

<https://doi.org/10.5016/1984-5529.2024.v52.1434>

## Chemical composition and seasonal variations in açai as it is consumed in the Brazilian Amazon

### Composição química e variações sazonais do açai na forma em que é consumido na Amazônia brasileira

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Recebido em: 20-09-2022; Aceito em: 07-11-2023

#### Abstract

The fruit of the açai palm, a native Amazon species, has received global attention due to its composition, which is rich in antioxidants. However, since ancient times, açai has been considered a staple food for the local population, where it is abundant. From rural and riverine populations to large urban centers in the Amazon, freshly extracted açai pulp is sold and consumed daily, making up a broad market. There are many scientific studies related to the nutritional and functional aspects of açai, but just a few related to this direct (artisanal) consumption. Thus, this research aimed to assess the characteristics of açai from points of sale in the city of Belém, PA, Brazil, during the season and off-season of the fruit over three years. The results indicated that açai is a low-acidity food with lipids as the predominant macronutrient in its composition. Although the variations in results were not significant according to Kruskal-Wallis statistical test, principal component analysis showed variations between season and off-season, among establishments, and among the years of the study. Although açai consumed during its season has relatively higher nutrient contents, particularly of bioactive compounds, artisanal açai consumed in the off-season may still be considered a valuable food for antioxidant compounds, thus enriching the regional diet.

**Additional keywords:** bioactive compounds; *Euterpe oleracea*; local processing; nutrition.

## Resumo

O fruto do açazeiro, espécie nativa da Amazônia, ganhou destaque no mundo em função de sua composição rica em antioxidantes. Entretanto, desde os tempos mais remotos, o açaí é considerado um alimento base para a população local, onde é encontrado em abundância. Desde populações rurais e ribeirinhas até os grandes centros urbanos da Amazônia, a polpa de açaí recém-extraída é comercializada e consumida diariamente, sendo um amplo mercado. Muitos estudos científicos sobre os aspectos nutricionais e funcionais existem sobre o açaí, mas poucos relacionados a esse alimento de consumo direto (artesanal). Dessa forma, o objetivo desse trabalho foi avaliar essas características no açaí proveniente de pontos comerciais situados na cidade de Belém-PA, durante a safra e entressafra do fruto, ao longo de três anos. Os resultados indicaram que o açaí é um alimento de baixa acidez com lipídios como macronutriente predominante em sua composição. Embora as variações dos resultados não tenham sido significativas pelo teste estatístico Kruskal-Wallis, a análise de componentes principais mostrou variações entre safra e entressafra, entre estabelecimentos, e entre os anos estudados. Embora o açaí consumido na safra apresente teores de nutrientes relativamente maiores, principalmente de compostos bioativos, o açaí artesanal na entressafra ainda pode ser considerado um valioso alimento para compostos antioxidantes, enriquecendo a dieta regional.

**Palavras-chave adicionais:** compostos bioativos; *Euterpe oleracea*; processamento local; nutrição.

## Introduction

The açai palm is native to the Brazilian Amazon region and, since the fruit raised interest worldwide for its chemical composition, rich in bioactive compounds, many scientific studies have been carried out to detect and quantify such compounds in pulps of different origins. Studies have shown significant variations in composition and many factors may be attributed to that, from high genetic variability (Torma et al., 2017) to different ways of processing the fruits, which requires adding water to obtain the pulp. Different commercial pulps, açai-based products, as well as its lyophilized form, have been widely studied for their composition and reported in the literature (Yamaguchi et al., 2015).

However, all those studies completely differ from artisanal açai in regions from where the fruit is native. Freshly harvested in the early morning, it is processed in small establishments, popularly known as açai beaters. After processing, the açai is immediately sold for direct consumption of the local population.

The Brazilian state of Pará is the largest açai producer, with 1,330,598 tons in 2019 according to the systematic survey of agricultural production (CONAB, 2019). Indeed, besides being a staple food of rural families in the Amazon estuary, açai has always been considered part of a regional identity and a source of income to many (Pepper & Alves, 2015). Santos et al. (2014), when studying the productive chain of açai, highlighted the importance of artisanal processors, who uphold a cultural role with their consumers and supply the Amazon population as part of a tradition and basic dietary source.

Despite the importance in the diet and culture of that population, where most people in both riverine communities and large urban centers in the Amazon consume açai daily, little is known about the composition of the product obtained in artisanal production. Furthermore, no studies have quantified changes in composition, both in nutritional and functional terms, between the season and off-season of the fruit over consecutive years.

Although the state of Pará is the largest açai producer during the off-season, Belém market is partially supplied by açai from other municipalities, whose productions focus opposite periods to the season in other locations in Pará. The transportation of açai to Belém is often done improperly, with poor storage conditions, exposure to heat and humidity, cross-contamination, etc. It travels long distances and, as a result, the processing is delayed. Thus, loss of bioactive compounds is expected as they may break down in face of transportation, storage, and processing conditions.

Since the nutritional and functional aspects of the açai artisanally processed in the Amazon are unknown, as are the variations in composition of this regional staple food, the present study aimed to assess

the açai sold at eight commercial establishments in the city of Belém, PA, Brazil for three consecutive years during the season and off-season of the fruit.

## Material and Methods

### Raw Material

The açai samples were purchased from eight commercial establishments from Belém and were transported and immediately frozen at  $-40\text{ }^{\circ}\text{C}$  (ultrafreezer model IULT 2430, Indrel Scientific, Brazil) for later lyophilization (lyophilizer model L101, Liobras, Brazil). All establishments complied with Decree no. 326 of January 24th, 2012 by Pará state government (PARÁ, 2012), which mandates, in addition to the fruit washing and sanitization steps, application of whitening, a thermal process that subjects açai berries to  $80\text{ }^{\circ}\text{C}$  for 10 s followed by a quick cooling prior to depulping in specific equipment. The berries were always collected from the same establishments during the season and off-season of 2015, 2016, and 2017. At the time of purchase, the establishments were asked to provide açai sold as medium type (11 to 14 % total solids).

### Nutritional Assessment and Bioactive Compounds

The pH value, total solids, ash, proteins and lipids were determined according to protocols by the Association of Official Analytical Chemists (AOAC, 2012). Total phenolic compounds were determined using the methodology described by Singleton & Rossi (1965) and modified by Georgé et al. (2005) using 70:30 acetone:water extract solution and Folin-Ciocalteu reagent with results expressed in mg of gallic acid equivalent (GAE)  $\text{kg}^{-1}$ . Monomeric anthocyanins were quantified using the differential pH method as described by Giusti & Wrolstad (2001) with results expressed in mg cyanidin 3-glucoside  $\text{kg}^{-1}$ . All analyses were carried out in triplicate for each establishment.

### Data Structure and Analysis

The results were submitted to Kolmogorov-Smirnov test to verify data normality. One-way ANOVA was used to check for differences among the datasets, with the application of Levene's test to assess homoscedasticity. Next, Kruskal-Wallis test was employed to identify where the differences among the data analyzed lie. The descriptive level (p-value) adopted in all tests was  $p \leq 0.05$ . The analyses were carried out using the software STATISTICA 12 (StatSoft). Also, the results were submitted to the MATLAB® R2016a software and the data were autoscaled, thus becoming non-dimensional, and analyzed using the unsupervised

pattern recognition method, principal component analysis (PCA). The calculations were carried out in the software PLS Toolbox 7.3.

## Results

Tables 1 and 2 show the results obtained in the analyses during the season and off-season over three years. The results, calculated in wet basis, exhibited normal data distribution except for the analyses of total solids, pH, and phenolic compounds. However, heterogeneity in variances was found for all analyses performed. Thus, the analysis by Kruskal-Wallis test was adequate to assess the differences among data at 5% probability. In addition, the presence of outliers in the dataset was assessed using Grubbs's test, which showed that the random variability is inherent to the data.

Unsupervised classification by PCA was applied to all data aiming at recognizing patterns or trends and identifying similarities and differences among the samples of the various establishments purchased at different times of distinct years.

For the exploratory analysis, three principal components (PCs) were selected that described 81.5 % of the total variance in the data (PC1 = 53.6 %, PC2 = 16.0 %, and PC3 = 11.8 %). The 3D score plot of PCA (Figure 1) shows a clear trend to separation between açai samples from the season and the off-season in the PC1 axis. Each point in Figure 1 represents an individual sample and was coded according to the year of purchase of the sample and time of harvest. Therefore, the açai samples were differentiated and categorized into two groups according to time of harvest: Group I (season açai) and Group II (off-season açai). Figure 1 also shows, in the PC3 axis (dashed ellipsis), a trend towards distinction of samples from 2015 (triangle) in relation to those from other years.

The best separation to distinguish Group I from Group II was observed in PC1. Hence, examining the variables responsible for the differentiation of groups in the PCA loading plot (Figure 2) shows that pH (negative loading) stands out, which indicates greater weight on the distinction between season and off-season açai. It is, therefore, deduced that the variable is positively correlated with Group II (not filled markers), i.e., it exhibits higher values for off-season açai samples, whereas the other variables, referring to the nutritional and functional value of the food, are positively correlated with Group I (filled markers), thus confirming the superior quality of season artisanal açai.

**Table 1.** Composition of medium type açai sold in Belém, PA, Brazil during the season and off-season over three years.

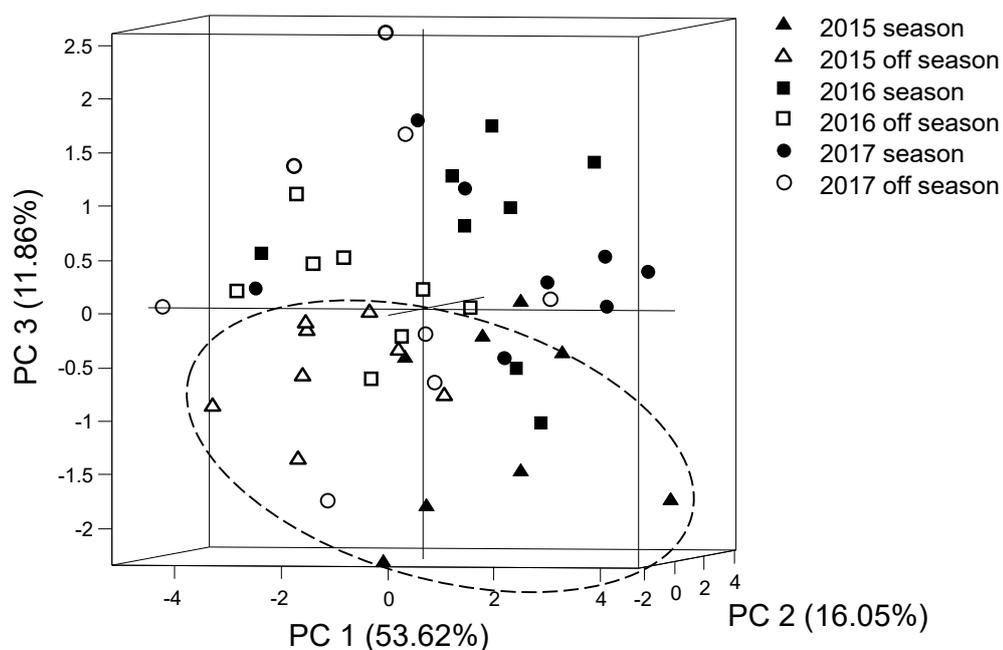
Est	pH		Total solids [%]		Proteins [%]		Lipids [%]		Ash [%]		Fibers [%]	
	S	OS	S	OS	S	OS	S	OS	S	OS	S	OS
2015												
A	4.58 <sup>aAB</sup>	5.11 <sup>aAB</sup>	18.6 <sup>aAB</sup>	12.8 <sup>aAB</sup>	1.6 <sup>aAB</sup>	1.2 <sup>aAB</sup>	9.3 <sup>aA</sup>	6.4 <sup>aAB</sup>	0.7 <sup>aAB</sup>	0.5 <sup>aAB</sup>	1.6 <sup>aAB</sup>	1.1 <sup>aAB</sup>
B	4.95 <sup>aAB</sup>	5.03 <sup>aAB</sup>	13.6 <sup>aAB</sup>	10.6 <sup>aAB</sup>	1.2 <sup>aAB</sup>	0.9 <sup>aAB</sup>	6.7 <sup>aAB</sup>	5.2 <sup>aAB</sup>	0.6 <sup>aAB</sup>	0.4 <sup>aAB</sup>	1.4 <sup>aAB</sup>	0.9 <sup>aB</sup>
C	4.68 <sup>aAB</sup>	4.94 <sup>aAB</sup>	17.11 <sup>aAB</sup>	14.9 <sup>aAB</sup>	1.6 <sup>aAB</sup>	1.3 <sup>aAB</sup>	7.6 <sup>aAB</sup>	7.3 <sup>aAB</sup>	0.7 <sup>aAB</sup>	0.6 <sup>aAB</sup>	1.9 <sup>aAB</sup>	1.4 <sup>aAB</sup>
D	4.69 <sup>aAB</sup>	4.77 <sup>aAB</sup>	16.6 <sup>aAB</sup>	13.7 <sup>aAB</sup>	1.4 <sup>aAB</sup>	1.2 <sup>aAB</sup>	7.9 <sup>aAB</sup>	6.1 <sup>aAB</sup>	0.7 <sup>aAB</sup>	0.4 <sup>aAB</sup>	1.6 <sup>aAB</sup>	1.2 <sup>aAB</sup>
E	4.60 <sup>aAB</sup>	4.99 <sup>aAB</sup>	14.6 <sup>aAB</sup>	14.6 <sup>aAB</sup>	1.3 <sup>aAB</sup>	1.3 <sup>aAB</sup>	7.5 <sup>aAB</sup>	6.9 <sup>aAB</sup>	0.6 <sup>aAB</sup>	0.7 <sup>aAB</sup>	1.0 <sup>aAB</sup>	1.4 <sup>aAB</sup>
F	4.72 <sup>aAB</sup>	4.94 <sup>aAB</sup>	17.7 <sup>aAB</sup>	13.8 <sup>aAB</sup>	1.5 <sup>aAB</sup>	1.2 <sup>aAB</sup>	8.6 <sup>aAB</sup>	6.8 <sup>aAB</sup>	0.7 <sup>aAB</sup>	0.5 <sup>aAB</sup>	1.9 <sup>aAB</sup>	1.5 <sup>aAB</sup>
G	5.00 <sup>aAB</sup>	5.12 <sup>aAB</sup>	18.1 <sup>aAB</sup>	14.8 <sup>aAB</sup>	1.5 <sup>aAB</sup>	1.4 <sup>aAB</sup>	8.8 <sup>aAB</sup>	7.9 <sup>aAB</sup>	0.8 <sup>aAB</sup>	0.5 <sup>aAB</sup>	1.7 <sup>aAB</sup>	1.2 <sup>aAB</sup>
H	4.69 <sup>aAB</sup>	5.07 <sup>aAB</sup>	14.8 <sup>aAB</sup>	11.9 <sup>aAB</sup>	1.5 <sup>aAB</sup>	1.2 <sup>aAB</sup>	7.1 <sup>aAB</sup>	5.9 <sup>aAB</sup>	0.6 <sup>aAB</sup>	0.5 <sup>aAB</sup>	1.3 <sup>aAB</sup>	1.0 <sup>aAB</sup>
2016												
A	5.07 <sup>aAB</sup>	4.88 <sup>aAB</sup>	18.9 <sup>aA</sup>	14.7 <sup>aAB</sup>	1.5 <sup>aAB</sup>	1.6 <sup>aAB</sup>	9.3 <sup>aAB</sup>	6.9 <sup>aAB</sup>	0.8 <sup>aA</sup>	0.5 <sup>aAB</sup>	1.9 <sup>aAB</sup>	1.7 <sup>aAB</sup>
B	5.01 <sup>aAB</sup>	5.10 <sup>aAB</sup>	11.4 <sup>aAB</sup>	13.1 <sup>aAB</sup>	0.9 <sup>aAB</sup>	1.4 <sup>aAB</sup>	5.2 <sup>aAB</sup>	5.8 <sup>aAB</sup>	0.5 <sup>aAB</sup>	0.5 <sup>aAB</sup>	1.3 <sup>aAB</sup>	1.7 <sup>aAB</sup>
C	5.13 <sup>aAB</sup>	4.89 <sup>aAB</sup>	17.1 <sup>aAB</sup>	16.1 <sup>aAB</sup>	1.3 <sup>aAB</sup>	1.5 <sup>aAB</sup>	7.7 <sup>aAB</sup>	7.8 <sup>aAB</sup>	0.7 <sup>aAB</sup>	0.5 <sup>aAB</sup>	2.0 <sup>aAB</sup>	1.8 <sup>aAB</sup>
D	5.01 <sup>aAB</sup>	4.94 <sup>aAB</sup>	16.7 <sup>aAB</sup>	12.9 <sup>aAB</sup>	1.4 <sup>aAB</sup>	1.2 <sup>aAB</sup>	8.1 <sup>aAB</sup>	4.6 <sup>aAB</sup>	0.7 <sup>aAB</sup>	0.4 <sup>aAB</sup>	1.9 <sup>aAB</sup>	1.5 <sup>aAB</sup>
E	4.83 <sup>aAB</sup>	5.14 <sup>aAB</sup>	16.4 <sup>aAB</sup>	12.9 <sup>aAB</sup>	1.4 <sup>aAB</sup>	1.3 <sup>aAB</sup>	8.5 <sup>aAB</sup>	5.8 <sup>aAB</sup>	0.7 <sup>aAB</sup>	0.6 <sup>aAB</sup>	1.4 <sup>aAB</sup>	1.4 <sup>aAB</sup>
F	5.00 <sup>aAB</sup>	4.84 <sup>aAB</sup>	17.0 <sup>aAB</sup>	15.6 <sup>aAB</sup>	1.3 <sup>aAB</sup>	1.5 <sup>aAB</sup>	8.7 <sup>aAB</sup>	7.2 <sup>aAB</sup>	0.6 <sup>aAB</sup>	0.5 <sup>aAB</sup>	1.9 <sup>aAB</sup>	2.0 <sup>aAB</sup>
G	5.01 <sup>aAB</sup>	5.10 <sup>aAB</sup>	16.3 <sup>aAB</sup>	14.0 <sup>aAB</sup>	1.5 <sup>aAB</sup>	1.5 <sup>aAB</sup>	8.3 <sup>aAB</sup>	6.9 <sup>aAB</sup>	0.7 <sup>aAB</sup>	0.4 <sup>aAB</sup>	1.2 <sup>aAB</sup>	1.6 <sup>aAB</sup>
H	5.05 <sup>aAB</sup>	5.04 <sup>aAB</sup>	16.4 <sup>aAB</sup>	13.5 <sup>aAB</sup>	1.5 <sup>aAB</sup>	1.3 <sup>aAB</sup>	8.0 <sup>aAB</sup>	6.7 <sup>aAB</sup>	0.7 <sup>aAB</sup>	0.5 <sup>aAB</sup>	1.5 <sup>aAB</sup>	1.1 <sup>aAB</sup>
2017												
A	5.35 <sup>aA</sup>	4.91 <sup>aAB</sup>	16.0 <sup>aAB</sup>	15.9 <sup>aAB</sup>	1.4 <sup>aAB</sup>	1.9 <sup>aA</sup>	8.6 <sup>aAB</sup>	9.2 <sup>aAB</sup>	0.6 <sup>aAB</sup>	0.5 <sup>aAB</sup>	1.2 <sup>aAB</sup>	1.4 <sup>aAB</sup>
B	5.20 <sup>aAB</sup>	4.99 <sup>aAB</sup>	9.8 <sup>aAB</sup>	9.5 <sup>aB</sup>	0.9 <sup>aAB</sup>	0.9 <sup>aB</sup>	4.4 <sup>aAB</sup>	4.4 <sup>aB</sup>	0.4 <sup>aAB</sup>	0.3 <sup>aB</sup>	1.1 <sup>aAB</sup>	1.2 <sup>aAB</sup>
C	5.09 <sup>aAB</sup>	5.12 <sup>aAB</sup>	16.9 <sup>aAB</sup>	16.9 <sup>aAB</sup>	1.5 <sup>aAB</sup>	1.5 <sup>aAB</sup>	8.5 <sup>aAB</sup>	8.9 <sup>aAB</sup>	0.6 <sup>aAB</sup>	0.5 <sup>aAB</sup>	1.6 <sup>aAB</sup>	1.4 <sup>aAB</sup>
D	5.11 <sup>aAB</sup>	5.01 <sup>aAB</sup>	16.5 <sup>aAB</sup>	15.4 <sup>aAB</sup>	1.3 <sup>aAB</sup>	1.0 <sup>aAB</sup>	6.3 <sup>aAB</sup>	6.3 <sup>aAB</sup>	0.6 <sup>aAB</sup>	0.5 <sup>aAB</sup>	1.7 <sup>aAB</sup>	1.7 <sup>aAB</sup>
E	5.0 <sup>aAB</sup>	4.91 <sup>aAB</sup>	16.0 <sup>aAB</sup>	13.9 <sup>aAB</sup>	1.4 <sup>aAB</sup>	1.4 <sup>aAB</sup>	8.0 <sup>aAB</sup>	6.7 <sup>aAB</sup>	0.7 <sup>aAB</sup>	0.6 <sup>aAB</sup>	1.5 <sup>aAB</sup>	1.5 <sup>aAB</sup>
F	5.08 <sup>aAB</sup>	5.07 <sup>aAB</sup>	14.7 <sup>aAB</sup>	16.1 <sup>aAB</sup>	1.1 <sup>aAB</sup>	1.3 <sup>aAB</sup>	7.1 <sup>aAB</sup>	7.2 <sup>aAB</sup>	0.5 <sup>aAB</sup>	0.5 <sup>aAB</sup>	1.8 <sup>aAB</sup>	2.4 <sup>aA</sup>
G	5.12 <sup>aAB</sup>	4.93 <sup>aAB</sup>	16.9 <sup>aAB</sup>	16.6 <sup>aAB</sup>	1.6 <sup>aAB</sup>	1.0 <sup>aAB</sup>	8.5 <sup>aAB</sup>	8.2 <sup>aAB</sup>	0.7 <sup>aAB</sup>	0.6 <sup>aAB</sup>	1.5 <sup>aAB</sup>	2.2 <sup>aAB</sup>
H	5.12 <sup>aAB</sup>	4.46 <sup>aB</sup>	14.9 <sup>aAB</sup>	14.7 <sup>aAB</sup>	1.6 <sup>aAB</sup>	1.4 <sup>aAB</sup>	7.3 <sup>aAB</sup>	7.8 <sup>aAB</sup>	0.6 <sup>aAB</sup>	0.5 <sup>aAB</sup>	1.1 <sup>aAB</sup>	1.4 <sup>aAB</sup>

Est. = commercial establishment; S = season; OS = off-season; Means of three replicates (wet basis). The same lower-case letters in the same line and same upper-case letters in the same column represent equal means according to Kruskal Wallis's test ( $p > 0.05$ ).

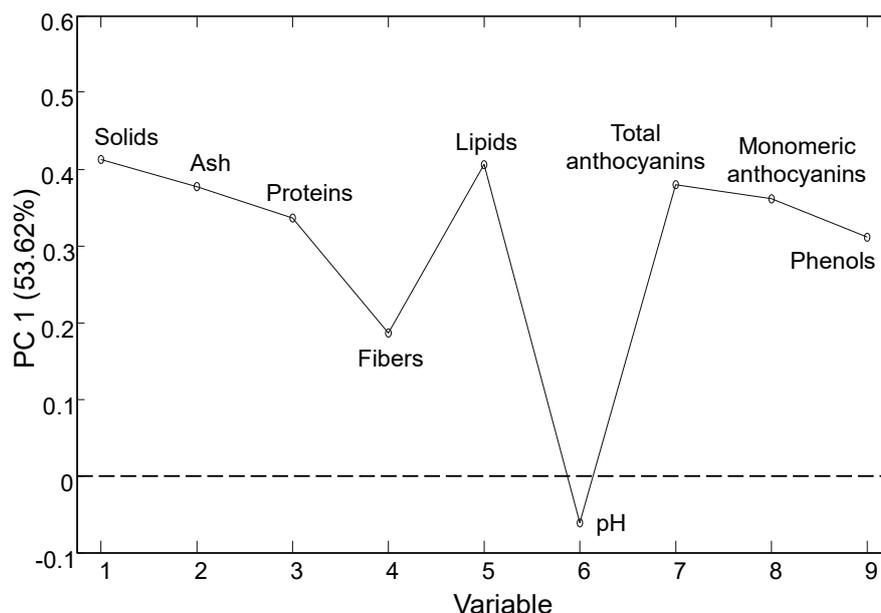
**Table 2.** Bioactive compounds of medium type açai sold in Belém, PA, Brazil during the season and off-season over three years.

Est.	Phenolic compounds [mg AGE kg <sup>-1</sup> ]		Total anthocyanins ** [mg kg <sup>-1</sup> ]		Monomeric anthocyanins ** [mg kg <sup>-1</sup> ]	
	S	OS	S	OS	S	OS
2015						
A	5910.08 <sup>aAB</sup>	2311.8 <sup>aAB</sup>	1960.9 <sup>aAB</sup>	822.8 <sup>aAB</sup>	1513.0 <sup>aA</sup>	621.8 <sup>aAB</sup>
B	3846.50 <sup>aAB</sup>	1312.2 <sup>aB</sup>	1223.5 <sup>aAB</sup>	768.5 <sup>aAB</sup>	977.7 <sup>aAB</sup>	602.1 <sup>aAB</sup>
C	5571.40 <sup>aAB</sup>	2795.8 <sup>aAB</sup>	1461.6 <sup>aAB</sup>	1314.7 <sup>aAB</sup>	1227.0 <sup>aAB</sup>	1230.3 <sup>aAB</sup>
D	3091.3 <sup>aAB</sup>	2229.6 <sup>aAB</sup>	1596.0 <sup>aAB</sup>	927.5 <sup>aAB</sup>	1193.1 <sup>aAB</sup>	812.8 <sup>aAB</sup>
E	2525.5 <sup>aAB</sup>	2365.9 <sup>aAB</sup>	1061.5 <sup>aAB</sup>	1062.6 <sup>aAB</sup>	795.3 <sup>aAB</sup>	847.4 <sup>aAB</sup>
F	2626.9 <sup>aAB</sup>	1709.8 <sup>aAB</sup>	1226.3 <sup>aAB</sup>	866.6 <sup>aAB</sup>	888.7 <sup>aAB</sup>	604.1 <sup>aAB</sup>
G	2264.1 <sup>aAB</sup>	2409.5 <sup>aAB</sup>	1337.4 <sup>aAB</sup>	847.4 <sup>aAB</sup>	1028.2 <sup>aAB</sup>	647.5 <sup>aAB</sup>
H	2744.1 <sup>aAB</sup>	2610.4 <sup>aAB</sup>	1242.6 <sup>aAB</sup>	879.4 <sup>aAB</sup>	954.4 <sup>aAB</sup>	784.0 <sup>aAB</sup>
2016						
A	5307.8 <sup>aAB</sup>	3174.7 <sup>aAB</sup>	1445.9 <sup>aAB</sup>	982.0 <sup>aAB</sup>	912.9 <sup>aAB</sup>	804.8 <sup>aAB</sup>
B	4168.9 <sup>aAB</sup>	2527.5 <sup>aAB</sup>	618.1 <sup>aAB</sup>	630.5 <sup>aAB</sup>	478.4 <sup>aAB</sup>	471.5 <sup>aAB</sup>
C	4355.6 <sup>aAB</sup>	3277.2 <sup>aAB</sup>	1134.7 <sup>aAB</sup>	1009.3 <sup>aAB</sup>	888.5 <sup>aAB</sup>	768.8 <sup>aAB</sup>
D	4547.5 <sup>aAB</sup>	2098.2 <sup>aAB</sup>	1286.2 <sup>aAB</sup>	737.5 <sup>aAB</sup>	960.8 <sup>aAB</sup>	472.5 <sup>aAB</sup>
E	4332.1 <sup>aAB</sup>	2123.1 <sup>aAB</sup>	1510.3 <sup>aAB</sup>	810.1 <sup>aAB</sup>	1204.7 <sup>aAB</sup>	623.6 <sup>aAB</sup>
F	3844.8 <sup>aAB</sup>	3758.6 <sup>aAB</sup>	911.1 <sup>aAB</sup>	1415.9 <sup>aAB</sup>	703.5 <sup>aAB</sup>	1168.8 <sup>aAB</sup>
G	4739.7 <sup>aAB</sup>	2543.2 <sup>aAB</sup>	1300.1 <sup>aAB</sup>	83.4 <sup>aAB</sup>	1061.7 <sup>aAB</sup>	649.6 <sup>aAB</sup>
H	5028.7 <sup>aAB</sup>	2978.3 <sup>aAB</sup>	980.1 <sup>aAB</sup>	1075.1 <sup>aAB</sup>	593.4 <sup>aAB</sup>	893.5 <sup>aAB</sup>
2017						
A	7531.8 <sup>aA</sup>	3609.1 <sup>aAB</sup>	2331.5 <sup>aA</sup>	796.5 <sup>aAB</sup>	1442.2 <sup>aAB</sup>	638.3 <sup>aAB</sup>
B	3320.5 <sup>aAB</sup>	2891.6 <sup>aAB</sup>	1017.6 <sup>aAB</sup>	560.3 <sup>aB</sup>	783.0 <sup>aAB</sup>	415.7 <sup>aAB</sup>
C	5503.1 <sup>aAB</sup>	5330.3 <sup>aAB</sup>	1839.9 <sup>aAB</sup>	1528.2 <sup>aAB</sup>	1459.8 <sup>aAB</sup>	1213.1 <sup>aAB</sup>
D	5439.6 <sup>aAB</sup>	3232.1 <sup>aAB</sup>	930.1 <sup>aAB</sup>	658.4 <sup>aAB</sup>	581.4 <sup>aAB</sup>	388.1 <sup>aB</sup>
E	7462.7 <sup>aAB</sup>	4406.6 <sup>aAB</sup>	1701.2 <sup>aAB</sup>	1171.3 <sup>aAB</sup>	1323.2 <sup>aAB</sup>	952.1 <sup>aAB</sup>
F	5790.7 <sup>aAB</sup>	3999.9 <sup>aAB</sup>	1275.4 <sup>aAB</sup>	777.5 <sup>aAB</sup>	1053.6 <sup>aAB</sup>	575.4 <sup>aAB</sup>
G	4570.5 <sup>aAB</sup>	3402.5 <sup>aAB</sup>	1475.1 <sup>aAB</sup>	989.8 <sup>aAB</sup>	1093.4 <sup>aAB</sup>	739.0 <sup>aAB</sup>
H	5180.3 <sup>aAB</sup>	3035.9 <sup>aAB</sup>	1435.7 <sup>aAB</sup>	704.6 <sup>aAB</sup>	987.3 <sup>aAB</sup>	502.8 <sup>aAB</sup>

Est. = commercial establishment; S = season; OS = off-season; Means of three replicates (wet basis). \*GAE: Galic acid equivalent. \*\* Expressed as cyanidin 3-glucoside. The same lower-case letters in the same line and same upper-case letters in the same column represent equal means according to Kruskal Wallis's test ( $p > 0.05$ ).



**Figure 1.** Score plot of principal component analysis (PCA) – 3D visualization (PC1xPC2xPC3) of the distribution and clustering of data from 48 açai samples purchased at eight commercial establishments from Belém, PA, Brazil, over three years, which describes 81.53 % of the total data variance. The symbols correspond to açai samples from the 2015 season (filled triangle), 2015 off-season (triangle), 2016 season (filled square), 2016 off-season (square), 2017 season (filled circle), and 2017 off-season (circle).



**Figure 2.** Loading plot of the principal component analysis (PCA) – visualization of the variables responsible for the separation of groups in PC1.

## Discussions

The lowest and highest pH values were observed in the off-season (4.46) and season (5.20) of 2017, respectively. The other years show a slight variation between season (pH 4.58 to 5.00) and off-season (pH 4.77 to 5.12) in 2015 and virtually no change in 2016 (season pH 4.83 to 5.13 and off-season pH 4.84 to 5.10). Such variations between the season and off-season were non-significant ( $p > 0.05$ ) in all years and only Kruskal-Wallis test indicated a difference between establishment H in the 2017 off-season and the value observed at establishment A in the 2017 season.

Even the lowest pH value found during the assessment indicates açai can be classified as a low-acidity fruit, which characterizes it as raw material prone to the growth of bacteria, including pathogens. The ranges observed also indicate acidity prone to the action of enzymes, particularly oxidative ones. Comparing the pH results obtained with the current legislation shows all samples were within the range established of between 4 and 6.2 for açai according to its Identity and Quality Standard (IQS) (BRASIL, 2018).

Since açai pulp is extracted with the addition of water, the best measure to compare samples in terms of pulp yield is the total solids content, which, even under the old IQS, allowed it to be classified into types (fine, medium, and coarse) (BRASIL, 2000). No establishments measure such content analytically, which is to this day done completely visually.

Based on that legislation, all samples assessed fall into the medium type (11 to 14 % total solids), except those from establishment B in the 2015 off-season, at 10.6 %, and in both the 2017 season (9.8 %) and off season (9.5 %). However, the new IQS in effect determines a minimum total solids content of 8 % for açai (12). Nonetheless, artisanal establishments never had any kind of analytical control, with water addition and visual consistency of the final process depending on the preference and experience of handlers. Except for the aforementioned establishment B (and three isolated samples), all samples were confirmed as medium type as requested when the products were purchased. That parameter of consistency, to this day, is what sets the price of the liter of açai.

Kruskal-Wallis test equally showed no significant difference between season and off-season in all years. Only in 2017 did the total solids content at establishment B differ from the value found in the 2016 season at establishment A.

The highest protein value found was 1.9 % from establishment A while the lowest was 0.9 % from establishment B, both during the 2017 off-season. The year 2015 had a variation from 1.2 to 1.6 % during the season and 0.9 to 1.3 % during the off-season. That range in 2016 was between 0.9 and 1.5 % during the season and 1.2 and 1.6 % in the off-season, whereas 2017 yielded values from 0.9 to 1.6 % in the season and 0.9 to 1.9 % in the off season. Those values, when converted as a function of the moisture content in the pulps, comply with the lowest limit of 7 % dry basis (BRASIL, 2018).

According to the statistical analysis performed, only protein content of establishment B in the 2017 off-season statistically differed from establishment A in the same year and off-season. For a food to be considered rich in protein, its content must be above 6% (BRASIL, 2012). Therefore, açai *in natura* cannot be considered rich in protein, not the least because it does not contain all essential amino acids as required by the legislation. The literature reports seven essential amino acids in açai pulp, with a profile similar to that of eggs (Bichara & Rogez, 2011).

Compared to other fruits, açai has significant protein content since the large majority of fruits have low levels of this nutrient, e.g., mango (0.4 %), white guava (0.9 %), pineapple (0.9 %), apple (0.2 %), melon (0.7 %), and papaya (0.5 %) (NEPA, 2011).

Lipids stand out in açai, whose content of this macronutrient is significant when compared with other fruits such as pineapple (0.1 %), acerola (0.2 %), banana (0.1 %), cashew (0.3 %), white guava (0.5 %), mango (0.4 %), papaya (0.5 %), and apple (0.2 %) (NEPA, 2011).

In 2015, lipid values in açai ranged from 6.7 to 9.3 % in the season and 5.2 to 7.9 % in the off-season; in 2016, from 5.2 to 9.3 % in the season and 4.6 to 7.8 % in the off-season; and in 2017, from 4.4 to 8.6 % in the season and 4.4 to 9.2 % in the off-season. The only significant variation observed by Kruskal-Wallis test was between establishment B in the 2017 off-season and establishment A in the 2015 season.

All values show fat is the predominant nutrient in açai. The IQS set by the current legislation does not determine a minimum value of lipids in açai. Those values are close to the lipid content of fruits such as avocado (8.4 %) and bacaba (7.4 %) and lower than those of fruits from other palm trees such as tucumã (19.1 %) (NEPA, 2011; Canuto et al., 2010).

The ash content in a food corresponds to the inorganic residue that remains after incineration of the organic matter and is a major indicative of its mineral content. No great variation in ash content was found among years in the açai samples. However, lower contents were found in the off-season than in the season, i.e., off-season values of 0.4 to 0.7 % in 2015, 0.4 to 0.6 % in 2016, and 0.3 to 0.6 % in 2017 against season values of 0.6 to 0.8 % in 2015, 0.5 to 0.8 % in 2016, and 0.4 to 0.7 % in 2017. Such variations between the season and off-season were non-significant ( $p>0.05$ ) according to Kruskal-Wallis test, except for establishment B in the 2017 off-season and establishment A in the 2016 season.

The legislation sets no parameters for ash content in açai, which could be very useful to detect tampering in commercial products. Higher ash contents might indicate tampering since values are normally below 1 % in fruit pulp. The pulps studied in this research are not suspected to have been tampered with since the highest ash contents found are related with the samples with the highest total solids content, such as those from establishments A, C, F, and G in the 2015 season, which were compatible with açai fruit.

No marked variation was found in fiber content in the samples studied according to time of harvest or among years. Kruskal-Wallis test confirmed data similarity and indicated significant difference only for the lowest (0.9 % in the 2015 off-season at establishment B) and the highest (2.4 % in the 2017 off-season at establishment F) fiber contents found.

The fiber data places açai in the same range as other fruits such as pineapple (1.0 %), acerola (1.5 %), banana (2 %), cashew (1.7 %), mango (1.6 %), papaya (1.8 %), and apple (2 %) (NEPA, 2011).

Overall, the literature on percentage composition of non-mixed (with guaraná, other fruits, etc.) commercial açai pulp with no thermal treatment or dehydration/lyophilization is scarce. That is very likely because açai, in the way it is processed and consumed in the Amazon, is still restricted to the places where the fruit is more accessible, i.e., the producing regions. Thus, comparing literature reports must be done

carefully since the pulp is obtained by adding water and the final solids content directly impacts its nutritional composition, not to mention external factors such as origin, climate, soil, harvest, transportation, and storage.

Alexandre et al. (2004), when studying medium-thickness-type açai from Tomé-Açu, PA, Brazil, found 1.5 % proteins, 6.75 % lipids, 0.43 % ash, and 4.37 % fibers. Da Silva et al. (19), when studying commercial açai pulp in Belém, observed 2.8 % proteins and 7.2 % lipids in a product with 14.6 % total solids.

Countless researches on bioactive compounds of açai have reported significant values of anthocyanins and phenolic compounds and their health benefits (Pacheco-Palencia et al., 2010; Rogez et al., 2011; Yamaguchi et al., 2015; Petruk et al., 2017; Torma et al., 2017)

Anthocyanins are the main pigment of the fruit and account for its off-violet color. The contents observed in this study (Table 2) show that, on average, they are higher during the season than in the off-season, particularly in 2015 and 2017. The highest total anthocyanin content was 2331.5 mg kg<sup>-1</sup> in samples from establishment A in the 2017 season, while the lowest was 618.1 mg kg<sup>-1</sup> from establishment B in 2016 off season, which was the only significant difference indicated by Kruskal-Wallis test ( $p \leq 0.05$ ) among all values observed.

The highest and lowest contents of monomeric anthocyanins, linked to greater potential antioxidant effects, was 1513.0 and 478.4 mg kg<sup>-1</sup>, from the same establishments mentioned above. During the off season, samples from establishment C had the highest contents of both total anthocyanins (1528.2 mg kg<sup>-1</sup> in 2017) and of monomeric anthocyanins (1230.3 mg kg<sup>-1</sup> in 2015). The lowest values observed in the off season were 560.3 and 388.1 mg kg<sup>-1</sup> for total and monomeric anthocyanins, respectively, both in 2017, from establishments B and D.

The values of total phenolic compounds observed show the same trend as for anthocyanins, with higher values in the season than in the off-season (Table 2). Samples from 2015 yielded 2264.1 to 5910.8 mg GAE kg<sup>-1</sup> in the season and 1312.2 to 2795.8 mg GAE kg<sup>-1</sup> in the off-season. In 2016, those values were 3844.8 to 5307.8 mg GAE kg<sup>-1</sup> in the season and 2098.2 to 3758.6 mg GAE kg<sup>-1</sup> in the off-season. In 2017, the last year studied, values ranged from 3320.5 to 7531.8 mg GAE kg<sup>-1</sup> in the season and 2891.6 to 5330.3 mg GAE kg<sup>-1</sup> in the off-season. In all seasons, samples from establishment A yielded the highest values, although Kruskal-Wallis test showed no significant difference ( $p > 0.05$ ).

Higher contents of bioactive compounds in the season are probably directly linked to fruit quality since no product needs to come from other regions to supply the market as occurs during the off-season. The far distances in the Amazon entail long transportation, which, without a doubt, leads to quality losses due to the

sensitivity of bioactive compounds to several factors, such as exposure to light and air, temperature, enzyme activity, etc. (Mazza & Miniati, 1993).

In addition, the very origin of açaí, whether due to genetic (1) or edaphoclimatic factors such as light availability and rainfall during growth, may result in changes in the chemical composition of the pulp as they impact the synthesis and concentration of phenolic pigments and the biosynthetic pathway of those pigments in the plant (Salisbury & Ross, 1991).

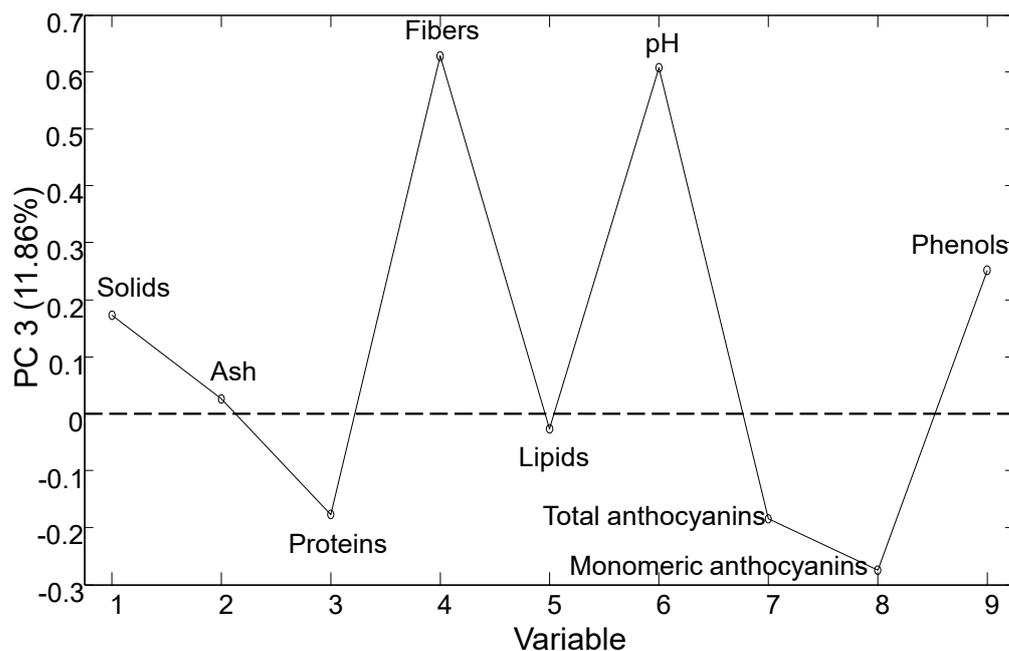
It is believed that the variations observed among establishments may also be directly caused by parameters such as storage time prior to processing, pre-steps (selection, hygienization, and maceration), form and time of processing, and time and temperature of packaging, among other factors dependent on the physical structure and conduct of handlers.

Rufino et al. (2010), when studying bioactive compounds in non-traditional tropical fruits, found 1110 mg kg<sup>-1</sup> and 4540 mg GAE kg<sup>-1</sup> for anthocyanins and total phenolic compounds, respectively, in açaí from Paraipaba, CE, Brazil. Neves et al. (2015) reported 381.9 to 432.5 mg kg<sup>-1</sup> and 5127.5 to 5585.6 GAE kg<sup>-1</sup> for anthocyanins and phenolic compounds, respectively, in artisanal açaí pulp from Boa Vista, RR, Brazil.

Rufino et al. (2010), when comparing contents of anthocyanins and phenolic compound in açaí with those of other red/purple fruits, reported values of 189 mg kg<sup>-1</sup> and 10630 mg GAE kg<sup>-1</sup> for acerola, 422 mg kg<sup>-1</sup> and 11760 mg GAE kg<sup>-1</sup> for camu-camu, 581 mg kg<sup>-1</sup> and 4400 mg GAE kg<sup>-1</sup> for jabuticaba, and 933 mg kg<sup>-1</sup> and 1850 mg GAE kg<sup>-1</sup> g for jambolan, respectively. Bobinaité et al. (2012), when studying raspberry varieties, detected variation from 21 to 3255 mg kg<sup>-1</sup> for total anthocyanins and 2786 to 7147 mg GAE kg<sup>-1</sup> for phenolic compounds. LI et al. (2017), when studying blueberry, reported 945 to 3010 mg kg<sup>-1</sup> and 1547 to 3980 GAE kg<sup>-1</sup> for total anthocyanins and phenolic compounds, respectively.

The PCA and plots shown in Figures 1 and 2 show the relation between the pH values observed in the season and off season are directly related to post-harvest alterations. As mentioned, off-season açaí comes from regions outside the city of Belém, which are more susceptible to chemical and microbiological changes prior to processing. According to Aguiar et al. (2013), one of the most important changes is related to spontaneous fruit fermentation, with the time and mean of transportation of açaí fruits strongly influencing the quality of the final product. Hence, since off-season fruits are much more impacted by the time and mean of transportation until they reach urban artisanal processing units in Belém, the trend seen in Figure 2 is perfectly defensible.

The loading plot of PCA in axis PC3 (Figure 3) shows the variables responsible for the separation of samples in 2015. The monomeric anthocyanins, total anthocyanins, and proteins are positively correlated with samples of that year, i.e., both season and off-season açai from 2015 exhibit higher values of those bioactive compounds and proteins when compared to the other years studied. Additionally, the plot indicates the samples from 2016 and 2017 have superior nutritional quality regarding fibers and total phenolic compounds as well as higher pH values.



**Figure 3.** Loading plot of the principal component analysis (PCA) – visualization of the variables responsible for the separation of groups in PC3.

The differences among years observed in the PCA shown in Figure 3 can very likely be justified as a function of açai being, as most raw materials of plant origin, susceptible to their growth sites and, consequently, the environmental factors around it, such as climate, rainfall, incidence of light, etc. (Salisbury & Ross, 1991). Although the açai purchased by beaters in the Belém metropolitan area often comes from the same outlet (açai fair at the Ver-o-Peso market), the fruits sold come from several locations, such as the municipalities of Ponta de Pedras, Acará, and Barcarena (Onças Island) (Bichara & Rogez, 2011). That prevents the present research from correlating the variations observed with environmental data of the years studied since there is no certification of origin as this is still a fully informal market.

## Conclusions

The pH values observed characterize artisanal açai as a low-acidity food and the samples studied are within the range set by the legislation. The total solids values confirmed the classification of açai purchased as medium type, as defined by the legislation in effect at the time, with only three samples of a single establishment (B) failing to meet minimum contents. Concerning macronutrients, the lipid content stands out as the predominant component of açai, which characterizes it as a food able to serve as a major source of calories. Even the lowest values observed for anthocyanins and total phenolic compounds show artisanal açai enriches the regional diet and is an important source of those antioxidants. The principal component analysis confirmed the superior quality of artisanal açai during the season of the fruit regarding nutritional aspects and the presence of bioactive compounds and showed that off-season açai tended to exhibit higher pH. Overall, it is believed that variations in the composition of artisanal açai will always be commonly observed since, although the fruit enjoys a consolidated market of indubitable magnitude in the Amazon region, many factors may impact its composition and there is still no effective control over them at artisanal processors.

## Acknowledgements

The authors thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for the financial support to the project in partnership with professor Antonio Gilberto Ferreira/Federal University of São Carlos (UFSCAR).

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