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ARTICLE

Polycyclic aromatic hydrocarbons in milk powders marketed in Uruguay

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) occurrence in forty-four samples of milk powder, marketed in Uruguay, was determined. A high-performance liquid chromatography (HPLC) method was applied with fluorescence detector (FLD) and UV-VIS diodes array detector (DAD). Milk powder was fortified with PAHs at three levels producing average recovery higher than 78.6% for all levels. The highest concentration of benzo(a)pyrene (BaP) was 2.85 μg kg^{-1} in milk powder. Contamination of samples expressed as the sum of 16 analysed PAHs varied between 5.77 and 427.28 μg kg^{-1} and as PAH4 (BaP, chrysene, benzo(a)anthracene and benzo(b)fluoranthene) was between below LOD and 11.54 μg kg^{-1}. Only one sample exceeded the maximum limit for BaP, but 84% of the commercial milk powders did not comply with the European Union maximum limit for PAH4.

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Milk powder; polycyclic aromatic hydrocarbons; PAHs; benzo(a)pyrene; PAH2; PAH4; PAH8

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that consist of two or more aromatic rings (Nagpal 1993). Up to date, more than 100 PAHs in nature have been characterised. On the basis of its occurrence and carcinogenicity studies, the Agency of environmental protection of the United States of America (USEPA) has selected 16 PAHs to be the main contaminants (Nieva-Cano et al. 2001). This group is called 16 USEPA PAHs and involves 2, 3, 4, 5 and 6 benzene rings in its structure. The high solubilities of PAHs in organic matrices lead to their accumulation in fat matrices.

Milk is widely used for human consumption, and due to its lipophilic nature (Aguinaga et al. 2007), it is susceptible to the bioaccumulation of environmental toxic compounds that have great relevance to human health and in particular growing children (Bianchi et al. 2008). The consumption of milk and dairy products makes Uruguay one of the more large consumers of Latin America, with 239 l annual by person (FAO, FEPALE 2012). Main destinations for export of Uruguayan milk powder are Venezuela, Brazil and China.

Naccari et al. (2011) determined that presence of PAHs in raw milk depends on environmental pollution. Dairy animal's exposure to PAHs is carried out mainly by breathing particles of the atmosphere, food intake of pasture and prepared food (Gutiérrez et al. 2015) or contact with a contaminated product. After body absorption, the PAHs are mainly excreted in the urine or faeces in the form of hydroxylated metabolites, or may accumulate in adipose tissue and be present in the milk (Chung et al. 2010). Yebra-Pimentel et al. (2012) established that the presence of PAHs in cow's milk is probably due to a contaminated atmosphere, which is transferred to plants in general, by the deposition of particles in waxy cuticle from the leaf or the uptake of PAHs from the gas phase through the stomata, or by ingestion of earth in the grazing of livestock in the fields (Ounnas et al. 2009). It has been evaluated that cows ingest 65 to 1000 times more PAHs than humans, which would indicate the potential risk of milk contamination (Bulder et al. 2006).

Kishikawa et al. (2003) stated that the degree of contamination of powdered milk, infant and milk formulas depends on the conditions of processing as well as the level of environmental pollution. Different studies on PAH contamination in milk powder, follow-on milk, infant and milk formulas are included in Table 1. The main aim of this study was to analyse the occurrence of PAHs in samples of milk powder commercialised in Uruguay during 2013 and 2014.

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Table 1. PAH4 occurrence in milk powder in different countries.

Food type	Country	*n*	min-max (µg kg^{-1})					Reference
			BaA	Chry	Bbf	BaP	PAH4	
Skimmed milk	Argentina	9	0.069–2.464	0.360–5.880	0.042–1.488	0.034–0.395	0.523–10.165	Garcia Londoño et al. (2013)
	Canada	3	< LOD-0.30	-	-	< LOD-0.1	-	Lawrence and Weber (1984)
	Nigeria	4	< LOD-18.90	< LOD	< LOD	< LOD	< LOD-18.90	Iwegbue and Bassey (2013)
Whole milk	Argentina	12	0.0025–1.249	0.002–3.800	0.0005–0.477	0.008–0.081	0.322–5.520	Garcia Londoño et al. (2013)
	Brazil	10	0–1.009	0.025–3.495	0.002–0.171	0.0005–0.570	0.0005–4.747	Garcia Londoño et al. (2013)
	Nigeria	12	< LOD-36.80	< LOD-20.90	< LOD-39.50	< LOD-176.00	< LOD-233.80	Iwegbue and Bassey (2013)
Infant formulae	Canada	1	1.70	-	-	1.20	-	Lawrence and Weber (1984)
(0–12 months)	Nigeria	3	<0.001–0.017	<0.001–0.032	<0.001–0.021	<0.001–0.032	< LOD-0.10	Iwegbue et al. (2014)
(0–6 months)	Nigeria	16	<0.001–0.050	<0.001–0.065	<0.001–0.039	<0.001–0.074	< LOD-0.128	Iwegbue et al. (2014)
(12–36 months)	Nigeria	8	<0.001–0.076	<0.001–0.063	<0.001–0.117	<0.001–0.163	< LOD-0.289	Iwegbue et al. (2014)
(6–12 months)	Nigeria	13	<0.001–0.211	<0.001–0.202	<0.001–0.133	<0.001–0.141	< LOD-0.652	Iwegbue et al. (2014)
	Spain	1	< LOD	< LOD	< LOD	< LOD	< LOD	Rey-Salgueiro et al. (2009)
	Spain	1	< LOD	< LOD	< LOD	< LOD	< LOD	Aguinaga et al. (2007)
	Japan	3	0.02–0.06	0.14–0.40	0.20–0.51	0.03–0.06	0.070[a]	Kishikawa et al. (2003)
	Korea	7	0.124[a]	0.136[a]	0.024[a]	0.074[a]	0.36[a]	Cho and Shin (2012)
	Poland	18	< LOD	< LOD	< LOD	< LOD	< LOD	Ciecierska and Obiedziński (2010)
	Rumania	5	< LOD	0.16–0.35	n.a.	< LOD	0.16–0.35	Dobrinas et al. (2016)
	United Kingdom	96	<0.01–0.19	<0.01–0.42	<0.01–0.19	<0.01–0.18	< LOD-0.89	White et al. (2004)
Mixed milk powder	Korea	1	0.146	0.193	0.023	0.060	0.42	Cho and Shin (2012)
Follow-on milk	Poland	36	< LOD	< LOD	< LOD	< LOD	< LOD	Ciecierska and Obiedziński (2010)

[a]mean value
n.a.: not analysed.

Materials and methods

Chemicals

Analytical standards of PAHs

Acenaphthene (ACE), acenaphthylene (ACY), anthracene (AN), benzo(a)anthracene (BaA), benzo(a)pyrene (BaP), benzo(b)fluoranthene (Bbf), benzo(g,h,i)perylene (BPe), dibenzo(a,h)anthracene (dBAn), and fluoranthene (FLUR) were acquired from Accustandard (New Haven, CT, USA); benzo(k) fluoranthene (Bfk), chrysene (Chry), and indeno (1,2,3-cd)pyrene (IcdP) were from Supelco-Analytical (Bellefonte, PA, USA); naphthalene (NA) and phenanthrene (PHEN) were from Sigma Aldrich (Tokyo, Japan); and fluorene (FL) and pyrene (PY) were from Sigma Aldrich (Buchs, Switzerland). The standard reference solution used for accuracy was a certified reference material of Supelco (No. CRM47940, Bellefonte, United States) with the following analytical concentrations: ACE 10.455 µg ml^{-1}, ACY 10.589 µg ml^{-1}, AN 10.544 µg ml^{-1}, BaA 10.720 µg ml^{-1}, BaP 10.725 µg ml^{-1}, Bbf 10.683 µg ml^{-1}, Bkf 10.404 µg ml^{-1}, BPe 10.636 µg ml^{-1}, Chry 10.493 µg ml^{-1}, dBAn 10.843 µg ml^{-1}, FL 10.484 µg ml^{-1}, FLUR 10.591 µg ml^{-1}, IcdP 10.463 µg ml^{-1}, NA 10.636 µg ml^{-1}, PHEN 10.820 µg ml^{-1} and PY 10.458 µg ml^{-1}.

Solvents

Acetonitrile (Tedia, Fairfield, OH, USA) and n-hexane (Carlo Erba, Milan, Italy) were HPLC grade and used as received. Water for all procedures was distilled in a 6 L capacity distiller Model 0716 (Rolco, Buenos Aires, Argentina) and purified through a Nano pure Diamond purification system, model D11911 (Bamstead International, Dubuque, IA, USA).

Samples

Forty-four samples milk powder produced in Uruguay were purchased in supermarkets of "Montevideo," "Maldonado" and "Treinta y Tres" during the years 2013 and 2014. The sampling was performed in accordance with the European Communities Regulations No 836/2011 (European Commission 2011b). The package size ranged between 0.5 and 1 kg. The samples were picked randomly from shelves where the number of products was less than 10. When the package sizes were smaller than 1 kg, more packages were bought to have a representative lot sample. Samples were kept in their original packages, properly identified, and stored under refrigeration (4 ± 1 °C) until were analysed.

Methodology for PAH determination

Extraction and clean-up

The extraction and clean up for determination of PAHs were performed using the procedure reported by Garcia Londoño et al. (2013).

Liquid chromatography

A high-resolution liquid chromatograph consisting of a module separations Alliance 2695 (Waters, Singapore), an ultraviolet-visible (UV–VIS) diodes array detector (Waters 2698) and a fluorescence detector (Waters 2475) was used for sample analyses. An analytical column Waters PAH C18 5 µm of particle size, 4.6 mm inner diameter and 250 mm length (Waters, Eschborn, Germany) fitted with a 1 cm Spherisorb S50DS2 guard column (Waters, Milford, MA, USA) were used. Chromatographic conditions were the same as reported by Garcia Londoño et al. (2013).

Data analysis

The Shapiro–wilk test was used to evaluate data distribution. Median values of experimental and reference data of PAH contamination were evaluated by Mann–Whitney (Wilcoxon) *W*-test (significance level $\alpha = 0.05$), using Statgraphics Centurion XVI Software (Statpoint Technologies Inc., Warrenton, Virginia, USA).

Results and discussion

Analytical quality assurance

The accuracy of the method was determined by spiking PAHs certified reference material Supelco No. CRM47940 on a milk powder sample at levels of 0.12, 13.49 and 53.06 µg kg^{-1} and analysing in triplicate. The recovery obtained for these 3 levels was equal to or greater than 78.6% (Table 2). These results were similar to those reported by Girelli et al. (2014) in milk samples and fulfil the recovery criteria (50 a 120%) set by Regulation (EC) 836/2011 (European Commission 2011b). The precision of the method was assessed by determining repeatability (r) and reproducibility (R). Repeatability was carried out by repeating analysis of a sample in a short period of time (intra-day) keeping the same analytical process, operator, measuring system and operating conditions. Reproducibility was determined by analysing a sample 3 times at three different days in the same laboratory with the same analytical process. RSD(r) was between 1.2 % and 9.4% and RSD(R) was between 5.8% and 16.7%, respectively (Table 2). The limit of detection (LOD) was defined as the concentration at which the signal-to-noise ratio was 3:1. The limit of quantification (LOQ) was defined as the lowest concentration of analyte that could be determined with acceptable precision and accuracy at a signal-to-noise ratio of 10:1. LOD and LOQ data are shown in Table 2. LODs of Bbf, Bkf, BPe, Chry and FLUR in milk powder were lower than those reported by Kishikawa et al. (2003). Quantification was carried out by the external standard method, constructing a calibration curve with successive dilutions of the 16 PAHs standard stock solution. Each dilution was determined in triplicate. Standard solutions were stored under refrigeration at 4 ± 1°C in amber silanised vials and were stable for 6 months. The linearity of the calibration curve was presented by three orders of magnitude. The linear correlation coefficient (R^2) was greater than 0.999. A reagent blank was analysed at each batch of 12 samples, which was prepared following the entire analytical procedure and using the same reagents and solvents as applied for the samples.

Table 2. Performance characteristics of the analytical method in milk powder.

			Average recovery (%)				
Analyte	LOD (µg kg^{-1})	LOQ (µg kg^{-1})	0.12 µg kg^{-1}	13.49 µg kg^{-1}	53.06 µg kg^{-1}	RSDr (%)	Accreditation
NA	0.04	0.13	n.q.	104.3	106.2	1.2; 9.4	No
ACY	4.9	16.4	n.q.	n.q.	84.9	n.q.	No
ACE	0.3	1.0	n.q.	82.2	80.8	3.8–7.5	No
FL	0.07	0.23	n.q.	87.8	99.8	2.2–9.4	No
PHEN	0.01	0.04	87.3	95.9	97.0	1.3–9.4	No
AN	0.003	0.01	79.2	80.3	83.1	2.4–9.3	No
FLUR	0.0004	0.0015	90.1	103.0	87.0	1.2–9.3	No
PY	0.005	0.018	83.3	92.9	78.6	1.2–9.4	No
BaA	0.005	0.017	89.2	90.4	105.2	3.8–9.2	No
Chry	0.004	0.014	82.7	98.4	86.9	1.8–9.1	No
Bbf	0.001	0.003	88.2	91.2	104.5	2.1–8.9	No
Bkf	0.0004	0.0014	85.2	93.3	99.2	1.3–7.6	No
BaP	0.001	0.002	86.4	88.5	92.8	2.8–8.7	No
dBAn	0.001	0.003	91.4	94.8	93.2	1.4–8.9	No
BPe	0.001	0.004	84.3	84.0	80.0	6.1–9.4	No
IcdP	0.07	0.23	n.q.	89.2	95.5	2.4; 9.0	No

n.q.: not quantifiable.

PAH content in samples

Mean, median, percentile 90, minimum and max of each PAH are shown in Table 3. By analysing normal probability graphics and applying the test of normality for each PAH, it was determined that PAH contamination does not follow a normal distribution (Shapiro-Wilk, α = 0,05; p-values < 0,05). ACY was not detected in any of the samples, regarding the determination of this analyte was performed by UV and thus had a higher limit of detection. ACE was not detected in more than 95% of the samples. NA, FL, and PHEN were detected in all samples. NA and PHEN were found in a higher concentration. The sample contamination expressed as the sum of analysed PAHs was between 5.77 and 427.28 μg kg^{-1} of milk powder. The median obtained was 148.19 μg kg^{-1} of milk powder. In the samples analysed by Iwegbue and Bassey (2013), the sum of 16 USEPA varied between 15.6 and 1711.8 μg kg^{-1}, a larger range than the results obtained in this study. Ciecierska and Obiedziński (2010) analysed 19 PAHs in infant and follow-on formulas on the Poland market, the range of the sum of PAHs contamination found, were between 0.28 and 7.45 μg kg^{-1}. In the present work, the range was between 0.01 and 27.60μg kg^{-1}, considering the sum of the same PAHs.

About 94% of PAHs contain 2 or 3 benzene rings (NA, ACY, ACE, FL, PHEN, AN and FLUR) in their chemical structure. This indicates that a low PAH percentage is considered as possible or probable carcinogenic for humans by the IARC or EPA. Ciecierska and Obiedziński (2010) obtained a similar profile for infant and follow – on formulas, where the predominant PAHs were from the three rings ones (no 2-ring PAHs were analysed). In the same way, Grova et al. (2002) determined that the lower molecular weight represented the PAHs highest contamination of raw milk of different farms, near and away from potential sources of contamination. In human milk samples, the predominant PAHs also correspond to low molecular weight (Yu et al. 2011). Dairy products from the Nigerian market presented PAH contamination predominant of 3 and 4 rings (Iwegbue and Bassey 2013). Gutiérrez et al. (2015) analysed PAH distribution in milk produced in farms near an industrial park during dry and rainy seasons. These authors observed that the 3 and 4 ring compounds were dominant in all samples, but especially in the rainy season. Girelli et al. (2014) found no PAHs of high molecular weight in pasteurised and UHT milk samples, except BaP, which presented high PAHs contamination. Iwegbue et al. (2014) only detected NA in 28% of the samples analysed (n = 40, infant formulas), this being the predominant PAH (3.6 to 33.8%) but in a low contamination range (0.002 to 0.851 μg kg^{-1}). Bkf, IcdP, BaP and BPe were not detected in 75, 50, 70 and 55% of the analysed samples, respectively. Contamination in the positive samples for BaA, BaP, Bbf and Chry (PAH4) was between 0.03 and 4.12 μg kg^{-1}, 0.01 and 2.85 μg kg^{-1}, 0. 01 and 2.72 μg kg^{-1} and 8.68 and 0.67 μg kg^{-1} of powdered milk, respectively. Cho and Shin (2012) analysed 7 PAHs (BaA, Chry, Bbf, Bkf, BaP, dBAn, BPe) in samples of infant formula (n = 58) and milk formula (n = 15) acquired in Korea with a mean of the sum of the seven analysed PAHs of 0.435 and 0.457 μg kg^{-1}, respectively. The median for the sum of these seven PAHs in the present study was 2.24 μg kg^{-1}, so an order of magnitude larger.

In skimmed powdered milk samples analysed in this work, the contamination of BaA and BaP is greater than obtained by Lawrence and Weber (1984) in Canadian samples. In case of whole milk powder samples, the maximum obtained for BaP in Nigeria (176 μg kg^{-1}) was much greater than the obtained for the samples in this study (2.85 μg kg^{-1}), where in only one of the samples the concentration of BaP was above the maximum limit as set by the European Commission (2011a). The median was 0.042 μg kg^{-1} in milk powder. In a study carried out by Garcia Londoño et al. (2013), none of the Argentinean and Brazilian samples exceeded the maximum limit. Iwegbue and Bassey (2013) found 30% of the analysed samples (n = 20) to be positive for BaP, with a range that varied from 7.8 to 88.2 μg kg^{-1}, and the median was greater (3.90 μg kg^{-1}) than the ones obtained in this survey (0.01 μg kg^{-1}). Chung et al. (2010) reported four positive samples for BaP in samples of fluid milk, with concentrations of 9–12 μg l^{-1}. Other authors reported that none of the samples

Table 3. PAH contamination in 44 milk powder samples obtained on the Uruguayan market.

PAH	Mean	Median	P90	Min	Max
NA	92.40	71.66	243.92	3.04	288.35
ACY	<4.9	<4.9	<4.9	<4.9	<4.9
ACE	<0.3	<0.3	<0.3	<0.3	0.75
FL	3.58	2.62	8.80	<0.23	13.08
PHEN	57.92	57.03	99.12	2.36	117.22
AN	0.51	0.31	1.23	<0.003	2.63
FLUR	5.51	3.23	12.19	<0.0004	28.15
PY	6.98	5.53	14.00	<0.005	39.72
BaA	0.31	0.14	0.44	<0.005	4.12
Chry	2.22	1.99	3.83	<0.004	8.68
Bbf	0.13	0.01	0.19	<0.001	2.72
Bkf	0.06	<0.0004	0.08	<0.0004	1.96
BaP	0.13	0.004	0.25	<0.001	2.85
dBan	0.04	0.02	0.08	<0.001	0.28
IcdP	0.09	0.04	0.12	<0.07	1.32
BPe	0.07	<0.001	0.14	<0.001	1.30
∑ PAHs	169.99	148.19	347.32	5.77	427.28
∑ PAH 4	2.36	2.01	3.83	<0.001	11.54
∑ PAH 2	2.80	2.21	4.20	2.80	2.21
∑ PAH 8	3.06	2.29	4.33	3.06	2.29

analysed exceeded the maximum limit as set for BaP (Rey-Salgueiro et al. 2009; Ciecierska and Obiedziński 2010; Cho and Shin 2012; Girelli et al. 2014; Iwegbue et al. 2014).

The range of contamination expressed as PAH4 was between 0.005 and 18.38 μg kg^{-1} of milk powder. In 37 samples (84%), PAH4 concentrations exceeded the maximum limit of 1 μg kg^{-1} in Regulation (EU) No 835/2011, whereas García Londoño et al. (2013) reported 40% (Argentina) and 76% (Brazil) of the samples exceeded that limit (Table 1). The maximum value for PAH4 obtained was 18.38 μg kg^{-1}, exceeding the maximum of 0.89 μg kg^{-1} found by White et al. in 2004, but below the maximum of 233.80 μg kg^{-1} reported by Iwegbue and Bassey (2013) in Nigerian samples. Median values obtained for Nigeria (9.55 μg kg^{-1}), Argentina (2.16 μg kg^{-1}) and Brasil (2.11 μg kg^{-1}) were of a lower order than for samples in Uruguay. Analysing the contamination levels between Argentina and Brazil revealed no significant difference in contamination (Mann–Whitney *W*-test, $\alpha = 0.05$, *p*-values > 0.05), but it exists between those countries and Uruguay. Analysing the contamination values of PAH2, PAH4 and PAH8 for the samples of those countries there was no significant difference (Kruskal-Wallis, $\alpha = 0.05$, *p*-values > 0.05). Although the large number of samples that exceeds the value set for PAH4, it is important to mention that the value which has been compared corresponds to that established for a group of risk as the infant population.

Evaluation of milk type (skimmed or whole)

Contamination of the samples in relation to the lipid content (whole: n = 39 and skimmed: n = 5) was assessed. Box and whisker plot for the sum of 16 PAHs is shown in Figure 1. No significant difference was found between samples with different lipid content for the sum of the analysed PAHs or for PAH4 (Mann–Whitney *W*-test, $\alpha = 0.05$, *p*-values>0.05). Contamination of BaP was significantly higher in the whole samples (Mann–Whitney *W*-test, $\alpha = 0.05$, *p*-values<0.05). Aguinaga et al. (2007) found no PAHs in samples of skimmed milk, maybe due to reduction during the skimming process. However, some studies determined greater PAH contamination in samples with higher lipid content (Kishikawa et al. 2003; Naccari et al. 2011; Garcia Londoño et al. 2013; Girelli et al. 2014). Battisti et al. (2015) reported that PAH concentrations were affected by fat level, particularly they found in the yogurt samples that PAH levels increased with an increase in triglyceride content. Other authors suggest that it is not possible to determine a correlation between the total fat content and PAHs concentration (Del Bubba et al. 2005; Zanieri et al. 2007). From the available data, it is not possible to establish a relationship between fat content and PAH levels. Perhaps other factors, such as raw milk quality, processing methods and environmental contamination have a larger influence.

Correlation between PAH2, PAH4 and PAH8

EFSA (2008) determined the co-occurrence of different groups of PAHs, as to establish a group that could serve as an indicator of contamination of samples according to its carcinogenic potential, since they considered that BaP itself just wasn't a good indicator. According to European Food Safety Authority Panel on Contaminants in the Food Chain, the correlation between PAH2 and PAH4 or PAH8 was 0.92, and between PAH4 and PAH8 was 0.99, based on analysis of only 84 milk or milk product samples. In the present study, the interrelationships between PAH2, PAH4 and PAH8 were evaluated using linear regression. Correlations between PAH2 and PAH4; PAH2 and PAH8; PAH4 and PAH8 are presented in Figures 2–4. It is generally observed that a positive relationship exists

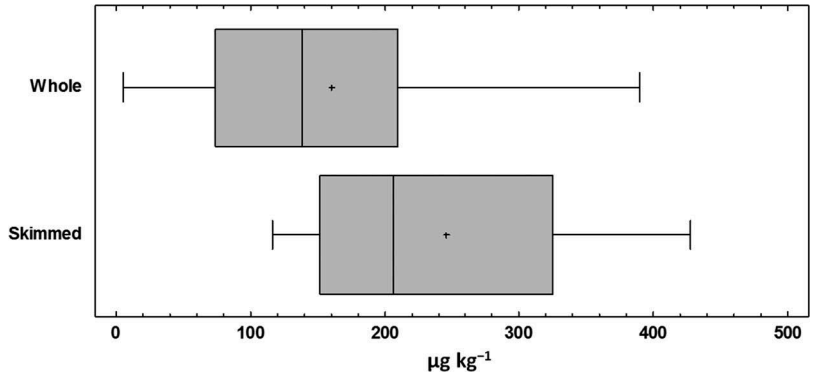

Figure 1. Box and Whisker Plot of Σ PAH of skimmed and whole powder milks.

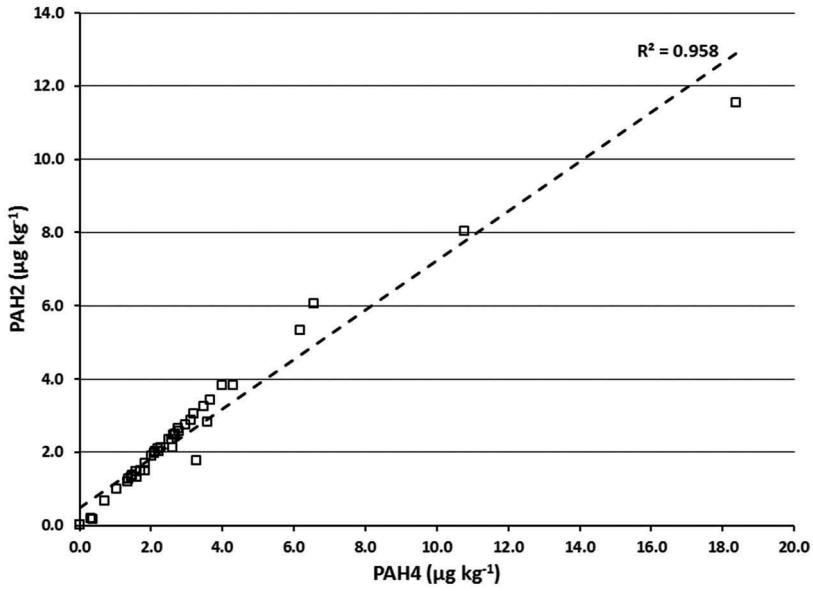

Figure 2. Linear relationship between PAH2 and PAH4.

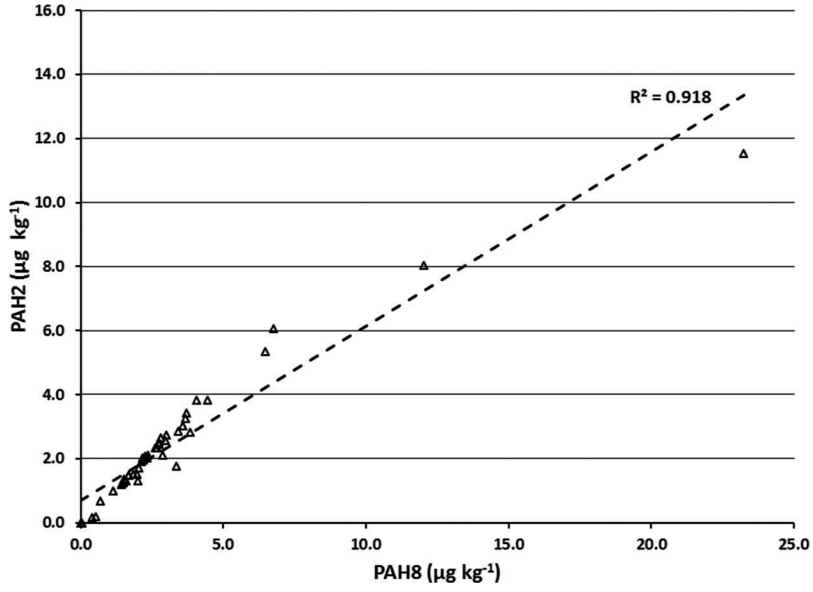

Figure 3. Linear relationship between PAH2 and PAH8.

between these three PAH categories. However, the most significant correlation was obtained for PAH4 against PAH8 (R^2 = 0.991), while between PAH2 and PAH8 (R^2 = 0.918) and PAH2 and PAH4 (R^2 = 0.958) these were lower than the study carried out by EFSA (2008).

Conclusions

PAH occurrence was determined in Uruguayan milk powders marketed during 2013 and 2014. There is evidence that PAHs of low molecular weight predominate in all powdered milk analysed from different countries. It was not possible to establish a relationship between fat content and PAH contamination. The best correlation was between PAH4 and PAH8, which coincides with the one carried out by EFSA for a group of PAHs that could serve as an indicator of the total contamination of the samples. Only one of the analysed samples exceeded the maximum limit set for infant formula by the European Commission (2011a) for BaP. However, 84% of the samples exceeded the maximum limit set for PAH4. This

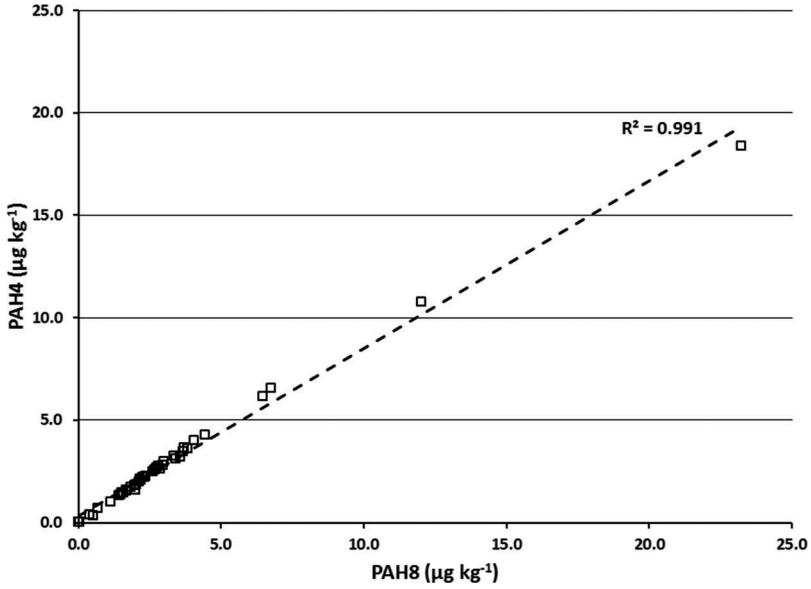

Figure 4. Linear relationship between PAH4 and PAH8.

study establishes the starting point for the establishment of a MERCOSUR regulation of PAH contamination in this type of food products.

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Disclosure statement

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