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Polycyclic aromatic hydrocarbons (PAHs) in yerba mate (Ilex paraguariensis) from the Argentinean market

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Polycyclic aromatic hydrocarbons (PAHs) in yerba mate (*Ilex paraguariensis*) from the Argentinean market

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Polycyclic aromatic hydrocarbons (PAHs) occurrence in 50 samples marketed in the main supermarkets from Argentina was surveyed. A high performance liquid chromatography (HPLC) method was applied with fluorescence detection (FLD) and UV—VIS diodes array detector (DAD) for the analysis of 16 PAHs in "yerba mate" (*Ilex paraguariensis*), with recoveries higher than 89% and limits of detection and quantification lower than that found by other methodologies in previous studies. Contamination expressed as the sum of 16 analysed PAHs ranged between 224.6 and 4449.5 μg kg^{-1} on dry mass. The contamination expressed as PAH4 (sum of benzo(a)pyrene, chrysene, benzo(a)anthracene and benzo(b)fluoranthene) varied between 8.3 and 512.4 μg kg^{-1}. The correlation coefficient for PAH2 (sum of benzo(a)pyrene and chrysene) and PAH4 groups was 0.99, for PAH2 and PAH8 (sum of benzo(a)pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, dibenzo(a,h)anthracene and indeno(1,2,3cd) pyrene) 0.97 and for PAH4 and PAH8 0.98.

Keywords: polycyclic aromatic hydrocarbons; "yerba mate"; *Ilex paraguariensis*; PAH; benzopyrene; organic contaminants

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Introduction

"Yerba mate" or "yerba" means the product made by dried leaves, lightly toasted and shredded, of exclusively *Ilex paraguariensis* (Aquifoliaceae), which has its origin in the subtropical regions of Argentina, Brazil, Paraguay and Uruguay. Polycyclic aromatic hydrocarbons (PAHs) are not essential for the development of plants, animals or human beings; however, they are ubiquitous in the environment. Some of them are carcinogenic and toxic for plants, animals and humans (EFSA 2008). PAHs are generally formed during the incomplete organic matter combustion. The transformation processes or food preparation which involve PAHs' formation are basically those in which food is subject to high temperatures and/or is in contact with flame or combustion gases (García-Falcón & Simal-Gándara 2005), roasted, air-dried smoked and "zapecado" (a rapid drying process by direct exposure to flames). Due to the drying and "zapecado" stages in the manufacturing of "yerba mate" and to the crop near to industrial areas, its contamination with PAHs may occur (García-Falcón et al. 2006; Rey-Salgueiro et al. 2008).

There are some studies performed about "yerba mate". Camargo and Toledo (2002), Kamangar et al. (2008) and Zuin et al. (2005) analysed samples of different Brazilian brands. Vieira et al. (2010) evaluated samples obtained from three Brazilian suppliers that were collected at three stages of processing and Ziegenhals et al. (2008) studied samples purchased from different manufactures with unknown origin. There are several reported methods for the determination of PAHs; Plaza-Bolaños et al. (2010) reviewed the extraction methodologies and the separation and detection techniques that are applied in the determination of PAHs in food and beverages. The determination of PAHs is carried out by high performance liquid chromatography (HPLC) coupled to a FLD (fluorescence detector) or with UV-VIS light detection or gas chromatography with mass spectrometry detector or liquid chromatography with mass spectrometry detector. Fluorescence is the most utilised detection system for the analysis of PAHs in food and beverages by HPLC because it is more selective and sensitive than UV detection with variable excitation and emission wavelengths. The limits of detection (LODs) are found at the 0.01 μg l^{-1} or μg kg^{-1} level. The LOD depends on pre-concentration techniques applied (such as solid phase extraction) and the programme of excitation and emission wavelengths. In this study, a HPLC method was applied with FLD and diode array detector (DAD) (UV-VIS DAD).

The aim of this study was to determine contamination levels of PAHs in "yerba mate" marketed in the main supermarkets from Argentina.

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Materials and methods

Chemicals

Analytical standards of PAH_S

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 purchased from Accustandard (New Haven, CT, USA), benzo(k)fluoranthene (Bkf), chrysene (Chry) and indeno(1,2,3cd) pyrene (IcdP) from Supelco Analytical (Bellefonte, PA, USA), phenanthrene (PHEN) from Sigma Aldrich (Tokyo, Japan), naphthalene (NA) from Sigma Aldrich (Munich, Germany), fluorene (FL), pyrene (PY) from Sigma Aldrich (Buchs, Switzerland). The standard reference solution utilised for accuracy was a PAH Calibration MIX of Supelco (No. 47940U, USA) with concentrations of ACE 9.03 ± 0.022 μg ml^{-1}, ACY 9.96 ± 0.008 μg ml^{-1}, AN 10.00 ± 0.019 μg ml^{-1}, BaA 10.02 ± 0.015 μg ml^{-1}, BaP 11.04 ± 0.008 μg ml^{-1}, Bbf 9.98 ± 0.005 μg ml^{-1}, BPe 10.07 ± 0.005 μg ml^{-1}, Bfk 9.95 ± 0.018 μg ml^{-1}, Chry 10.20 ± 0.013 μg ml^{-1}, dBAn 9.96 ± 0.026 μg ml^{-1}, FLUR 9.95 ± 0.026 μg ml^{-1}, FL 9.99 ± 0.007 μg ml^{-1}, IcdP 9.66 ± 0.011 μg ml^{-1}, NA 10.06 ± 0.013 μg ml^{-1}, PHEN 9.95 ± 0.011 μg ml^{-1} and PY 9.98 ± 0.013 μg ml^{-1}.

Solvents

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

Samples

Fifty "yerba mate" samples of different brands marketed in supermarkets from Buenos Aires during 2012–2013 were analysed. 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 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. In the lab, all samples were quartered and crushed in a hammer mill (Moulinex, Code No.215, Buenos Aires, Argentina). Then they were packed in bags with hermetic closure and stored in a freezer at –18ºC for their subsequent analysis.

Methodology for the determination of PAH_S

The method of extraction employed was a modification of the method by Vieira et al. (2010) and the clean-up step was based on methodologies proposed by García-Falcón et al. (2005), Lin et al. (2005) and Garcia Londoño et al. (2013).

Extraction of PAH_S from "yerba mate" samples

Approximately 0.5 g of samples were weighed, 15 ml of hexane were added and then the mixture was mixed in a vortex for 20 seconds. It was sonicated (Branson Ultrasonics, model 2510E-MT, Danbury, LT, USA) for 30 min at 35°C; once the sonication ended, it was centrifuged (Rolco, model 2036, Buenos Aires, Argentina) at 3000 rpm for 10 min. Then, the supernatant was taken and placed in a 100 ml flask. This procedure was repeated twice. The extract was partially evaporated in a rotary evaporator with a thermostated bath at 55°C, adjusting the rotor speed at 120 rpm and with a vacuum pressure of 7 inches of mercury through Venturi water trap. The extract was evaporated to an approximate volume of 3 ml and filtered through a nylon filter of 0.45 μm. The filtrate was recollected in glass test tubes, washed three times with 0.75 ml of hexane to the flask where the extract was present and passed through the filter. Finally, 1 ml of additional hexane was used to clean the filter. The total volume (6.25 ml approximately) was recollected in another glass test tube and it was taken to a thermostated bath at 36°C with nitrogen current (PIERCE ReactiTherm III, Rockford, IL, USA) and reduced to an approximate 1 ml volume.

Clean-up and preparation of the extract for chromatographic analysis

In order to perform the extract cleaning, an extraction column in solid phase (SPE) Waters Sep-PakSilica Plus with 690 mg filler and 55–105 μm of particle size (Code No. WAT020520) was used. A vacuum filtration station for SPE 12-position Vacuum manifold (Phenomenex, AHO6023, Torrance, CA, USA) was utilised to carry out the purification of various extracts simultaneously. SPE column conditioning was performed with 3 ml of hexane at the speed of 1.2 ml min^{-1}. Sample extract was subsequently loaded with 1 ml of hexane in order to avoid the column to get dried. Hexane (7 ml) was used for PAHs' elution.

Once the purified extract was obtained, the change of solvent was performed avoiding its dryness (in order to avoid the volatilisation of PAHs of lower molecular weight). Acetonitrile (0.75 ml) were added to the extract and then placed in a thermostated dry bath at 36°C with nitrogen current until the hexane was evaporated and the volume of acetonitrile was 0.2 ml approximately. Then, ultrapure water was added and carried to a relation of

Table 1. Mobile phase gradient.

Time (min)	Acetonitrile (%)	Water (%)	Curve[a]
0	60	40	6
12	90	10	9
29	90	10	6
34	60	40	6

Note: [a]Gradient curve linear (6) and non-linear (9).

acetonitrile/water 60:40 (p/p). Finally, it was filtered by a nylon membrane of 0.45 µm and placed in amber vials of 2 ml with teflon septa for their subsequent injection in HPLC.

HPLC–DAD/FLD

A HPLC composed of a module separations Waters Alliance 2695 (Singapore), a DAD Waters 2698 (USA) and a FLD Waters 2475 (USA) was used. An analytical column Waters PAH C18 5 µm of particle size, 4.6 mm of inner diameter and 250 mm of length (Waters, Code No. 186001265, Germany) fitted with a guard column Spherisorb S50DS2 of 1 cm (Code No. PSS830053, Waters, USA) was utilised. The column temperature was set at 30°C. The injection volume was of 50 µl. A gradient elution composed of two solvents, acetonitrile and water (Table 1), was carried to a flux of 1.2 ml min^{-1}. The determination was carried out using FLD and DAD detectors, because one of the analysed PAHs (ACY) does not possess fluorescentic properties.

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Results and discussion

Optimisation of detection

Emission and excitation spectra for 15 PAHs with fluorescence were obtained to optimise FLD determining the highest emission and excitation wavelength for each of them, programming them in time in order to increase detection sensibility (Table 2). An excitation and emission wavelength was established together for ACE and FL, BaA and Chry, because even though the resolution of these peaks were greater than 1.5, the time interval was not wide enough to ensure that the change in the wavelengths does not affect the base line. In order to determine the excitation and emission wavelength for these two pairs of compounds, more detailed spectra were obtained and a proper wavelength for both compounds was evaluated, taking into account the detection sensitivity for each of them (slope of the calibration curve) and the average concentration found in the samples. In case of DAD, a resolution of 1.2 mm and a wavelength scanning range from 210 to 400 nm were set. UV spectra for each PAH were determined and compared with libraries built

Table 2. Wavelength programme for measurement of PAHs.

Time (min)	λ Ex (nm)	λ Em (nm)	PAH
0.0	277	330	NA
7.2	291	318	ACE, FL
9.4	252	365	PHEN
11.0	250	402	AN
12.1	284	467	FLUR
13.3	332	378	PY
14.8	277	384	BaA, Chry
17.5	298	436	Bbf
19.0	303	432	Bkf
20.5	280	410	BaP
23.2	294	398	dBAn
24.7	290	420	BPe
26.5	305	480	IcdP

previously. The contrast spectral angle tool was used to determine peaks purity.

Analytical quality assurance

The calibration curves were obtained using a series of standard solutions. Calibration curves for all analysed PAHs had correlation coefficients higher than 0.998. The linearity of all calibration curves was present in three or more orders of magnitude according to the analysing PAH. The LOD and the limit of quantification (LOQ) were calculated as a relation of signal-to- noise = 3 or 10, respectively (Table 3). LOQ value for the regulatory compound (BaP) was below the lowest value established by European Communities of 1 µg kg^{-1} (European Commission 2011a). LOD and LOQ values for BaP, BaA, Bbf and Chry were also lower than 0.30 and 0.90 µg kg^{-1}, respectively, complying with the performance criteria of the European Communities Regulations 836/2011 (European Commission 2011b).

Samples were spiked with individual PAHs at three levels from 0.1 to 53 µg kg^{-1} depending on the PAH, by triplicate. The recovery percentages were higher than 89% for all tested PAHs. The standard relative recovery deviations ranged from 1.2% to 9.4%. The average recoveries were shown in Table 3.

Due to the lack of certified material for PAHs in "yerba mate" (Lerda 2011), the accuracy of the developed analytical method was verified also through a reference solution. A standard reference solution was injected daily by triplicate into the HPLC equipment. A blank was prepared following the entire analytical procedure and using the same reagents and solvents as samples, and it was analysed periodically. The precision of the proposed methods was investigated by intra- and inter-day determinations of standard solution and expressed by relative standard deviations (RSD). For intra-day studies, each concentration was assessed by performing three repeated

Table 3. Performance characteristics of the analytical method (n = 3).

Analyte	Matrix	LOD (μg kg^{-1} dry mass)	LOQ (μg kg^{-1}dry mass)	Average Recovery (%)	RSDr% range	Accreditation yes/no
NA	Yerba Mate	0.1	0.4	100.5	1.7–20.6	No
ACY	Yerba Mate	0.7	2.5	94.5	1.0–9.0	No
ACE	Yerba Mate	0.1	0.3	100.4	6.2–18.5	No
FL	Yerba Mate	0.02	0.08	99.0	0.1–12.2	No
PHEN	Yerba Mate	0.02	0.08	99.8	0.5–9.6	No
AN	Yerba Mate	0.01	0.03	100.3	0.2–9.9	No
FLUR	Yerba Mate	0.04	0.14	97.5	0.4–10.9	No
PY	Yerba Mate	0.01	0.04	100.2	0.1–8.1	No
BaA	Yerba Mate	0.02	0.06	100.1	0.5–11.3	No
Chry	Yerba Mate	0.04	0.13	98.4	0.2–10.2	No
Bbf	Yerba Mate	0.1	0.3	99.8	1.0–10.4	No
Bkf	Yerba Mate	0.01	0.03	99.8	0.3–10.6	No
BaP	Yerba Mate	0.01	0.02	105.9	1.5–10.1	No
dBAn	Yerba Mate	0.02	0.06	108.7	5.5–18.6	No
BPe	Yerba Mate	0.03	0.12	89.0	0.9–8.8	No
IcdP	Yerba Mate	0.1	0.3	97.0	0.3–10.3	No

Notes: NA, naphthalene; ACY, acenaphthylene; ACE, acenaphthene; FL, fluorene; PHEN, phenanthrene; AN, anthracene; FLUR, fluoranthene; PY, pyrene; BaA, benzo(a)anthracene; Chry, chrysene; Bbf, benzo(b)fluoranthene; Bkf, benzo(k)fluoranthene; BaP, benzo(a)pyrene; dBAn, dibenzo(a,h) anthracene; BPe, benzo(g,h,i)perylene; IcdP, indeno(1,2,3cd) pyrene.

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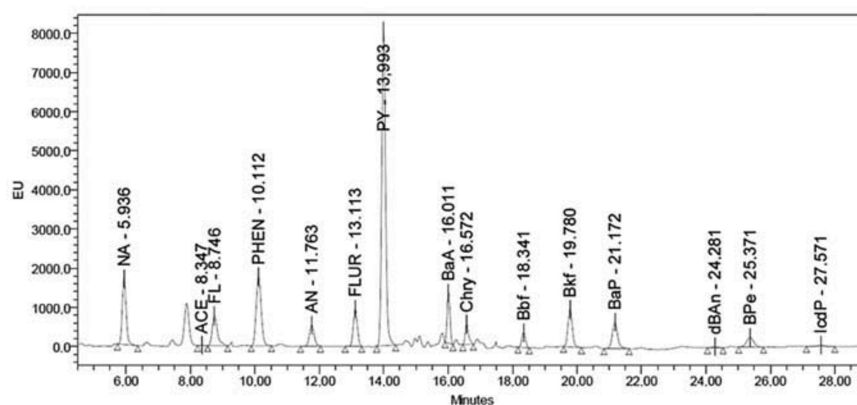

Figure 1. Typical chromatogram of “yerba mate” sample by FLD detection.

measurements for three times during a working day. The inter-day measurement studies were performed over 1 week. RSD values ranged from 0.4% to 7.6% and 1.2% to 9.5% for intra-day and inter-day assays, respectively. Figure 1 shows a chromatogram corresponding to 15 PAHs detected by fluorescence in a typical “yerba mate” sample. Triplicate determinations were made on all samples. The RSDr % of individual compounds ranged between 0.1% and 20.6%.

PAH content

Contamination expressed as the sum of 16 PAHs

The contamination found in 50 commercial tested samples expressed as the sum of 16 analysed PAH was between 224.6 and 4449.5 μg kg^{-1} on dry mass and the average was 1664.1 μg kg^{-1} on dry mass. “Box and Whisker Plots” for each analysed PAHs grouped in such a way that the scale of the ordinate axis (axis *Y*) clearly allows to see the distribution type of concentration data obtained for each PAH in the analysed samples as shown in Figure 2, the spacing between the different parts of the box indicate the degree of dispersion and skewness in data. The PAHs contamination had positive asymmetry and leptokurtic distribution. PAHs were found in all samples. ACE was not detected in nine samples and ACY in only one of them. Contamination for BaA, BaP, Bbf and Chry ranged from 2.21 to108.8 μg kg^{-1}, 1.33 to 125.2 μg kg^{-1}, 1.7 and 85.3 μg kg^{-1}, 3.11 and 210.5 μg kg^{-1}, respectively. NA (mean = 589.9 μg kg^{-1}) and PHEN (mean = 404.2 μg kg^{-1}) had the highest PAH levels, but these PAHs are not

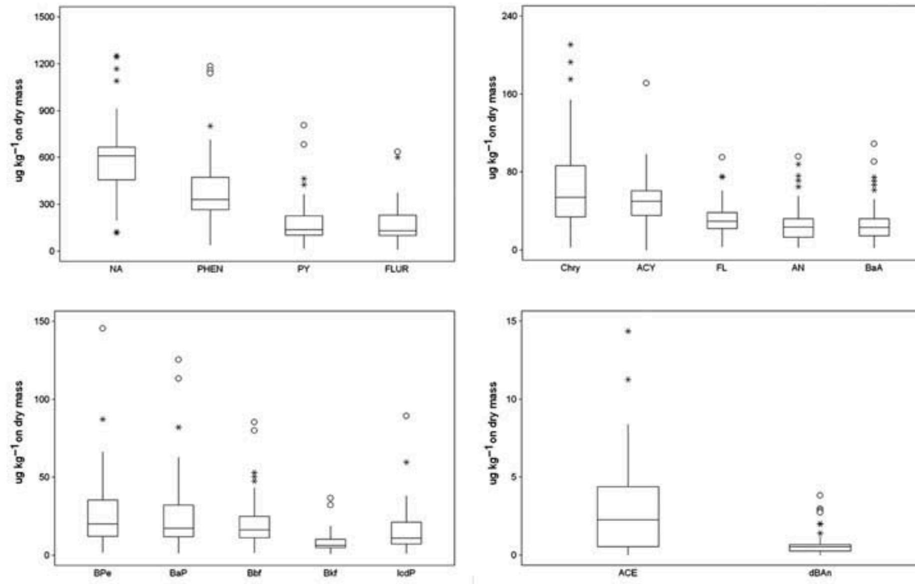

Figure 2. Box and Whisker plot for each PAH in all samples.

classifiable as carcinogenic to humans by the International Agency for Research on Cancer.

The comparison of the contaminations found in this study with the studies developed by Kamangar et al. (2008), Ziegenhals et al. (2008) and Vieira et al. (2010) are shown in Table 4. Kamangar et al. (2008) analysed 21 PAHs; however, we compared only 16 PAHs which matched with our research. Ziegenhals et al. (2008) analysed 16 PAHs which are classified as priority by the Scientific Committee on Food and the Joint FAO/WHO Experts Committee on Food Additives; for discussion, we took into account only the PAHs in common with the present study (BaA, Chry, Bbf, bkf, BaP, dBAn, BPe and IcdP).

The contamination expressed as the sum of 16 analysed PAHs had similarities with the study developed by Kamangar et al. (2008), the contaminations found by Vieira et al. (2010) were five times higher. In Ziegenhals et al. (2008) research, eventhough if the sum of the PAH values were lower than that obtained in present study, it was not comparable because they did not analyse those PAHs with low mass weight.

The distribution of the contamination, according to the number of benzene rings, is shown in Table 4. The criterion employed was the number of benzene rings established by Nagpal (1993). The five groups were: two benzene rings (ACE, ACY, FL and NA), three benzene rings (AN, FLUR and PHEN), four benzene rings (BaA, Bbf, Bkf, Chry, and PY), five benzene rings (BaP, dBAn and IcdP) and six benzene rings (BPe). The contamination results of PAHs with two benzene rings were lower than those published by Vieira et al. (2010), but higher than those reported by Kamangar et al. (2008). For the other groups (3, 4, 5 and 6 rings), the contamination obtained in this work was lower than the mentioned studies. The samples analysed by Vieira et al. (2010) and Kamangar

Table 4. Comparison of average contamination (μg kg^{-1}dry mass) and distribution by number of benzene rings with other studies (dry mass).

	Number of	Average contamination						Number of benzene type rings				
Reference	samples (*n*)	∑ PAHs	BaP	Chry	BaA	BbF	PAH4	2	3	4	5	6
This study	50	1664.2	26.9	67.6	28.7	21.9	145.1	676.6	602.4	313.4	43.4	28.4
Kamangar et al. (2008)[a]	8	1699.4	37.1	121.4	72.8	51.0	282.3	85.9	811.2	618.3	104.9	79.1
Ziegenhals, Jira, and Speer (2008)a	8	871.5	106.6	276.2	147.0	105.2	635.0	n.a.	n.a.	570.0	205.8	95.7
Vieira et al. (2010)[b]	1	8830.2	38.6	128.0	135.0	91.0	392.6	1476.0	5210.7	1917.9	177.1	48.5

Notes: [a]Mean of analysed samples obtained for PAHs which coincide with this study;
[b]values for PAHs in DMCC (dried mate cultivated from processor C);
n.a.: not analysed.

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et al. (2008) were of Brazilian origin, where the manufacturing process is different from the Argentinean one. The Brazilian process during "zapecado" had more contact with combustion fumes.

Analysis of the contamination compared to regulation (EC) 835/2011

The European Communities Regulation 835/2011 (European Commission 2011a) fixes maximum values for different groups of food (oils and fats, cocoa beans, coconut oil, meats and smoked fish, smoked sprats, molluscs, cereal food, infant food and infant formulae), expressed as BaP and PAH4. So far in the European Community there does not exist an established limit value for dried herbs and spices.

Taking into account all groups of food established by the European Community, all samples in this study exceeded the minimum value regulated for BaP and PAH4 (1 μg kg^{-1}). Meanwhile, the maximum level established for BaP (6 μg kg^{-1}) and PAH4 (35 μg kg^{-1}) was exceeded by 92% and 94% of the samples, respectively. The lowest contamination found for BaP and PAH4 was 1.3 and 8.3 μg kg^{-1} and the highest was 125.2 and 512.4 μg kg^{-1}, respectively. The median for BaP and PAH4 was 17.4 and 112.1 μg kg^{-1}, respectively. The values of the samples analysed by Kamangar et al. (2008), Ziegenhals et al. (2008) and Vieira et al. (2010) also exceeded the maximum level established for BaP as well as PAH4. On the other hand, the average contamination of BaP, Chry, BaA, Bbf and PAH4 was lower than those reported by Kamangar et al. (2008), Ziegenhals et al. (2008) and Vieira et al. (2010) (Table 4).

Relation between PAH2, PAH4 and PAH8

The Scientific Opinion of the Panel on Contaminants in the Food Chain (EFSA 2008) expressed that BaP itself was not an adequate indicator of PAHs occurrence in food and probed different groups of substances. PAH2, PAH4 and PAH8 were used for the exposure calculation as well as the estimation of margins of exposure. Subsequently, EFSA came to the conclusion that a system of eight substances (PAH8) would not provide much more added value with regard to a system of four substances (PAH4). The analysis performed by the Panel on Contaminants in the Food Chain (EFSA 2008) considered 9714 samples from which only 111 correspond to the category that included similar products as "yerba mate" such as tea, coffee and cocoa.

In the same way that the analysis performed by EFSA (2008), the correlation between PAH2 and PAH4, PAH2 and PAH8 and PAH4 and PAH8 were evaluated (Figure 3a, 3b and 3c). The best correlation obtained was between PAH2 and PAH4 (r^2 = 0.99), higher to the one observed in the study developed by EFSA (2008). The relationships

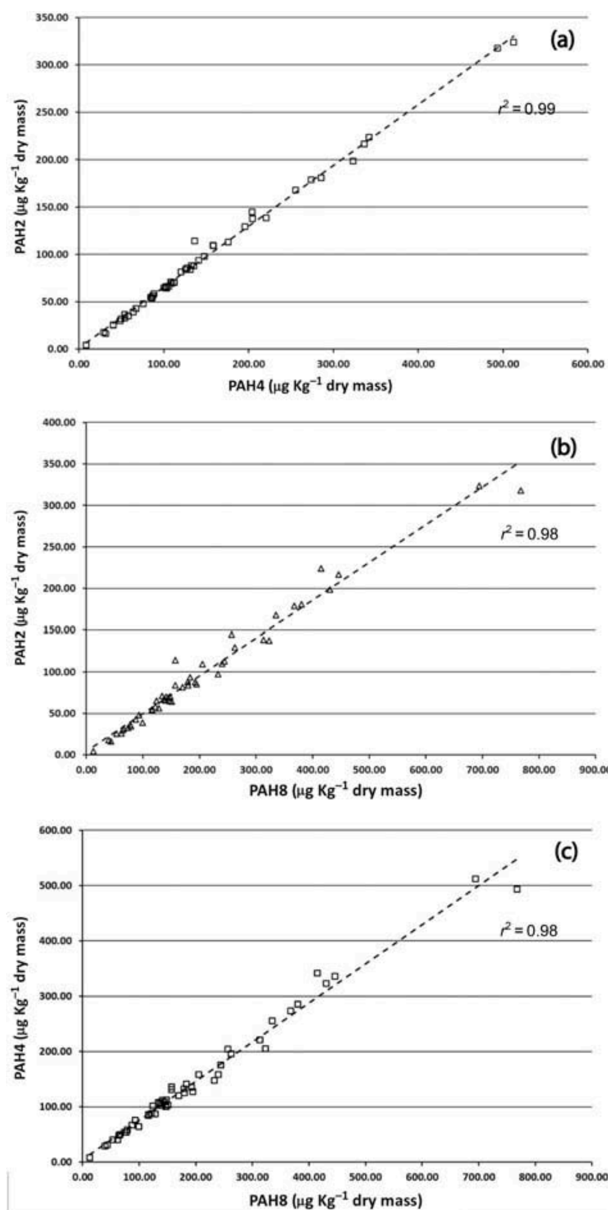

Figure 3. Linear relationship between: (a) PAH2 and PAH4, (b) PAH2 and PAH8 and (c) PAH 4 and PAH8.

between PAH2 and PAH8 (r^2 = 0.98) and PAH4 and PAH8 (r^2 = 0.98) were slightly lower than those observed in the study developed by EFSA (2008). The correlations obtained in this work are equivalent with the analysis developed by EFSA (2008). The contamination of PAHs in this type of sample (yerba mate) behaves similar to other matrices analysed by EFSA (2008).

Conclusion

A PAHs survey was performed in 50 samples of "yerba mate" marketed in the main supermarkets from Buenos

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Aires. The contamination expressed as the sum of 16 analysed, PAHs, PAH4 or BaP was lower than samples previously reported, most of them from Brazil. It was noted that concentrations of the samples were above the limits established by the European Community for foodstuffs. Correlations between PAH2, PAH4 and PAH8 were similar to the ones obtained by EFSA (2008) for tea, coffee and cocoa. The results obtained could help to extend the food categories established by EFSA. In order to evaluate the exposure of the population to these contaminants, it is necessary to perform studies to establish what quantity of PAHs is transferred to an infusion, after traditional Argentinean preparation.

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