds containing 4–6 condensed benzene rings in a molecule. The common distinctive mark of PAHs is their restricted local effect and long period between first contacts with a compound before appearance of a tumour. They are dangerous even in trace amounts; therefore, controlling the PAH level seems to be a substantial contemporary ecoanalytical problem.

Total PAHs levels (Table 3) varied from 88 to 4240 ng/kg. The measurements for the three replicates were pooled together for direct comparisons among the different plants. Variations were due to the various growth stages pooled. Among the different PAHs found in the plant food samples, concentrations of Chr and B[*b*]F were the highest ranging from 29 to 1320 ng/kg and from 11 to 920 ng/kg, respectively. B[*a*]A, B[*k*]F and B[*a*]P were also identified in all samples. Nisbet and LaGoy (1992) proposed that based on its carcinogenic potency relative to BaP, an individual PAH may be expressed in terms of its equivalent; the carcinogenic potency of the mixture could then be estimated from the sum of BaP equivalents. They reviewed approaches to the calculation of exposure to PAHs and applied several data to derive a set of equivalent toxicity factors (ETF) that more accurately reflects the state of knowledge on the relative potencies of different PAHs (Table 3). The results found, expressed in B[*a*]P equivalents, were always lower than 1003 ng/kg. No EU maxima levels for PAHs are regulated in plant foods. Nevertheless B[*a*]P concentrations in the selected samples are lower than maximum levels regulated in other foods (Commission Regulation (EC) No. 208/, 2005), ranging between 1000 ng/kg in baby foods and 10,000 ng/kg in bivalve molluscs. These concentrations found after fire were not alarming (the highest levels were found in cabbage; Fig. 2) and the intensive horticultural area in O Salnés could be considered not affected by the fire because of the smooth winds blowing the days after.

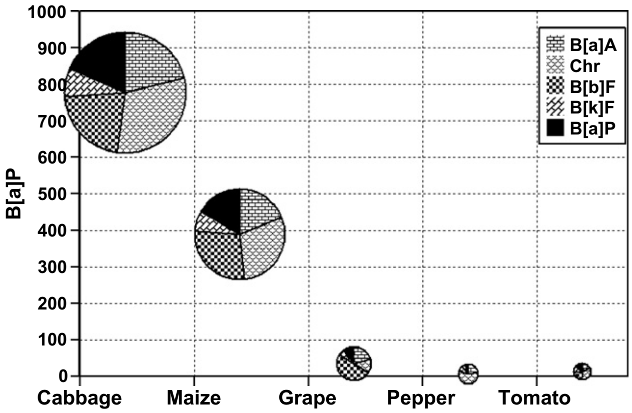


Fig. 2. Average PAHs concentrations ($n = 3$) in different plant foods (*x*-axis). Circle areas are proportional to total PAHs in the plants, and *y*-axis takes into consideration the level of B[*a*]P (ng/kg).

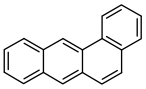
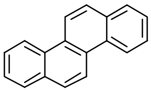
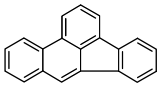
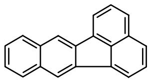
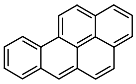
The degree of total PAH pollution by plant surface unit is not so variable as by plant weight, ranging from 36 to 305 pg/cm^2. This finding can be considered indicative of PAH pollution coming from the same air source, explaining why the highest PAH concentrations occur in leaves. PAHs may enter plant tissue either via the gaseous phase or deposit bound to atmospheric particles in the air to accumulate on plant surfaces (Barber, Thomas, Kerstiens, & Jones, 2004). Increased PAH concentrations in aerial plant tissues with large exposed surface were also reported in the literature. For example Kipopoulou, Manoli, and Samara (1999) observed the highest PAH burden in the leafy vegetables with a large surface area exposed to the atmosphere. Böhme, Welsch-Pausch, and McLachlan (1999) found that variation of PAH accumulation among 10 species could partially be explained by differences in

Table 3
PAH concentrations (average ± standard deviations; $n = 3$) found in samples, together with PAH equivalent toxicity factors (ETF) (Nisbet & LaGoy, 1992) to estimate B[*a*]P equivalents in samples, and the external surface/weight ratio of plant foods

	ETF	Cabbage leaves (14 cm^2/g)	Maize leaves (36 cm^2/g)	Grape fruits (1.9 cm^2/g)	“Padron-type” pepper fruits (3.4 cm^2/g)	Tomato fruits (0.55 cm^2/g)
B[*a*]A (ng/kg)	0.10	900 ± 827	450 ± 350	72 ± 57	27 ± 8.0	16 ± 12
Chr (ng/kg)	0.01	1320 ± 1055	700 ± 600	47 ± 35	70 ± 28	29 ± 9.0
5-Mch (ng/kg)	0.01	–	–	–	–	–
B[*j*]F (ng/kg)	0.10	–	–	–	–	–
B[*b*]F (ng/kg)	0.10	920 ± 723	660 ± 410	173 ± 111	11 ± 10	21 ± 9.0
B[*k*]F (ng/kg)	0.10	325 ± 215	175 ± 150	20 ± 16	7.0 ± 3.0	10 ± 8.0
B[*a*]P (ng/kg)	1.0	775 ± 725	388 ± 260	35 ± 10	6.0 ± 2.0	12 ± 6.0
DB[*al*]P (ng/kg)	5.0	–	–	–	–	–
DB[*ah*]P (ng/kg)	5.0	–	–	–	–	–
B[*ghi*]P (ng/kg)	0.01	–	–	–	–	–
I[1,2,3-*cd*]P (ng/kg)	0.10	–	–	–	–	–
Σ5-ring PAH Σ4-ring PAH		0.90	1.1	1.9	0.20	1.0
ΣPAH (ng/kg)		4240	2373	347	121	88
B[*a*]P eq. (ng/kg)		1003	524	62	11	17
ΣPAH (pg/cm^2)		305	67	176	36	160
B[*a*]P eq. (pg/cm^2)		72	15	32	3.3	31

–: not detected (4 ng/kg for the first nine PAHs and 80 for the last two).

Table 4
Structure, chemical abstract service number, molecular weight, water solubility and log P (octanol-water partition coefficient) for detected PAHs (from ACS SciFinder Scholar, v. 2006)

PAH	CAS no.	Bioconcentration factor	pm g mol^{-1}	S mol l^{-1}	Log P	TEFs
 benzo[a]anthracene	56-55-3	18,300	228	6.4×10^{-8}	5.9 ± 0.2	0.1
 chrysene	218-01-9	18,300	228	4.2×10^{-8}	5.9 ± 0.2	0.01
 benzo[b]fluoranthene	205-99-2	43,200	252	2.0×10^{-8}	6.4 ± 0.2	0.1
 benzo[k]fluoranthene	207-08-9	43,200	252	1.3×10^{-8}	6.4 ± 0.2	0.1
 benzo[a]pyrene	50-32-8	43,200	252	7.4×10^{-9}	6.4 ± 0.2	1.0

Toxic equivalency factors(TEFs) based on Nisbet and LaGoy (1992).

the surface area. The most reasonable explanation for the observed decreasing trend of PAHs for fruits seems to be dilution because of the increase in biomass (Fig. 2), since the absolute quantities of PAHs by surface unit are more similar (Table 3).

The analysed vegetal material can be divided in two main categories, leaves and fruits. For leaves and quasi-spherical fruits (grapes and tomatoes), the ratio between 5- and 4-ring PAHs was between 0.9 and 1.9. This ratio for the quasi-conical pepper fruits was much lower (0.2) due to their lower content in 5-ring PAHs, those with higher octanol/air partitioning coefficients and, therefore, bioconcentration factors (Table 4). This lower content of 5-ring PAHs in peppers could be explained by its own characteristics (shape and/or surface cuticula). Anyway, Edwards (1983) suggested that lower molecular weight PAHs which predominate the atmosphere can easily penetrate the cuticular surface of the foliage, while the higher molecular weight PAHs, mainly associated with the atmospheric particulates, are only superficially deposited on plant foliage and are thus more easily washed away by rain (133 mm in September 2006). High-molecular weight PAHs bond to coarse particles are prone to dry deposition and have shorter transfer distance, and there is weak effect to the other further areas, where pepper samples were collected (in the area of Cambados). Conversely, the fine particles float in the atmosphere for a long time, as it is reported that the 0.1–1 μm particles stayed in the air about 10 days (Warneck, 1988). Voutsa and Samara (1998) also reported that the total PAH burden in vegetables grown in an industrial area in Greece was dominated by low molecular weight compounds. By measuring 10 PAHs in rice from Tokushima, Japan, Liu and Korenaga (2001) found that PAH ratios for the lighter molecular weights (152–202) to the heavier molecular weights (228–252) in rice and paddy leaves were approximated to 70:30.

To summarize, PAHs found in this study were lower than those measured by Kluska (2003); content of PAH in fruits and vegetables depend on pollution of environment (mainly on air pollution) and on area of contact: Apples contain usually 200–500 ng/kg, tomatoes 200 ng/kg, spinach 6600 ng/kg, and cabbage (savoy) 20,400 ng/kg, what provide a basis for estimating a low potential biological impact associated with the levels found. In a previous work, we screened for the presence of PAHs in soil of rural areas (García-Falcón, Soto-González, & Simal-Gándara, 2006): Total PAHs were always lower than 13,000 ng/kg. As a conclusion, the selected plant foods will not give a chance for adverse biological effects to take place. In Tianjin (China), a PAH contaminated site, total PAHs of rice leaves from various growth stages ranged from 58,900 to 548,000 ng/kg with a mean value of 216,000 ng/kg (Tao et al., 2006).

4. Conclusions

The proposed method helps to cover some of the most important research and development needs in this area of PAHs fate in vegetation to asses the state of fire-induced pollution. The selected method is relatively rapid and reliable for determining PAHs in the selected plant foods. PAH pollution in vegetation was produced by their deposition from combustion smoke, since there were similarity in PAH profiles between most of the plant tissues. The results revealed that the company fire did not constitute a health risk. This low level of bioaccumulation depended on the limited exposure of the plants to smoke thanks to the smooth winds blowing in the direction of the intensive horticultural area of O Salnés. Surface area appeared to be an important factor controlling PAH levels in various exposed tissues of plants, indicating that the contribution of soil/water PAHs to plants (aerial part) accumulation was insignificant.

Acknowledgements

E. Martínez-Carballo is funded under a Parga Pondal contract (Galicia's Council of Education).

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