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# Polycyclic Aromatic Hydrocarbons (PAHs) in “Yerba Mate” (*Ilex paraguariensis*) Fractions

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## ABSTRACT

The aim of this study was to evaluate polycyclic aromatic hydrocarbons (PAHs) contamination, distribution, and toxicity in “yerba mate” fractions, and to propose actions to reduce its pollution. Sixteen PAHs were quantified using a recently developed methodology by HPLC-DAD/FLD, obtaining recoveries higher than 84.5% and relative standard deviation of individual compounds from 0.2% to 9.6%. The PAHs distribution was not normal. The Inverse Gaussian, Birnbaum-Saunders, Lognormal, Gamma, and Weibull were the models that best described benzo(a)pyrene and PAH4 distribution. The fraction that was significantly less contaminated was stem. Also, there was significant difference between leaf and powder fractions, the latter being the one that presented higher PAHs concentration. This may be due to the products generated in the pyrolysis of wood, used in the drying process of “yerba mate.” If powder were removed, a reduction of ~3.5% of  $\sum$ PAHs and 6.5% of TEQ would be achieved. Although eliminating powder could be a strategy to reduce PAHs contamination, this would not be enough to diminish PAHs levels below the regulatory limits.

## ARTICLE HISTORY

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## KEYWORDS

Benzo(a)pyrene; *Ilex paraguariensis*; organic contaminants; PAH; polycyclic aromatic hydrocarbons; “yerba mate”

## Introduction

*Ilex paraguariensis*, commonly called “yerba mate” or “yerba” is native of the subtropical regions of Argentina, Brazil, Paraguay and Uruguay. Argentina is the leading producer worldwide, followed in importance by Brazil and Paraguay. Its use as an infusion has spread widely, and has been extended to many countries such as Syria, Lebanon, United States, Chile, Germany and Spain, among many others.<sup>1</sup>

According to the “Código Alimentario Argentino,” the law that rules food in Argentina, “yerba mate” is the product exclusively formed by the dried, lightly toasted and crumbled *I. paraguariensis* (Aquifoliaceae) leaves, mixed or not with fragments of young dry twigs, petioles and flower stems, commonly known as stem. As for the traditional category, not less than 65% must correspond to dried, broken or powdered leaves and not more than 35% has to be gross and finely crushed stem, chips and fibers, setting the mesh size that must be used to separate those fractions.<sup>2</sup> Argentinian legislation also determines the suitable proportion of each fraction according to the different commercialized varieties, being “yerba mate” denominated “low powder content” one of the most appreciated by consumers.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants generated primarily during the incomplete combustion of organic materials (e.g. coal, oil, petrol and wood). This group is conformed of several hundreds of chemically related compounds that are environmentally persistent, with various structures and varied toxicity.<sup>3</sup> Some studies prove PAHs contamination in “yerba mate.” For example, Vieira et al.<sup>4</sup> determined the contamination in three samples of “yerba mate” from different producers at Catanduvas, in the State of Santa Catarina, Brazil. Camargo and Toledo,<sup>5</sup> Kamangar et al.<sup>6</sup> and Zuin et al.<sup>7</sup> analyzed PAHs concentration of 9, 8 and 11 commercial samples of Brazilian “yerba mate,” respectively. Ziegenhals, Jira and Speer<sup>8</sup> studied the contamination of eight samples bought in the German market. The only study carried out in Argentina was reported by García Londoño, Reynoso and Resnik<sup>9</sup> in which new methodology was developed, based on solid phase extraction and high resolution liquid chromatography, in order to quantify PAHs occurrence in a total of 50 samples of “yerba mate” in the Buenos Aires city market.

Through “yerba mate” production, when the drying process occurs, the fumes from the wood or wood chips combustion are in direct contact with raw material, strongly increasing PAHs contamination, as in the case of tea elaboration.<sup>10–13</sup>

The Agency of environmental protection of the United States of America (USEPA) has mentioned the 16 PAHs studied in this work as in priority pollutant lists.<sup>14</sup>

The European Commission Regulation 2015/1933<sup>15</sup> maximum values for dried herbs are 10 and 50  $\mu\text{g kg}^{-1}$  expressed as Benzo(a)pyrene (BaP) and PAH4 (sum of Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene and BaP), respectively.

Given the different toxicity of each PAH, several methods were reported in order to explain global toxicity of a contaminated sample. The total toxic equivalent (TEQ) indicates the total toxicity of a sample, attributable to several substances, expressed as equivalent of a particular compound. This corresponds to the sum of each PAH concentration multiplied by their respective toxic equivalent factor (TEF). In this case, the TEQ is expressed in equivalents of BaP.

The aim of this study was to evaluate PAHs contamination levels, distribution and TEQ in different mesh size fractions of “yerba mate” commercial samples.

## Materials and methods

### Chemicals

#### Analytical standards of PAHs

Acenaphthene (ACE), acenaphthylene (ACY), anthracene (AN), benzo(a)anthracene (BaA), BaP, benzo(b)fluoranthene (Bbf), benzo(g,h,i)perylene (BPe), dibenzo(a,h)anthracene (dBAn), fluoranthene (FLUR) were purchased from Accustandard (New Haven, CT, United States), benzo(k)fluoranthene (Bkf), chrysene (Chry), indeno(1,2,3cd)pyrene (IcdP) from Supelco Analytical (Bellefonte, PA, United States), 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 used for accuracy was a PAH Calibration MIX of Supelco (No. 47940 U, United States) with concentrations of ACE  $9.03 \pm 0.022 \mu\text{g ml}^{-1}$ , ACY  $9.96 \pm 0.008 \mu\text{g ml}^{-1}$ , AN  $10.00 \pm 0.019 \mu\text{g ml}^{-1}$ , BaA  $10.02 \pm 0.015 \mu\text{g ml}^{-1}$ , BaP  $11.04 \pm 0.008 \mu\text{g ml}^{-1}$ , Bbf  $9.98 \pm 0.005 \mu\text{g ml}^{-1}$ , BPe  $10.07 \pm 0.005 \mu\text{g ml}^{-1}$ , Bkf  $9.95 \pm 0.018 \mu\text{g ml}^{-1}$ , Chry  $10.20 \pm 0.013 \mu\text{g ml}^{-1}$ , dBAn  $9.96 \pm 0.026 \mu\text{g ml}^{-1}$ , FLUR  $9.95 \pm 0.026 \mu\text{g ml}^{-1}$ , FL  $9.99 \pm 0.007 \mu\text{g ml}^{-1}$ , IcdP  $9.66 \pm 0.011 \mu\text{g ml}^{-1}$ , NA  $10.06 \pm 0.013 \mu\text{g ml}^{-1}$ , PHEN  $9.95 \pm 0.011 \mu\text{g ml}^{-1}$  and PY  $9.98 \pm 0.013 \mu\text{g ml}^{-1}$ .

### Solvents

Acetonitrile (Tedia, Fairfield, OH, United States) and n-Hexane (Carlo Erba, Milan, Italy) were High performance liquid chromatography (HPLC) grade. The water for all the procedures was

distilled in a 6 L capacity distiller, model number 0716 (Rolco, Buenos Aires, Argentina) and purified through Nano pure Diamond purification system, D11911 (Barnstead International, Dubuque, IA, United States).

### **Samples**

Ten commercial samples of traditional “yerba mate” from different trade marks were analyzed. The sampling was performed according to the European Commission Regulations No 836/2011,<sup>16</sup> that establishes the number of packages or units (incremental samples) to form the aggregate sample.

Samples were entirely sieved using three screen sizes, getting four fractions A to D, being A: stem (Zonytest Agrícola, 1.75 mm), B: small stem – big leaf (mesh 14 A.S.T.M, 1.410 mm), C: leaf (mesh 40 A.S.T.M, 425  $\mu\text{m}$ ) and D: powder (<425  $\mu\text{m}$ ). The sieving process was performed hermetically in order to lose the least amount of dust as possible. Once finished, each fraction was entirely grinded (Moulinex, model 215, Argentina), obtaining a particle size of 425  $\mu\text{m}$  at most (40 A.S.T.M mesh size), and then, its content of PAHs was determined. The analysis of the samples was performed by triplicate.

### **Methodology for the determination of PAHs**

#### **Extraction and clean-up of PAHs from “yerba mate” fractions**

The extraction and clean-up for PAHs determination was performed using the procedure reported by García Londoño, Reynoso, and Resnik.<sup>17</sup>

#### **HPLC – DAD/flid**

HPLC equipment composed of a separation module Waters Alliance 2695 (Singapore), UV-VIS diodes array detector (DAD) Waters 2698 (United States) and fluorescence detector (FLD) Waters 2475 (United States) was utilized. The analytical column used was Waters PAH C18, 5  $\mu\text{m}$  of particle size, 4.6 mm of inner diameter and 250 mm of length (Waters, Code No. 86001265, Germany) fitted with a guard column Spherisorb S50DS2 of 1 cm (Code No. PSS830053, Waters, United States). The column temperature was set at 30 °C. The injection volume was 50  $\mu\text{l}$ . The binary mobile phase consisted of acetonitrile (solvent A) and water (solvent B), and a gradient program was optimized as follows: non-linear gradient (curve 9) from 40% to 10% B in 12 min, 10% isocratic B during 17 min, linear gradient from 10% to 40% B in 5 min. Then, post-run time was set up for 6 min to equilibrate the system. The flow rate was 1.2 ml  $\text{min}^{-1}$ . The FLD and DAD conditions were the same as reported by García Londoño, Reynoso and Resnik.<sup>18</sup>

### **Data analysis**

For TEQ calculation, TEFs reported by Nisbet and LaGoy (1992) were used and the following equation (1) was applied:

$$\text{TEQ} = \sum (C_{\text{PAHi}} \times \text{TEF}_{\text{PAHi}}) \quad (1)$$

TEQ of a mixture is defined by the sum of the concentrations of individual compounds ( $C_{\text{PAHi}}$ ) multiplied by their relative toxicity ( $\text{TEF}_{\text{PAHi}}$ ). Shapiro-Wilks normality test was applied and graphics of normal probability (“rankit”) were evaluated, as well as the homoscedasticity, using the F-test when the analysis involved two data groups, or the Levene test for 3 or more groups. The median values were evaluated by Mann-Whitney (Wilcoxon) W-test (significance

level  $\alpha=0.05$ ) using Statgraphics Centurion XVI Software (Statpoint Technologies Inc., Warrenton, Virginia, USA).

In order to evaluate the distribution of BaP, Chry, BaA, Bbf, PAH2 (Sum of BaP and Chry), PAH4, PAH8 (Sum of BaP, Chry, BaA, Bbf, Bkf, BPe, dBA<sub>n</sub> and IcdP),  $\sum$ PAHs and TEQ in the different fractions, fourteen distribution curves were assessed: Birnbaum-Saunders, Exponential, Gamma, Inverse Gaussian, Laplace, Largest Extreme Value, Logistic, Loglogistic, Lognormal, Normal, Pareto, Smallest Extreme Value, Uniform and Weibull. Log-likelihood value was determined and then the Kolmogorov-Smirnov test was applied to determine the goodness of fit.

## Results and discussion

### Analytical quality assurance

Calibration curves for all analyzed PAHs were obtained using a series of standard solutions obtaining correlation coefficients higher than 0.998. The linearity of all calibration curves was present in three or more orders of magnitude. The detection limit (LOD) and the quantification limit (LOQ) were calculated as signal to noise ratio 3 or 10, respectively (Table 1). LOD and LOQ values for BaP, BaA, Bbf and Chry were lower than 0.30 and 0.90  $\mu\text{g kg}^{-1}$ , respectively, complying with the performance criteria of the European Commission Regulations 836/2011.<sup>19</sup> Samples were spiked with individual PAHs at three levels (0.12, 13.49 and 53.06  $\mu\text{g kg}^{-1}$ ) by triplicate (Table 1). The recovery percentages were higher than 84.5% for all tested PAHs in different fractions. The standard relative recovery deviations (RSD) ranged from 0.2% to 9.6%. Due to the lack of certified material for PAHs in “yerba mate”<sup>20</sup> the accuracy of the developed analytical method was verified also through a reference solution. A standard reference solution was daily quantified by triplicate during HPLC analysis. A blank prepared following the entire analytical procedure and using the same reagents and solvents as used with samples, was periodically analyzed. The precision of the proposed method was assessed by intra-day ( $\text{RSD}_r$ ) and inter-day ( $\text{RSD}_R$ ) determinations. For intra-day studies, each PAH concentration was studied by performing three repeated measurements, three different times during a working day.  $\text{RSD}_r$  values ranged from 0.2% to 25.5% (Table 1).

**Table 1.** Performance characteristics of the PAHs analytical method.

PAH	LOD ( $\mu\text{g kg}^{-1}$ )	LOQ ( $\mu\text{g kg}^{-1}$ )	Average recovery ( $n=3$ )			RSD, range			
			(%)			(%)			
			0.12 $\mu\text{g kg}^{-1}$	13.49 $\mu\text{g kg}^{-1}$	53.06 $\mu\text{g kg}^{-1}$	A	B	C	D
NA	0.12	0.40	nq	90.9	94.2	5.3–24.3	2.7–15.8	5.4–22.3	2.1–22.3
ACY	0.74	2.47	nq	91.1	85.1	nd	nd	nd	nd
ACE	0.09	0.30	nq	84.8	87.9	0.2–23.2	9.1–23.2	11.9–25.5	8.7–10.0
FL	0.02	0.08	84.3	88.1	100.2	8.3–15.8	3.0–18.3	4.5–12.6	2.8–16.6
PHEN	0.02	0.08	87.2	96.2	97.5	1.0–25.0	2.3–20.4	2.1–19.9	0.7–11.2
AN	0.01	0.03	89.1	89.5	85.2	3.1–19.0	1.0–24.4	4.3–25.4	0.6–16.8
FLUR	0.04	0.14	nq	103.2	105.6	2.2–12.6	2.0–22.3	0.8–21.7	0.6–9.2
PY	0.01	0.04	84.5	93.6	99.4	2.8–17.1	2.4–23.2	0.3–20.4	1.2–9.0
BaA	0.02	0.06	89.5	90.2	87.3	0.2–23.2	5.0–21.7	1.2–23.3	1.8–16.4
Chry	0.04	0.13	nq	98.4	87.2	4.7–18.7	0.7–22.9	1.4–22.7	1.1–8.4
Bbf	0.08	0.27	nq	88.4	105.0	2.4–21.5	2.6–21.6	2.5–22.0	0.7–10.3
Bkf	0.01	0.03	95.0	93.1	99.2	2.8–23.6	3.4–19.5	1.4–20.1	1.8–10.7
BaP	0.01	0.02	96.7	98.3	93.0	3.1–20.8	3.0–22.4	1.7–23.3	1.6–10.9
dBA <sub>n</sub>	0.02	0.06	91.4	95.1	93.9	9.9–16.6	2.4–17.7	4.1–16.2	0.2–13.6
BPe	0.03	0.12	94.4	98.2	98.3	1.5–20.6	3.1–23.4	1.9–23.7	3.4–17.4
IcdP	0.08	0.27	nq	99.9	96.7	0.2–25.5	4.2–23.4	3.7–23.6	0.2–23.6

nq: not quantifiable; nd: not detected.

### PAHs levels in ‘yerba mate’ fractions

The contamination values of PAHs (median, minimum and maximum) of the different fractions are presented in Table 2. Regarding BaP and PAH4, all fractions except A (stem) exceed the UE limits. These results are in agreement to those obtained by Vieira et al.,<sup>21</sup> Kamangar et al.,<sup>22</sup> Zuin et al.<sup>23</sup> and Ziegenhals, Jira and Speer<sup>24</sup> in whole ‘yerba mate’ samples.

No significant differences (Kruskal–Wallis,  $\alpha=0.05$ ,  $P$ -values  $> 0.05$ ) were found for NA concentration. However, for all the other PAHs, fraction A was the less contaminated. Also, contamination expressed as PAH4 and  $\sum$ PAHs of A fraction presented significant differences with the other evaluated fractions. This indicates that global contamination of stems (A) is significantly lower than the other fractions.

As can be seen in Figure 1, PAHs contamination varies among the fractions, according to the number of benzene rings.

The A fraction had higher proportion of the more volatile PAHs, of two and three benzene rings (generally regarded as the less toxic PAHs). Fractions B, C and D present similar amount of volatile PAHs, however, fraction D (powder) was the fraction that presented greater contamination of PAHs of 4, 5 and 6 rings (generally regarded as more toxic). The powder present in the yerba mate corresponds to the ground leaf to an impalpable point. However, due to the drying conditions during ‘yerba mate’ elaboration process, a portion of the products generated in the pyrolysis of wood or woodchips, would settle with powder.

### Total toxic equivalent

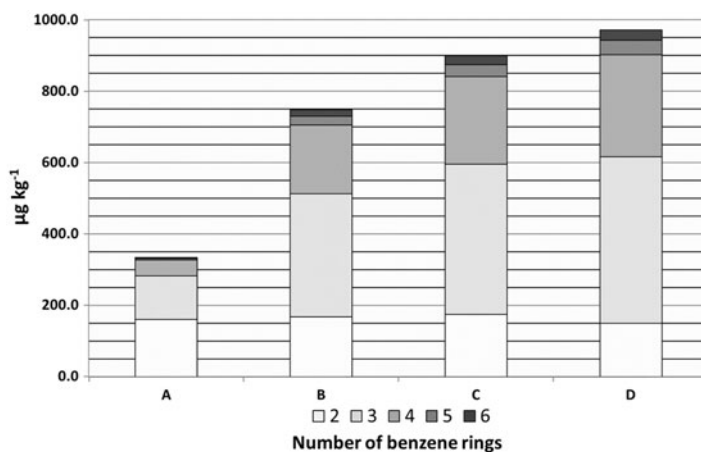
In agreement with the contamination results, A fraction presented significantly low TEQ levels and D was the fraction that showed highest TEQ, comparing with the other fractions, as can be seen in Figure 2.

If powder were removed, a reduction of approximate 3.5% of  $\sum$ PAHs would be achieved. At the same time, TEQ would be reduced by more than 6.5%. Moreover, if the powder were replaced by stem in the same proportion, a reduction of approximate 10% of  $\sum$ PAHs and 15%

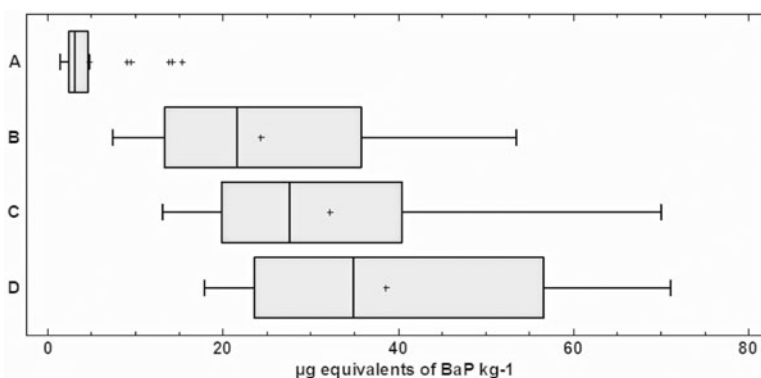
**Table 2.** PAHs contamination (median, minimum and maximum) of the different fractions ( $\mu\text{g kg}^{-1}$ ).

PAH	Fraction ( $\mu\text{g kg}^{-1}$ )											
	A			B			C			D		
	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max
NA	98.1	44.1	528.6	66.8	40.4	595.9	92.0	63.5	549.6	79.9	29.5	360.7
ACY	nd				nd			nd			nd	
ACE	0.1	<LOD	0.9	0.2	<LOD	0.4	0.1	<LOD	0.6	0.2	<LOD	0.8
FL	1.6	1.0	7.2	2.0	0.9	10.7	2.8	1.2	9.8	2.4	1.1	10.4
PHEN	79.7	57.7	171.4	205.3	136.3	519.0	259.6	184.1	616.8	281.0	187.7	636.0
AN	1.5	0.8	7.3	8.4	3.4	34.0	11.5	5.4	42.4	13.4	7.2	48.9
FLUR	18.8	12.2	57.0	83.3	50.6	220.0	112.2	69.4	271.2	128.0	73.1	283.1
PY	22.1	15.9	69.6	95.5	60.2	255.5	127.7	86.1	307.4	144.9	85.1	312.1
BaA	0.8	<LOD	7.8	14.1	6.2	40.8	20.4	10.3	49.0	25.8	13.1	52.4
Chry	6.3	4.3	24.0	34.8	18.9	64.4	47.1	29.2	75.0	56.2	36.5	84.3
Bbf	1.9	0.9	8.0	12.3	5.8	25.4	16.5	9.0	32.4	19.8	11.4	34.2
Bkf	0.7	0.4	3.0	4.3	2.2	10.4	6.0	3.5	13.5	7.2	4.3	14.3
BaP	1.4	0.3	8.0	12.4	4.4	29.8	17.4	7.2	37.5	21.0	9.6	41.4
dBan	0.1	0.1	0.5	0.4	0.1	1.3	0.7	0.2	1.5	0.7	0.3	1.9
lcdP	1.3	0.3	4.4	8.7	2.3	21.6	12.8	4.3	27.2	15.7	5.7	32.1
BPe	1.7	<LOD	9.2	15.5	4.5	35.7	22.7	7.3	45.8	26.6	9.3	50.3
PAH4	10.3	3.6	50.3	73.8	29.7	176.2	94.8	51.5	213.9	121.4	69.8	209.8
$\sum$ PAHs	214.9	132.9	931.1	672.4	305.5	1583.2	805.4	471.3	1833.1	906.9	484.1	1758.7

n.d.: not detected.



**Figure 1.** PAHs contamination in fractions A to D discriminated as a function of the number of benzene rings.



**Figure 2.** Box and Whisker plots for TEQ in the different fractions.

TEQ would be obtained, since the percentage of PAHs from 4 and 5 benzene rings in the A fraction (stem) is significantly less than in D (powder).

This strategy would be applicable since some consumers prefer “yerba mate” with low powder content. Currently, there are in Argentinian market different brands with the low powder content denomination, which according to the “Código Alimentario Argentino,” should not exceed 10% powder content (fraction  $<425\ \mu\text{m}$ ).

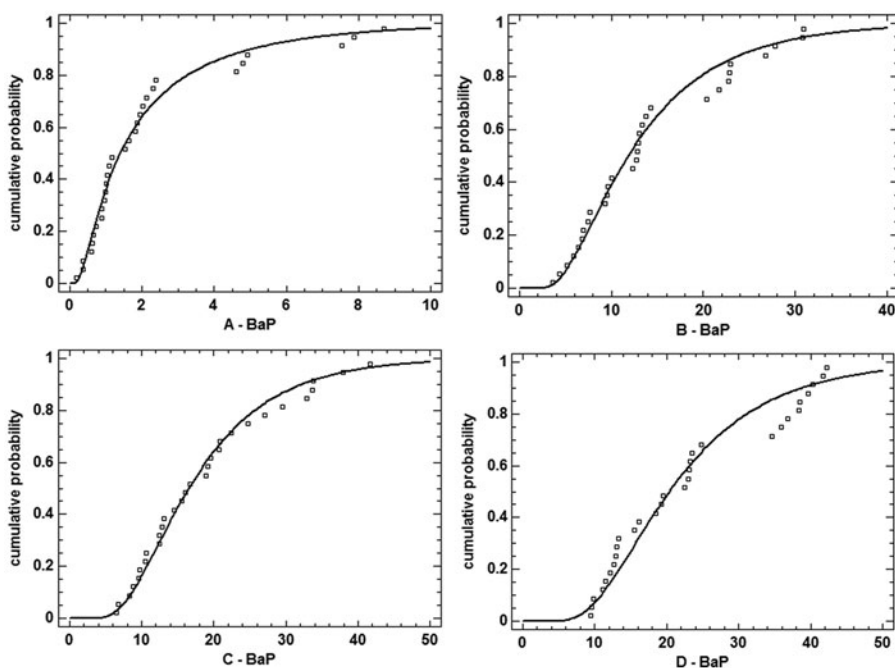
### **PAHs distribution in “yerba mate” fractions**

The distribution of the contamination of BaP, Chry, BaA, BbF, PAH2 and PAH4, PAH8 and  $\sum\text{PAHs}$  in the analyzed samples fractions, did not fit a normal distribution (Shapiro-Wilk,  $\alpha = 0,05$ ,  $P$ -values  $< 0.05$ ). This behavior coincides with other food contaminants, such as mycotoxins.<sup>25</sup> In those cases, distributions commonly used have been the negative binomial, the lognormal and the exponential, in low pollution samples.

The log-likelihood determines the goodness of the adjustment of the data to different distributions, higher value indicating a better fit (Table 3). There are different types of distributions that fit contamination data. In the case of the BaP and PAH4, distribution curves, which presented the best fit were the Inverse Gaussian, Birnbaum-Saunders, Lognormal, Gamma and Weibull. As an example, Figure 3 presents cumulative probability versus quartiles for BaP in the different fractions and the Inverse Gaussian distribution curve adjustment.

**Table 3.** Log-likelihood values for distributions that best fitted PAHs contamination in the different fractions.

Fraction	Distribution	BaP	Chry	BaA	Bbf	PAH2	PAH4	PAH8	$\Sigma$ PAHs
A	Birnbaum-Saunders	-51.52	-84.76	-48.96	-49.90	-92.64	-104.17	-113.35	-194.43
	Gamma	-53.80	-87.62	-70.27	-53.15	-95.88	-107.82	-116.95	-197.18
	Inverse Gaussian	-51.58	-85.04	-61.66	-50.01	-92.82	-104.45	-113.44	-194.67
	Largest Extreme Value	-54.19	-87.97	-71.31	-53.88	-96.70	-109.50	-118.61	-198.04
	Loglogistic	-54.44	-89.76	-77.94	-55.18	-97.88	-109.51	-118.70	-198.98
	Lognormal	-52.15	-85.10	-66.26	-50.37	-93.00	-104.63	-113.81	-195.80
	Weibull	-58.72	-91.16	not fit	-56.45	-99.67	-111.94	-121.12	-200.47
B	Birnbaum-Saunders	-99.16	-121.09	-105.06	-91.99	-133.17	-148.51	-160.40	-214.59
	Gamma	-101.32	-121.27	-106.15	-94.53	-133.70	-149.09	-160.93	-216.96
	Inverse Gaussian	-100.82	-121.11	-105.07	-94.14	-133.44	-148.53	-160.44	-215.78
	Largest Extreme Value	-101.91	-121.52	-106.75	-94.77	-133.80	-149.48	-161.02	-217.30
	Loglogistic	-102.15	-121.86	-107.43	-95.39	-134.37	-149.72	-161.31	-217.45
	Lognormal	-101.18	-121.23	-106.02	-94.38	-133.60	-148.98	-160.80	-216.16
	Weibull	-102.20	-122.24	-109.86	-95.39	-134.64	-150.09	-161.76	-218.22
C	Birnbaum-Saunders	-106.52	-120.22	-111.15	-98.91	-135.05	-152.16	-164.67	-216.50
	Gamma	-107.16	-122.07	-111.90	-99.59	-136.34	-152.69	-165.18	-217.73
	Inverse Gaussian	-106.55	-121.94	-111.16	-98.92	-136.08	-152.17	-164.68	-216.89
	Largest Extreme Value	-107.60	-122.25	-112.00	-100.00	-136.52	-152.79	-165.27	-218.17
	Loglogistic	-107.90	-122.88	-113.20	-100.00	-137.13	-153.22	-165.67	-218.24
	Lognormal	-106.82	-122.03	-111.84	-99.36	-136.21	-152.58	-165.16	-217.14
	Weibull	-108.07	-123.67	-114.47	-101.14	-137.89	-154.33	-166.66	-220.29
D	Birnbaum-Saunders	-104.73	-119.27	-111.56	-96.08	-132.77	-148.25	-162.18	-214.51
	Gamma	-112.45	-127.00	-116.24	-103.91	-141.45	-157.07	-169.48	-218.94
	Inverse Gaussian	-111.79	-126.81	-115.94	-103.52	-141.12	-156.70	-169.07	-218.29
	Largest Extreme Value	-113.04	-127.13	-116.64	-104.08	-141.56	-157.19	-169.65	-218.95
	Loglogistic	-113.05	-127.57	-116.83	-104.60	-142.08	-157.78	-170.22	-220.01
	Lognormal	-112.20	-126.97	-116.23	-103.77	-141.34	-156.93	-169.31	-218.54
	Weibull	-113.71	-127.81	-117.47	-105.22	-142.69	-158.35	-170.67	-220.09

**Figure 3.** Cumulative probability versus quantiles for BaP in the different fractions and the Inverse Gaussian distribution curve.



## Conclusions

The fraction that presented significantly lower levels of contamination was stem. There was significant difference between leaf and powder, the latter being the most contaminated fraction. Apparently, the pyrolysis products generated in the drying process of “yerba mate” are mostly incorporated in this fraction. Eliminating powder could be a strategy to reduce PAHs contamination, regarding the consumers acceptance of the low powder category. Although, this would not be enough to diminish PAHs levels below the regulatory limits. Control and innovation of drying procedures seem more accurate for this purpose.

The PAHs concentrations in the different fractions did not fit normal distribution. BaP and PAH4 contamination best fitted the Inverse Gaussian, Birnbaum-Saunders, Lognormal, Gamma and Weibull models. This information would be useful to design accurate sampling plans.

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## References

1. SAGPyA, “Informe de Coyuntura Cadena Infusiones: YERBA MATE (erva mate, maté),” 2010. [http://www.minagri.gov.ar/SAGPyA/economias\\_regionales/index.php](http://www.minagri.gov.ar/SAGPyA/economias_regionales/index.php) (accessed March 29, 2017).
2. ANMAT, “Administración Nacional de Medicamentos, Alimentos y Tecnología Médica. Capítulo XV - Productos estimulantes o frutivos,” *Código Alimentario Argentino* 15 (2018): 1193–5.
3. H. I. Abdel-Shafy and Mona S. M. Mansour, “A Review on Polycyclic Aromatic Hydrocarbons: Source, Environmental Impact, Effect on Human Health and Remediation,” *Egyptian Journal of Petroleum* 25, no. 1 (2016): 107–23.
4. Manoela Alano Vieira, Marcelo Maraschin, Ângela Angeloni Rovaris, Renata Dias de Mello Castanho Amboni, Cristiane Manfê Pagliosa, José Júnior Mendonça Xavier, and Edna Regina Amante, “Occurrence of Polycyclic Aromatic Hydrocarbons Throughout the Processing Stages of Erva-Mate (*Ilex paraguariensis*),” *Food Additives & Contaminants: Part A* 27, no. 6 (2010): 776–82.
5. Mônica Cristiane Rojo de Camargo and Maria Cecília Figueiredo Toledo, “Chá-mate e café como fontes de hidrocarbonetos policíclicos aromáticos (HPAs) na dieta da população de Campinas,” *Ciência e Tecnologia de Alimentos* 22 (2002): 49–53.
6. Farin Kamangar, Michele M. Schantz, Christian C. Abnet, Renato B. Fagundes, and Sanford M. Dawsey, “High Levels of Carcinogenic Polycyclic Aromatic Hydrocarbons in Mate Drinks,” *Cancer Epidemiology Biomarkers and Prevention* 17, no. 5 (2008): 1262–8.
7. Zuin Vânia Gomes, Larisse Montero, Coretta Bauer, and Peter Popp, “Stir Bar Sorptive Extraction and High-Performance Liquid Chromatography-Fluorescence Detection for the Determination of Polycyclic Aromatic Hydrocarbons in Mate Teas,” *Journal of Chromatography A* 1091, no. 1–2 (2005): 2–10.
8. Katja Ziegenhals, Wolfgang Jira, and Karl Speer, “Polycyclic Aromatic Hydrocarbons (PAH) in Various Types of Tea,” *European Food Research and Technology* 228, no. 1 (2008): 83–91.
9. Victor Alonso García Londoño, Marcela Reynoso, and Silvia Resnik, “Polycyclic Aromatic Hydrocarbons (PAHs) in yerba mate (*Ilex paraguariensis*) from the Argentinean Market,” *Food Additives & Contaminants: Part B* 7, no. 4 (2014): 247–53.
10. Daohui Lin, Youying Tu, and Lizhong Zhu, “Concentrations and Health Risk of Polycyclic Aromatic Hydrocarbons in Tea,” *Food and Chemical Toxicology* 43, no. 1 (2005): 41–8.
11. Daohui Lin and Lizhong Zhu, “Polycyclic Aromatic Hydrocarbons: Pollution and Source Analysis of a Black Tea,” *Journal of Agricultural and Food Chemistry* 52, no. 26 (2004): 8268–71.
12. L. Duedahl-Olesen, M. A. Navaratnam, J. Jewula, and A. H. Jensen, “PAH in Some Brands of Tea and Coffee,” *Polycyclic Aromatic Compounds* 35, no. 1 (2015): 74–90.
13. Omowunmi H. Fred-Ahmadu and Nsikak U. Benson, “Polycyclic Aromatic Hydrocarbons (PAHs) Occurrence and Toxicity in *Camellia sinensis* and Herbal Tea,” *Polycyclic Aromatic Compounds* (2017): 1–11.
14. Zuzana Zelinkova and Thomas Wenzl, “The Occurrence of 16 EPA PAHs in Food – A Review,” *Polycyclic Aromatic Compounds* 35, no. 2–4 (2015): 248–84.

15. European Commission, "Commission Regulation (EU) 2015/1933 of 27 October 2015 Amending Regulation (EC) No 1881/2006 as Regards Maximum Levels for Polycyclic Aromatic Hydrocarbons in Cocoa Fibre, Banana Chips, Food Supplements, Dried Herbs and Dried Spices," *Official Journal of the European Union L* 282 (2015): 11–3.
16. European Commission, "Commission Regulation (EU) No 836/2011 of 19 August 2011 amending Regulation (EC) No 333/2007 Laying Down the Methods of Sampling and Analysis for the Official Control of the Levels of Lead, Cadmium, Mercury, Inorganic Tin, 3-MCPD and Benzo(a)pyrene in Foodstuffs," *Official Journal of the European Union L* 215 (2011): 9–16.
17. García Londoño et al., "Polycyclic Aromatic Hydrocarbons (PAHs) in yerba mate (*Ilex paraguariensis*)," 247–53.
18. Ibid.
19. European Commission, "Commission Regulation (EU) No 836/2011 of 19 August 2011 amending Regulation (EC) No 333/2007," 9–16.
20. Donata Lerda "Polycyclic aromatic hydrocarbons (PAH) Factsheet," 2011. [https://ec.europa.eu/jrc/sites/jrcsh/files/Factsheet%20PAH\\_0.pdf](https://ec.europa.eu/jrc/sites/jrcsh/files/Factsheet%20PAH_0.pdf).
21. Vieira et al., "Occurrence of Polycyclic Aromatic Hydrocarbons," 776–82.
22. Kamangar et al., "High Levels of Carcinogenic Polycyclic Aromatic Hydrocarbons," 1262–8.
23. Gomes et al., "Stir Bar Sorptive Extraction and High-Performance Liquid Chromatography," 2–10.
24. Ziegenhals et al., "Polycyclic Aromatic Hydrocarbons (PAH) in Various Types of Tea," 83–91.
25. T. Whitaker, A. Slate, J. Adams, T. Birmingham, and F. Giesbrecht, "Comparing the Performance of Sampling Plans That Use a Single Regulatory Limit Based upon Total Aflatoxins to Sampling Plans That Use Dual Limits Based upon B1 and Total Aflatoxins," *World Mycotoxin Journal* 3, no. 1 (2010): 35–44.