

# Levels of Minor and Trace Elements of Some Commercial Fruit Juices and Syrup Produced in Artisanal and Semi-Industrial Units in Benin Republic

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## Abstract

Fruit juices have been gaining interest in recent years for their contributions of minerals and other essential vitamins. But, with the development of intensive agriculture massively using pesticides and mineral fertilizers, the risk of contamination of these juices is high along the production chain. In this study, we evaluated the concentrations of arsenic (As), cadmium (Cd), beryllium (Be), aluminium (Al), strontium (Sr), tin (Sn), barium (Ba), mercury (Hg), thallium (Tl), lead (Pb), thorium (Th), uranium (U) for 92 commercial samples of pineapple juice, cocktail of pineapple and watermelon and pineapple syrup of Benin and France using Inductively Coupled Plasma-Source Mass Spectrometry (ICP-MS). The concentrations vary in the following ranges: As <QL at 39.3 ppb, Cd <QL at 0.7 ppb, Be <QL at 0.59 ppb, Al 26.4 ppb at 30620 ppb, Sr 130 ppb at 4049 ppb, Sn <QL at 43 ppb, Ba 42 ppb at 1582 ppb, Hg <QL at 31.7 ppb, Tl <QL at 21.3 ppb, Pb <QL at 608 ppb, Th <QL at 24.7 ppb and U <QL at 1.04 ppb. Se, Ag and Pt have concentrations below the quantification limit (<QL). The levels of Ba, Hg and Pb exceeded the norms for some samples. The presence of aluminum, arsenic and cadmium in the tested samples of fruit juices can be toxic since they have no nutritional value, and hence may be treated as potential contaminants in these beverages. The classification of concentration levels of metallic contaminants reveals two main groups, the minor and the trace elements. These results make it possible to classify the contaminants in the decreasing order of the concentrations in the following way: Al > Sr > Ba > Pb > Sn > Tl > As > Th > Hg > Cd > Be > U. The average concentrations' levels of trace elements are generally in accordance with the levels obtained for French pineapple juices chosen as reference, national and international standards for the quality of beverages.

**Keyword:** metallic contaminants, pineapple, watermelon, syrup, juice, ICP-MS

## 1. Introduction

### 1.1 Contamination Factors

According to Sodjinou and al. (2011) quoted by Hotegni and al. (2015), the increase of the pineapple production in Benin Republic is more dependent on the expansion of the planted areas than on the improvement of yield in the sense that during the period from 2000 to 2010, the yield of pineapple production increased only 19% from 44 tons/ha to 52 tons/ha with a production rising from 51 151 tons to 222 223 tons during the same period, an increase of 334%. According to Arouna and Afomasse (2005) quoted by Hotegni and al. (2012 and 2015), in the technical itineraries of production of pineapple in Benin, the phytosanitary treatment and the use of synthetic fertilizers is systematic. It should also be noted that in place of the recommended equipment, pineapple producers use cans of 20 or 25 liters for the treatment of floral induction which is not without negative consequences on the treatment and even on the health of the producers. However, several factors can contribute to the observed variations in element concentrations, including the availability of elements for uptake by plants (strictly related to soil characteristics, mineral composition and soil pH),

agricultural practices and plant nutrients. The procedures applied during the growth of the fruiting plants (the application of fertilizers and irrigation, water and climatic conditions), and finally, the variation of treatments at the plant, in addition to the type and maturity of the fruits at harvest (Paula and al., 2014). The use of synthetic chemicals, such as fertilizers or pesticides to maintain or improve soil fertility, is known to have a significant effect on micronutrient concentrations in fruit juices. The use of agrochemicals, for instance, insecticides or fungicides used during the growth of fruit plants, is responsible for reducing the nutritional quality and safety of these products due to an increased risk of human exposure to toxic metals (eg, Cd and Pb) (Williams and al. 2010; Szymczycha-Madeja and al. 2014; Kiliç and al. 2015; Lopez and al. 2002; Tufuor and al. 2011).

### 1.2 Choice of Mineralisation Method of Fruit Juices 's

In this study, we mineralized the samples taken to destroy organic matter due to the high viscosity and high solid content; direct analysis of fruit juices under these conditions often causes many non-spectral difficulties (mainly matrix effects) and spectral interferences in spectrometric measurements. Spectrochemical methods are used for the determination of elements in fruit juices after wet mineralization, eg, with atomic flame absorption spectrometry (FAAS) (Krejpcio and al. 2005), graphite furnace atomic absorption spectrometry (GF- AAS) (Oliveira and al. 2005; Liu and al. 1999), inductively coupled plasma optical emission spectrometry (ICP-OES) (Simpkins and al. 2000; WHO, 1996) and inductively coupled plasma source mass spectrometry (ICP-MS) (Lai and al. 2016). This can be avoided when fruit juice samples are mineralized before analysis (Liu and al. 1999; Lai and al. 2016). Tables 1 and 2 summarize the literature review on analytical methods and concentration ranges of elements in fruit juices.

Table 1. Methods of analysis of elements in fruit juices

N°	Auteurs et année	Matrices	Méthodes	Éléments
1	Akan and al., 2010	Juice	AAS	Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn, Pb
2	Chmara and al., 1996	Pineapple juice and nectars.	AAS	Ca, Mg, Cu, Fe, Mn, Zn
3	Beattie and al., 2000	pineapple juice	FAAS and EPR	Mn
4	Francisco and al., 2015	Fruit Juices	GFAAS and FAAS	GFAAS (Cd, Cr, Pb, Ni) and FAAS (Zn, Fe)
5	Santos Froes and al., 2009	Fruit Juices	ICP OES	Al, Cu, Fe, Mn, Zn, Ni, Cd, Pb, Sn, Cr, Co, Ba
6	Szymczycha-Madeja and al., 2014	Fruit Juices	XRFS, INAA, ICP-OES, ICP-MS, FAAS, GF, AAS	Mg, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Cd, Al, Sr, Mo, Sn, Ba, Hg, Pb
7	Szymczycha-Madeja and al., 2013	Commercial fruit juices	ICP -OES	Mg, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Cd, Al, Sr, Mo, Sn, Ba, Hg, Pb
8	Tormen and al., 2011	Commercial fruit juices	ICP-MS	Ca, V, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sr, Mo, Pb

Table 2. Concentration ranges of elements (ppm) in fruit juices according to the authors

Elements	Mg	Ca	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Authors N°	2, 6, 7	2, 6, 7, 8	6, 8	1, 4, 5, 6, 7	1, 2, 3, 5, 6, 7, 8	2, 4, 5, 6, 7, 8	1, 5, 8	1, 4, 5, 6, 7, 8	1, 2, 5, 6, 7, 8	1, 2, 4, 5, 6, 7, 8
Concentrations (ppm)	7 - 750	0.14 - 980.1	0.005 - 0.052	ND - 2.767	0.06 - 23	0.009 - 179.2	ND - 0.004	0.04 - 73.37	ND -0.49	0.04 -545.9
Elements	Se	Cd	Al	Sr	Mo	Sn	Ba	Hg	Pb	
Authors N°	6	1, 4, 5, 6, 7, 8	5, 6, 7	6, 7, 8	6, 8	1, 5, 6	5, 6, 7	6	6, 7, 8	
Concentrations (ppm)	0.014 -0.015	0 -0.012	0 - 4.2	0.088 - 0.88	0.0487 -0.049	0 - 0.45	0.038 - 0.114	0 - 3	ND - 0.24	

Auteurs N° = authors indicated in the table 1; ND= Not detected

### 1.3 Levels of juice contaminants

According to Szymczycha-Madeja and al. (2014) the concentrations of chemical elements in pineapple juices vary in the ranges shown below in Table 3.

Table 3. Concentrations (in  $\mu\text{g. mL}^{-1}$ ) of different elements in pineapple juices

Elements	Al	Ba	Cd	Co	Cr	Mo	Pb	Rb
Concentrations	ND-4.2	0.04–0.11	ND-0.012	ND-0.004	ND-0.017	0.049	ND-0.24	0.45–1.1
Elements	Se	Sn	Sr	Ti	V	Zr		
Concentrations	0.014–0.015	ND-0.45	0.088–0.62	0.30	0.005	0.2		

Source: Szymczycha-Madeja and al. (2014); ND= Not detected

#### 1.4 Hypotheses

The underlying hypothesis of this study was that the quality juices produced in Benin is affected by the use of fertilizers, pesticides, transport conditions, juice extraction and conditioning conditions etc. The verification of this hypothesis will be done through the analysis of the conformity with the national and international standards of quality of the water and food of Codex alimentarius (table 4) and according to the literature review.

In international legislation concerning micronutrients in foods, environment or occupational health, most regulations are based on the total content of elements and are often indicated as maximum or guideline limits. However, several techniques are developed for research and determination of metallic and metalloid contaminants in foods and beverages (Akman and al., 2007, Varadi and al., 2007). Specifically, most contaminants are not regulated, but juices can be compared to drinking water. The WHO guidelines for drinking water quality, updated in 2006, are the benchmark for safe drinking water. The legislation varies from one country to another, table 4 below summarizes the standards of WHO (2006) and that of Benin, Brazil, Codex Alimentarius (Codex, 1997) and Canadian one.

Table 4. Some quality standards for water and beverages

Contaminants	Standards (ppb)				
	Benin*	Brazilian Legislation	Codex Alimentarius	WHO (2006)	Canadian **
As	50	-	-	10	50
Se	10	-	-	10	10
Ag	-	-	-	No guide value	50
Al	-	-	-	200	-
Ba	1000	-	-	700	1000
Be	-	-	-	No guide value	-
Cd	5	200	50	3	10
Cr				50	
Hg	1			1	
Pb	50	200	50	10	50
Pt	-	-	-	-	-
Sn	-	250	150	No guide value	
Sr	-	-	-	-	-
Th	-	-	-	-	-
Tl	-	-	-	50	-
U	-	-	-	15	5000

\* physico-chemical standards for water intended for human consumption

\*\* maximum permissible concentration for drinking water

## 2. Material and Methods

### 2.1 Juices Sampling

Juice sampling was carried out in variable numbers per unit in order to take into account various factors of variability such as the environment of growing of pineapple, juices production environment, the dates of manufacture or of expiry, the packaging of products etc. The environment of the growing area, the soil and the place of production of the juices

were taken into account in terms of rays compared to the city of Cotonou taken as origin (0 Km). In practice, eighty-five (85) juice bottles (kept in glass containers of varying size and volume) were randomly sampled from about twenty juice producers located primarily near the growing areas of the pineapple (Figure 1). It counted 69 bottles of 33cl, 15 of 50cl and 1 of 50 cl high and of gray color. The dates of storage from production to laboratory analysis are also variable, as are the colors of the bottle packaging, of which there are 30 green bottles, 54 colorless bottles and 1 gray bottle. It should be noted here that pineapple products for export mainly consist of pineapple juice. For the analyses, a bottle of pineapple syrup was taken from a processing unit. Table 5 summarizes and describes the different samples analyzed per processing unit. The samples are in variable numbers per unit according to the different criteria observed such as the place and dates of manufacture, the nature of the juice (cocktail or pineapple juice), the species of pineapple fruit used (Sugarloaf, Smooth Cayenne etc.). Basing on the self-regulatory principles of researchers in research ethics, we opted for the non-disclosure of unit names or their marks which will be abbreviated using the three-letter initials (Table 5) and the corresponding samples will be distinguished by numerical indices on these abbreviated names.

Table 5. Presentation of the samples with their identification codes or Codec

City/country	NS	sample identification names
ABOMEY	7	JUA <sub>1</sub> - JUA <sub>6</sub> , SYR
AKASSATO	6	BRA <sub>1</sub> - BRA <sub>6</sub> ,
ALLADA	13	CHA <sub>1</sub> - CHA <sub>6</sub> , OJA <sub>1</sub> - OJA <sub>5</sub> , TRO <sub>1</sub> - TRO <sub>2</sub>
AVAKPA	9	SAN <sub>1</sub> - SAN <sub>9</sub>
CALAVI	8	ALA <sub>1</sub> - ALA <sub>2</sub> , PAS <sub>1</sub> - PAS <sub>6</sub>
COME	6	JUV <sub>1</sub> - JUV <sub>6</sub>
COTONOU	7	VIP <sub>1</sub> - VIP <sub>7</sub>
EKPE	6	ALO <sub>1</sub> - ALO <sub>6</sub>
FRANCE	6	JAF <sub>1</sub> - JAF <sub>2</sub> , INN <sub>1</sub> - INN <sub>2</sub> , VIB <sub>1</sub> - VIB <sub>2</sub>
LOGBOZOUKPA	6	FRU <sub>1</sub> - FRU <sub>6</sub>
PORTO-NOVO	9	FRE <sub>4</sub> - FRE <sub>5</sub> , LAS, JUD <sub>1</sub> - JUD <sub>3</sub>
SEKOU	3	JUS <sub>1</sub> - JUS <sub>3</sub>
ZE	6	VIT <sub>1</sub> - VIT <sub>6</sub>
TOTAL	92	

NS.: Number of samples

Once collected, these bottles of juice and syrup are conveyed to the laboratory for investigations of chemical contaminants, which are detected and measured out by appropriate analysis techniques. The Codec or sample code is the identification number of each sample and the code is its acronym derived from the name of the processing unit to which a serial number is associated (Table 5).

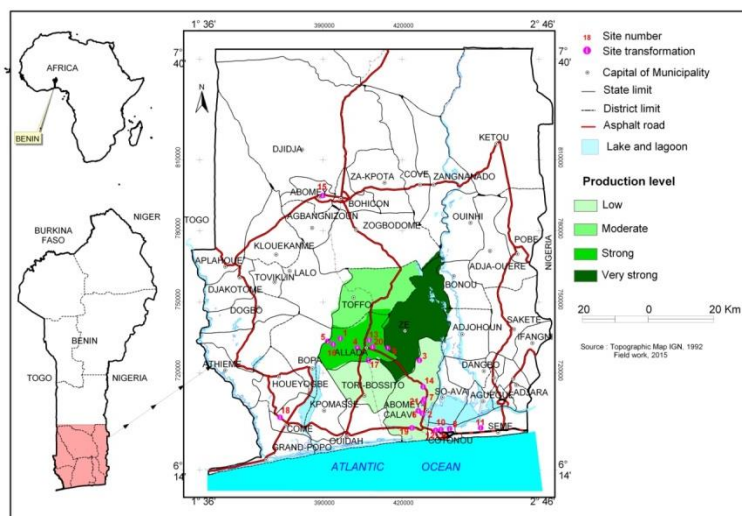


Figure 1. Location of processing units and growing areas of pineapple

### 2.2 Choice of Method of Mineralization and Quantification of Samples

We adopted conventional wet digestion in open systems by using DigiPrep digestion blocks for the decomposition of fruit juice samples with concentrated nitric acid ( $\text{HNO}_3$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) at 30% (Szymczycha-Madeja and al. 2013; Santos Froes and al. 2009). To succeed in this, 2 ml of ultra-pure  $\text{HNO}_3$  and 1 ml of hydrogen peroxide were added to 2 ml of juice samples in a Teflon container, closed untightly to let the vapors escape. The entire system was put in a programmable oven with two temperature stages ( $45^\circ$  and  $90^\circ$ ). This feature of DigiPrep allowed the samples to be progressively brought to  $45^\circ\text{C}$  for 20 min and then held at this temperature for 40 min and then progressively brought to  $90^\circ\text{C}$  for 30 min and finally maintained at this temperature for 160 min.

### 2.3 Criteria for Validation of the Analytical Method

The validation of the method consisted in evaluating: the linearity through the calibration (external and internal), the repeatability and the reproducibility, the limits of detection (LD) and of quantification (QL). To do this, standard certified mixed reference solutions of the desired elements are prepared in the range of 0 to 100 ppb and injected. The mass spectra  $m/z$  are determined and the external and internal calibration curves are plotted with the slopes, the coefficients of determination  $R^2$  and the ordinates at the origin. The results of the repeatability tests are presented in Table 7. The coefficients of variation % CV are determined in each case. MRC certified water standards are digested under the same conditions; which allowed us to obtain good recovery rates for the chemical elements recorded with recovery rates between 80% and 105% maximum except for zinc and cadmium with SRM SLRS-5 (table 6).

Table 6. Recovery rates and concentrations ( $\pm$  sd) of metals in reference materials in  $\mu\text{g}\cdot\text{L}^{-1}$ 

Analyte	SRM NIST 1640a			SRM SLRS-5		
	Certified value ( $\mu\text{g}/\text{L}$ )	Sample value ( $\mu\text{g}/\text{L}$ )	Recovery (%)	Certified value ( $\mu\text{g}/\text{L}$ )	Sample value ( $\mu\text{g}/\text{L}$ )	Recovery (%)
Be	3.026 $\pm$ 0.028	2.938 $\pm$ 0.080	97.1	0.005*	0.005 $\pm$ 0.001	100.0
Al	53.0 $\pm$ 1.8	54.3 $\pm$ 3.1	102.5	49.5 $\pm$ 5.0	42.8 $\pm$ 1.1	86.0
V	15.05 $\pm$ 0.25	12.16 $\pm$ 0.32	80.8	0.317 $\pm$ 0.033	0.284 $\pm$ 0.003	89.6
Cr	40.54 $\pm$ 0.30	38.20 $\pm$ 0.09	94.2	0.208 $\pm$ 0.023	0.108 $\pm$ 0.005	51.9
Mn	40.39 $\pm$ 0.36	39.05 $\pm$ 1.31	94.4	4.33 $\pm$ 0.18	4.37 $\pm$ 0.09	100.9
Co	20.24 $\pm$ 0.24	18.97 $\pm$ 0.26	93.7	0.05*	0.05 $\pm$ 0.01	100.0
Ni	25.32 $\pm$ 0.14	25.33 $\pm$ 0.44	100.0	0.476 $\pm$ 0.064	0.471 $\pm$ 0.020	98.9
Cu	85.75 $\pm$ 0.51	87.40 $\pm$ 1.36	101.9	17.4 $\pm$ 1.3	19.7 $\pm$ 0.4	113.2
Zn	55.64 $\pm$ 0.35	53.23 $\pm$ 1.25	95.7	0.845 $\pm$ 0.095	1.90 $\pm$ 0.05	224.9
As	8.075 $\pm$ 0.070	7.190 $\pm$ 0.332	89.0	0.413 $\pm$ 0.039	0.412 $\pm$ 0.015	99.8
Se	20.13 $\pm$ 0.17	19.16 $\pm$ 1.41	95.2	-	-	-
Mo	45.60 $\pm$ 0.61	45.74 $\pm$ 0.11	100.3	0.27 $\pm$ 0.04	0.20 $\pm$ 0.01	74.1
Ag	8.081 $\pm$ 0.046	9.370 $\pm$ 0.251	116.0	-	-	-
Cd	3.992 $\pm$ 0.074	3.711 $\pm$ 0.15	93.0	0.0060 $\pm$ 0.0014	0.0083 $\pm$ 0.0014	138.3
Ba	151.80 $\pm$ 0.83	146.66 $\pm$ 1.38	96.6	14.0 $\pm$ 0.5	14.0 $\pm$ 0.1	100.0
Ca**	-	-	-	10.5 $\pm$ 0.4	10.2 $\pm$ 0.3	97.1
Tl	1.619 $\pm$ 0.016	1.571 $\pm$ 0.011	97.0	-	-	-
Pb	12.101 $\pm$ 0.050	11.927 $\pm$ 0.122	98.6	0.081 $\pm$ 0.006	0.072 $\pm$ 0.002	88.9
Mg**	-	-	-	2.54 $\pm$ 0.16	2.59 $\pm$ 0.08	102.0
U	25.35 $\pm$ 0.27	24.12 $\pm$ 0.09	95.1	0.093 $\pm$ 0.006	0.092 $\pm$ 0.001	98.9
Fe	36.8 $\pm$ 1.8	28.2 $\pm$ 0.6	76.7	91.2 $\pm$ 5.8	80.3 $\pm$ 2.8	88.0
Sr	126.03 $\pm$ 0.91	110.10 $\pm$ 0.73	87.4	53.6 $\pm$ 1.3	52.9 $\pm$ 0.5	98.7

Note: concentrations are given with the same number of significant figures found in the certificate of analysis of the SRM

\*Values not certified in the SRM; given for information only

\*\*Concentration reported in  $\text{mg L}^{-1}$

#### 2.4 Analytical Method

A Perkin Elmer ELAN DRC device equipped with a nebulizer was used with a Meinhardt silica cyclone chamber for continuous spraying and nebulization. The operating conditions were optimized using an 8-level standard aqueous solution (for calibration of the apparatus) containing: 0; 0.05; 0.1; 0.5; 1; 5; 20 and 100 ppb and internal standards for the control of isotope intensities. The internal standards used are indium (In), bismuth (Bi) and scandium (Sc) of concentrations 5 ppb. Two types of reference materials (SRM NIST 1640a and SRM SLRS-5) were used to determine coverage percentages.

Table 7. Repeatability test results

Samp	Concentrations in elements (ppb)											
	As	Cd	Be	Al	Sr	Sn	Ba	Hg	Tl	Pb	Th	U
CHA4a	1.06±0.21	<QL	0.067±0.010	5052±221	671±5	21.2±0.1	86.2±0.6	<QL	0.13±0.01	9.03±0.11	2.43±0.01	0.076±0.002
CHA4b	0.93±0.03	<QL	0.063±0.008	5074±250	663±5	18.3±0.3	84.6±1.2	<QL	0.14±0.01	9.00±0.11	2.67±0.04	0.065±0.002
CHA4c	<QL	<QL	0.056±0.011	5158±230	669±5	16.9±0.2	84.7±0.9	<QL	0.14±0.01	9.05±0.03	2.53±0.06	0.064±0.001
JAF1a	<QL	0.61±0.05	0.070±0.016	138±5	816±16	6.88±0.07	292±4	<QL	0.60±0.01	0.35±0.01	2.53±0.06	0.069±0.004
JAF1b	<QL	0.61±0.06	0.092±0.012	148±9	801±7	6.11±0.09	287±3	<QL	0.59±0.03	0.39±0.01	2.12±0.02	0.066±0.004
JAF1c	<QL	0.57±0.08	0.079±0.008	135±7	796±9	4.83±0.05	286±1	<QL	0.60±0.01	0.26±0.01	1.87±0.01	0.062±0.007
JUA1a	<QL	<QL	0.15±0.02	913±54	649±1	9.17±0.05	218±1	<QL	1.14±0.02	3.63±0.02	1.72±0.02	0.037±0.002
JUA1b	<QL	<QL	0.18±0.03	911±35	645±7	12.8±0.4	217±2	<QL	1.13±0.01	3.64±0.02	1.78±0.03	0.036±0.004
JUA1c	<QL	<QL	0.16±0.03	899±46	650±7	7.92±0.05	219±3	<QL	1.14±0.03	3.77±0.07	1.84±0.04	0.044±0.006
LASa	<QL	<QL	0.086±0.021	3043±93	1106±15	6.95±0.07	119±2	<QL	1.52±0.05	23.1±0.3	1.58±0.05	0.072±0.004
LASb	<QL	<QL	0.088±0.017	3014±123	1112±12	5.97±0.08	118±1	<QL	1.50±0.04	22.9±0.1	1.54±0.09	0.073±0.006
LASc	<QL	<QL	0.076±0.005	2999±128	1119±9	7.26±0.12	119±2	<QL	1.50±0.03	22.1±0.1	1.48±0.06	0.074±0.007
OJA1a	1.06±0.21	<QL	0.067±0.010	5052±221	671±5	21.2±0.1	86.2±0.6	<QL	0.13±0.01	9.03±0.11	2.43±0.01	0.076±0.002
OJA1b	0.93±0.03	<QL	0.063±0.008	5074±250	663±5	18.3±0.3	84.6±1.2	<QL	0.14±0.01	9.00±0.11	2.67±0.04	0.065±0.002
OJA1c	<QL	<QL	0.056±0.011	5158±230	669±5	16.9±0.2	84.7±0.9	<QL	0.14±0.01	9.05±0.03	2.53±0.06	0.064±0.001
VIB1a	<QL	0.46±0.07	0.027±0.004	154±5	313±6	10.5±0.1	266±2	<QL	0.20±0.01	1.47±0.03	1.98±0.08	0.051±0.004
VIB1b	<QL	0.46±0.08	0.034±0.017	161±9	314±4	10.0±0.2	281±4	<QL	0.19±0.02	1.48±0.03	1.87±0.04	0.050±0.002
VIB1c	<QL	0.42±0.07	0.038±0.009	161±6	306±4	11.3±0.1	276±2	<QL	0.19±0.01	1.40±0.03	2.01±0.02	0.049±0.005
VIP1a	<QL	<QL	0.073±0.016	130±5	730±10	8.93±0.06	138±1	<QL	1.49±0.02	2.95±0.01	2.38±0.01	0.051±0.003
VIP1b	<QL	<QL	0.063±0.010	118±4	733±10	8.43±0.08	137±1	<QL	1.49±0.03	3.03±0.05	1.88±0.05	0.052±0.004
VIP1c	<QL	<QL	0.068±0.018	130±7	732±5	9.69±0.14	138±1	<QL	1.47±0.05	3.00±0.09	1.68±0.03	0.051±0.001

keys to abbreviations: Samp= sample name

### 2.5 Statistical Analysis Method

The data was first recorded on excell and the statistical analysis is done for this purpose using SPSS (Statistical Package for Social Science), version 20.0 for the representation of boxplots.

## 3. Results

### 3.1 Contamination Levels of Elements in Fruit Juices

The data in Table 8 show Al in first place followed by Sr, the concentrations of which are significantly higher than those of the other metals.

Table 8. Classification of contaminants according to the nature and origin of the juice

Elements	FPJ	BPJ 100%	PWC	SYR	Overall average
Minor Elements (ppb)					
Al	1853,00	3999,29	1600,67	162	3582,98
Sr	860,00	953,59	1088,11	317	953,76
Ba	270,00	173,34	332,28	233	195,87
Trace Elements (ppb)					
Pb	0,56	28,52	6,69	1,36	24,26
Sn	8,00	9,03	8,79	10,3	8,74
Tl	0,38	3,23	2,06	0,21	2,88
As	1,00	3,09	1,53	<QL	2,72
Th	2,33	2,17	5,57	2,21	2,36
Hg	<QL	1,7	<QL	<QL	1,41
Cd	1,00	0,13	0,3	0,47	0,13
Be	<QL	0,08	0,18	<QL	0,09
U	0,05	0,07	0,07	0,05	0,07
Ultra trace Elements (ppb)					
Se	<QL	<QL	<QL	<QL	<QL
Pt	<QL	<QL	<QL	<QL	<QL
Ag	<QL	<QL	<QL	<QL	<QL

keys to abbreviations: FPJ= French pineapple juice; BPJ= Beninese 100%Pineapple juice; PWC= Pineapple and Watermelon Cocktail from Benin; SYR= Syrup.

The statistical comparison of average concentrations based on the 92 samples analyzed shows groupings at 5 classification levels. The first group consisted of the element Al who is of the order of ppm, the second group consisted of the element Sr of the order of one tenth of a ppm (0.1 ppm), the third consisted of the element Ba intermediate between the second and fourth groups and the fourth group with the lead (of the order of ppb) at the upper end , and

Uranium at the lower end. The fifth group of elements consisted of the triad (Ag, Pt and Se) has concentrations below the limit of quantification. These will not be taken into account for the analysis of the results, because the contents of these elements are below the various accepted standards in the matter. However, we will retain a classification at three levels of grouping, namely the microelements consisted of Al, Sr and Ba which are of the order of ppm to some tens of ppm, the trace elements consist of Pb, Sn, Tl, As, Th, Hg, Cd, Be and U (which are of the order of ppb to a few tens of ppb) and ultra trace elements consisted of Se, Ag and Pt whose concentrations are below the limit of quantification. It should be noted that despite the high values of Al (first position) and Sr (second position), no reference standard for these two elements could be found either in relation to drinking water or by report to Codex Alimentarius (table 4).

The analysis of concentrations average shows only cases of non-compliance with respect to Hg compared to Benin standards and the WHO directive (1972) (see Table 4).

These results make it possible to classify the contaminants in the decreasing order of the concentrations in the following way: Al> Sr> Ba> Pb> Sn> Tl> As> Th> Hg> Cd> Be> U (Table 8).

The classification according to contamination levels shows similar results regardless of the nature of the juice except for pineapple syrup which differs in size (table 8) and in the classification. It is as follows:

- Al> Sr> Ba> Pb> Sn> Tl> As> Th> Hg> Cd> Be> U for the 100% pineapple juice produced in Benin (BPJ 100%);
- Al> Sr> Ba> Sn> Th> Cd> As> Pb> Tl> U for the 100% pineapple juice produced in France (FPJ 00%);
- Al> Sr> Ba> Sn> Pb> Th> Tl> As> Cd> Be> U for Pineapple and Watermelon Cocktail (CPW) and
- Sr> Ba> Al> Sn> Th> Pb> Cd> Tl> U> As> Be> Hg for pineapple syrup (SYR).

These results highlight the influence of the process in the intake of metallic contaminants in food, the syrup being less contaminated.

Overall, the three-class classification is valid regardless of the nature and origin of the fruit as well as the process of processing the fruit into juice. About 10% of Benin's juice samples contain traces of Hg, representing four juice-producing units, this is due to possible accidental contamination.

### 3.2 Comparative Analysis of Metallic Contaminant Levels Against Standards

In order to assess the quality of the juices, we have taken for reference several national and international standards which are as follows: Beninese standards, Brazilian legislation, CODEX (1997), WHO (2006), Canadian legislation.

Thus, according to the results presented in Table 9 and Table 10, the maximum concentrations of chemical elements are below the norms except those of the FRE<sub>2</sub> sample for Ba (1582 ppb) (Beninese and Canadian standards), of the sample (JUA<sub>6</sub>) for Hg (31.7 ppb) Beninese and WHO standards (1972) and the OJA<sub>4</sub> sample for lead (608 ppb) (all reference standards used for water and Codex). Overall sample averages are below standard (Table 3) except for Hg (1.41 ppb). These three elements with high maxima will be further analyzed for contaminated samples as well as the production units affected by this contamination. According to the results in Table 9, the concentrations of Ba in 95% of samples comply with Beninese, Canadian and WHO legislation. For Al concentrations around 25% of the samples analyzed comply with the WHO regulations, while more than 90% (percentile 0.90) of the analyzed samples have a concentration in Hg higher than the Beninese and WHO standards. For Pb, 95% of the samples comply with the Brazilian legislation, 90% with the Beninese standard and 50% with that of the WHO.

Table 9. Characteristics of dispersion of contaminant concentrations in juices (ppb)

Elements	Minimum	Maximum	SD	Percentiles					
				0.25	0.50	0.75	0.90	0.95	0.99
As	<QL	39.3	6.57	0.00	0.97	1.99	4.30	12.41	34.15
Cd	<QL	0.7	0.22	0.00	0.00	0.35	0.48	0.57	0.68
Be	<QL	0.59	0.1	0.00	0.08	0.12	0.18	0.21	0.50
Al	26.4	30620	5979	219	848	4093	10367	15840	28563
Sr	130	4049	494	704.50	819.50	1075	1395.60	1771.40	2421.52
Sn	<QL	43	7.4	1.26	9.06	11.55	16.46	18.74	32.42
Ba	42	1582	198	116.70	162	217	287.67	311.40	1278.40
Hg	<QL	31.7	5.89	0.00	0.00	0.00	0.00	6.96	28.48
Tl	<QL	21.3	4.01	0.72	1.41	2.88	7.06	11.22	19.55
Pb	<QL	608	74.7	3.09	5.15	13.80	39.18	79.56	342.12
Th	<QL	24.7	3.47	0.00	1.68	2.99	5.63	6.27	17.98
U	<QL	1.04	0.14	0.02	0.04	0.06	0.09	0.22	0.63

Here the concentrations lower than quantification limit (QL) are taken approximately equal to zero SD: Standard Deviation



Table 10. Results of Metallic Contaminants Analyses

Samp	Concentrations in elements (in ppb)											
	As	Cd	Be	Al	Sr	Sn	Ba	Hg	Tl	Pb	Th	U
ALA1	0.92±0.04	0.42±0.04	0.12±0.01	82.7±4.1	1200±10	7.77±0.02	213±1	<QL	1.30±0.01	3.71±0.03	1.93±0.07	0.032±0.006
ALA2	<QL	0.38±0.09	0.14±0.01	65.2±4.0	1158±12	<QL	268±3	<QL	2.61±0.03	5.72±0.04	1.65±0.07	0.026±0.002
ALO1	<QL	<QL	0.11±0.04	111±6	752±5	11.4±0.23	77.9±0.4	<QL	1.34±0.01	0.99±0.02	2.85±0.13	0.034±0.007
ALO2	0.97±0.12	0.55±0.04	0.13±0.01	39.7±1.5	1035±14	7.54±0.10	222±2	<QL	1.16±0.01	2.07±0.03	2.49±0.08	0.031±0.001
ALO3	2.42±0.12	<QL	<QL	79.4±3.0	1083±14	<QL	229±2	<QL	5.82±0.05	2.80±0.02	<QL	<QL
ALO4	<QL	0.38±0.07	0.12±0.01	39.8±2.0	1041±14	6.60±0.11	223±1	<QL	1.16±0.02	2.49±0.07	2.51±0.07	0.032±0.005
ALO5	1.67±0.32	<QL	<QL	55.1±1.3	788±12	<QL	85.7±0.5	<QL	6.52±0.21	1.02±0.02	<QL	<QL
ALO6	<QL	<QL	0.12±0.01	26.4±1.2	751±5	6.00±0.08	76.6±0.4	<QL	1.30±0.02	0.92±0.01	2.49±0.10	0.023±0.003
BRA1	<QL	<QL	0.078±0.010	389±18	996±6	9.70±0.13	136±2	<QL	1.21±0.03	3.32±0.02	1.50±0.03	0.039±0.004
BRA2	<QL	<QL	0.11±0.02	424±21	1019±9	13.3±0.1	140±1	<QL	1.23±0.02	4.22±0.13	1.35±0.02	0.036±0.003
BRA3	0.93±0.10	0.31±0.04	0.11±0.04	412±17	1032±6	13.7±0.1	144±1	<QL	1.21±0.02	4.37±0.03	1.22±0.03	0.035±0.002
BRA4	<QL	<QL	0.083±0.001	425±14	1021±7	11.6±0.1	138±1	<QL	1.24±0.02	3.43±0.04	1.30±0.03	0.034±0.005
BRA5	<QL	0.36±0.05	0.11±0.01	416±21	1034±5	12.0±0.1	143±1	<QL	1.20±0.03	4.55±0.02	1.33±0.02	0.037±0.005
BRA6	<QL	<QL	0.067±0.016	375±20	1019±9	7.68±0.08	123±1	<QL	1.38±0.03	1.69±0.02	1.21±0.05	0.025±0.004
CHA1	2.70±0.06	<QL	<QL	3196±122	1923±13	<QL	291±3	<QL	11.1±0.2	8.41±0.03	<QL	<QL
CHA2	3.25±0.20	<QL	<QL	4620±144	2001±16	<QL	299±4	<QL	11.4±0.1	12.3±0.1	<QL	<QL
CHA3	<QL	<QL	0.082±0.003	2616±100	1390±9	14.2±0.13	294±2	<QL	2.16±0.02	12.9±0.1	2.12±0.05	0.066±0.007
CHA5	1.21±0.16	<QL	<QL	2655±131	545±6	14.6±0.04	71.0±0.6	<QL	0.12±0.01	8.53±0.03	3.05±0.04	0.038±0.003
CHA6	3.50±0.26	<QL	<QL	6213±28	655±13	<QL	96.5±1.2	<QL	0.50±0.02	12.8±0.1	<QL	0.074±0.009
FRU1	1.63±0.16	<QL	<QL	6603±212	786±5	<QL	74.6±1.3	<QL	2.69±0.04	4.18±0.05	<QL	<QL
FRU1	<QL	0.50±0.06	0.092±0.011	16455±869	1146±7	13.0±0.2	187±2	<QL	0.82±0.05	9.94±0.07	2.02±0.04	0.056±0.005
FRU2	1.55±0.33	<QL	<QL	4152±88	816±11	<QL	77.7±0.9	<QL	2.82±0.01	4.91±0.11	<QL	<QL
FRU2	<QL	0.42±0.04	0.085±0.023	16203±741	1133±15	11.9±0.1	182±1	<QL	0.79±0.01	9.64±0.06	2.05±0.01	0.058±0.004
FRU3	1.33±0.15	<QL	<QL	4095±128	816±5	<QL	77.5±1.1	<QL	2.90±0.06	4.67±0.06	<QL	<QL
FRU3	<QL	0.42±0.05	0.088±0.016	16701±665	1137±15	13.0±0.1	184±1	<QL	0.79±0.02	10.0±0.1	2.05±0.01	0.055±0.006
FRU4	1.37±0.20	<QL	<QL	3942±46	924±4	<QL	170±1	14.6±0.2	7.48±0.10	3.98±0.06	<QL	<QL
FRU5	1.22±0.12	<QL	<QL	4088±127	926±7	<QL	170±1	25.4±0.2	7.47±0.11	3.97±0.02	<QL	<QL
FRU6	1.29±0.03	<QL	<QL	4004±75	934±10	<QL	170±1	<QL	7.51±0.13	4.21±0.10	<QL	<QL
INN1	0.92±0.31	0.42±0.02	0.11±0.02	135±6	1257±10	5.09±0.05	292±2	<QL	0.27±0.01	0.29±0.01	2.54±0.05	0.027±0.002
INN2	0.93±0.04	<QL	0.12±0.02	108±6	1226±10	<QL	283±4	<QL	0.27±0.01	0.44±0.01	2.24±0.05	0.031±0.002
JAF2	0.91±0.16	0.56±0.02	0.080±0.007	139±8	790±12	5.05±0.07	267±1	<QL	0.57±0.01	0.27±0.01	2.72±0.04	0.060±0.002
JUA2	3.46±0.32	<QL	0.081±0.007	1188±48	600±2	19.9±0.4	184±2	1.86±0.11	3.83±0.02	4.19±0.02	4.24±0.18	0.077±0.006
JUA3	6.48±0.20	<QL	<QL	472±17	609±1	<QL	189±2	<QL	21.3±0.1	5.05±0.07	<QL	<QL
JUA4	1.97±0.18	0.37±0.01	0.10±0.03	413±14	617±8	18.7±0.1	203±1	0.99±0.03	4.37±0.04	6.66±0.14	1.61±0.03	0.077±0.003
JUA5	5.41±0.40	<QL	<QL	143±6	584±9	<QL	176±1	<QL	19.4±0.2	2.37±0.03	<QL	<QL
JUA6	4.85±0.08	<QL	<QL	304±9	678±9	<QL	151±2	31.7±0.6	7.08±0.08	3.03±0.02	<QL	0.075±0.005
JUD1	2.14±0.15	0.45±0.10	0.30±0.02	2528±135	735±3	10.5±0.1	159±1	<QL	1.50±0.02	11.4±0.1	<QL	0.27±0.006
JUD2	2.69±0.24	<QL	0.49±0.02	21488±925	1765±5	10.6±0.1	173±2	<QL	1.65±0.06	15.3±0.6	24.7±1.0	0.54±0.01
JUD3	2.89±0.46	<QL	0.59±0.04	30620±1145	2280±18	9.12±0.02	181±1	<QL	1.69±0.05	16.8±0.2	17.4±0.4	0.59±0.01
JUS1	<QL	0.48±0.07	0.070±0.017	8523±469	903±9	14.9±0.1	168±1	<QL	1.44±0.04	31.4±0.1	1.21±0.06	0.039±0.002
JUS2	2.04±0.18	0.70±0.07	0.086±0.004	16109±871	879±7	31.5±0.4	161±1	<QL	1.44±0.01	49.8±0.3	<QL	0.091±0.009
JUS3	1.99±0.03	<QL	0.096±0.012	8282±369	912±5	16.9±0.1	163±1	<QL	1.50±0.03	31.1±0.4	<QL	0.063±0.002
JUV1	1.08±0.30	<QL	0.10±0.01	225±11	985±15	10.0±0.04	143±2	<QL	0.42±0.01	24.8±0.2	5.77±0.08	0.043±0.004
JUV2	1.02±0.15	<QL	0.14±0.03	788±41	1052±7	9.16±0.18	146±1	<QL	0.43±0.01	25.1±0.1	5.53±0.12	0.051±0.008
JUV3	<QL	<QL	0.10±0.01	3558±146	910±8	12.9±0.12	135±1	<QL	0.41±0.03	16.9±0.1	7.32±0.24	0.048±0.002
JUV4	0.91±0.11	<QL	0.19±0.03	290±16	516±7	5.49±0.05	89.9±0.6	<QL	0.93±0.03	7.06±0.08	3.62±0.04	0.057±0.005
JUV5	0.96±0.09	<QL	0.21±0.05	349±12	520±6	6.31±0.07	84.7±0.9	<QL	0.96±0.01	7.40±0.09	3.73±0.08	0.057±0.003
JUV6	0.91±0.07	<QL	0.21±0.05	318±17	518±4	6.37±0.11	84.8±0.7	<QL	0.97±0.01	7.09±0.13	3.58±0.04	0.057±0.001
OJA2	18.3±0.6	<QL	<QL	1167±21	770±2	17.3±0.1	94.2±1.4	<QL	4.06±0.06	208±1	<QL	<QL
OJA2	0.93±0.03	<QL	0.063±0.008	5074±250	663±5	18.3±0.3	84.6±1.2	<QL	0.14±0.01	9.00±0.11	2.67±0.04	0.065±0.002
OJA3	33.7±1.3	<QL	<QL	1075±21	1141±4	18.6±0.3	226±3	26.0±0.4	14.2±0.3	319±1	<QL	<QL
OJA3	<QL	<QL	0.056±0.011	5158±230	669±5	16.9±0.2	84.7±0.9	<QL	0.14±0.01	9.05±0.03	2.53±0.06	0.064±0.001
OJA4	24.3±1.4	<QL	<QL	8256±197	1397±12	43.0±0.7	242±3	<QL	16.8±0.2	608±1	<QL	<QL
OJA5	25.5±1.3	<QL	<QL	3974±52	811±9	16.7±0.1	60.6±0.7	<QL	3.54±0.04	59.9±0.6	<QL	<QL
VIB2	<QL	0.47±0.06	<QL	162±5	317±3	10.3±0.1	233±3	<QL	0.21±0.02	1.36±0.03	2.21±0.06	0.047±0.004
VIP2	2.16±0.02	0.41±0.06	<QL	150±6	712±10	18.8±0.6	154±2	0.62±0.02	1.52±0.05	3.89±0.13	0.86±0.03	0.061±0.003
VIP3	8.49±0.44	<QL	<QL	67.2±1.7	326±2	<QL	44.3±0.6	<QL	<QL	1.02±0.03	<QL	<QL
VIP4	1.76±0.13	0.37±0.04	0.084±0.003	301±14	654±10	11.1±0.1	108±1	<QL	1.36±0.01	3.54±0.02	0.57±0.01	0.087±0.007
VIP5	3.90±0.15	<QL	<QL	320±10	720±7	<QL	123±1	28.2±1.0	6.98±0.01	3.73±0.02	<QL	0.086±0.005
VIP6	1.47±0.10	0.36±0.01	<QL	291±14	654±3	10.1±0.05	108±1	0.77±0.01	1.36±0.01	3.25±0.02	1.04±0.03	0.088±0.003
VIP7	3.88±0.09	<QL	<QL	363±11	663±2	<QL	119±1	<QL	6.88±0.03	3.67±0.12	<QL	0.10±0.01
VIT1	1.12±0.17	<QL	0.12±0.02	4717±146	816±3	30.0±0.3	180±1	<QL	1.12±0.03	62.6±0.7	5.65±0.09	1.04±0.03
VIT2	0.92±0.22	<QL	0.11±0.02	217±11	814±9	8.11±0.03	145±1	<QL	1.04±0.02	32.3±0.2	4.56±0.14	0.032±0.004
VIT3	<QL	<QL	0.095±0.012	507±20	777±6	5.38±0.05	145±1	<QL	1.02±0.03	19.8±0.2	3.59±0.07	0.033±0.003
VIT4	<QL	<QL	0.11±0.01	497±25	1167±3	10.3±0.1	155±2	<QL	0.57±0.03	40.9±0.5	5.04±0.29	0.052±0.005
VIT5	1.06±0.25	<QL	0.12±0.01	1018±54	1198±9	9.88±0.11	157±1	<QL	0.53±0.01	115±1	4.06±0.04	0.032±0.003
VIT6	<QL	<QL	0.096±0.009	493±19	1177±13	10.1±0.1	158±1	<QL	0.57±0.01	41.1±0.2	3.64±0.06	0.056±0.008

keys to abbreviations: Samp: Samples

The purpose of the analysis of dispersion characteristics around the median (percentiles) and the average is to highlight the proportion of samples affected by the contamination of juices (Table 9).

Thus, more than 75% of the samples have a concentration lower than the average in As, Hg and Pb elements. On the other hand, for As, Tl and U, more than 75% of the values are lower than or equal to the average, whereas the elements Cd, Be, Al, Sr, Sn, Ba, Th have more than 75% above average values ( $Q_3$ ). Nevertheless, Be, Sn and Ba in a lesser measure are uniformly distributed around the mean (average close to the median). The calculated averages of the samples comply with the different standards except Hg, of which more than 75% ( $Q_1$ ) of the samples comply with international standards (Table 4). Box-and-mustache graphs will further identify certain manufacturing units that do not meet the standards for Ba, Hg and Pb.

The analysis of average concentrations (Table 4) shows only cases of non-compliance with respect to Hg compared to Benin standards and the WHO directive (1972). These are FRU (6.67 ppb), JUA (5.76 ppb), OJA (5.20 ppb) and VIP (4.14 ppb). Further analysis by sample will allow us to highlight any major contaminations to the elements studied.

### 3.3 Comparative Analysis of Pineapple Juices and Syrup Versus Microelements (or Minor Elements)

Although Al, Sr and Ba were at the higher end of the classification in increasing order of element concentrations, only Sr is not regulated on human drinking water. The representation of the concentrations of the samples according to the unit highlights the contributions of the different units in the distribution with respect to the mean and median.

A comparative analysis of the four types of beverage compared to the minor elements shows that 100% pineapple juice has the highest levels of Al while the cocktail has similar levels of Sr to those of French juice (Table 8). On the other hand, the contents of Sr are similar in the juices. The distribution of Ba is on average the same as the process.

Compared to the minor elements and the same juice manufacturer, the comparison of 100% juice of pineapple with the cocktail reveals on the whole a higher rate of Al and Sr (Table 8).

### 3.4 Comparative Analysis of Pineapple Juices and Syrup Versus Trace Elements

As for trace elements, Pb is predominant in Benin juices and much larger in 100% pineapple juice than in other products (Table 8). On the other hand, Sn contents are uniform in all products. In addition, there is a slight increase in the Cd concentration in cocktails compared to other products.

Apart from Sn, which is uniform in all juices, the syrup is generally less contaminated with toxic metals. Lead (Pb) concentration levels are determined by the contaminated soil because pineapple plantations are generally located near roads. The tin (Sn) appears in 100% pineapple juice samples and is not found at all in cocktails. The cocktail proved to be more contaminated by Tl than 100% pineapple but the Pb is in similar rates in the juice as in the cocktail. Watermelon is believed to be the main source of Tl, while other trace elements, especially Sn, are thought to be tributaries of pineapple.

### 3.5 Contamination by Microelements in Some Units

#### 3.5.1 Intra-Unit Variability of Microelements

Although Al, Sr and Ba are at the higher end of the classification in increasing order of element concentrations, only Ba is regulated on human drinking water. The representation of the concentrations of the samples according to the unit highlights the contributions of the different units in the distribution with respect to the average and the median (Figure 2). JUD, SAN units more particularly; JUS and JAF are the most determinant in this distribution for Aluminum (Table 11). On the other hand FRE, JUD and SAN for the Sr and finally FRE and SAN for the Ba are the most determinants for the strong values obtained. However, there is no standard for classifying the Al and Sr elements despite their preponderance (Table 10). For Ba, FRE juices show above-standard concentrations of 1000 ppb while FRE<sub>2</sub> and FRE<sub>4</sub> have concentrations of 1582 ppb and 1252 ppb respectively (Table 10). These values are higher than those obtained in the literature review (tables 1 & 2).

Table 11. Average concentrations according to chemical elements and juice production units

Unit	N	Element concentrations (in ppb)											
		As	Cd	Be	Al	Sr	Sn	Ba	Hg	Tl	Pb	Th	U
ALA	2	0.46	0.40	0.13	73.95	1179	3.88	240.50	< QL	1.96	4.71	1.79	0.03
ALO	6	0.84	0.16	0.08	58.60	908	5.26	152.40	< QL	2.88	1.72	1.72	0.02
BRA	6	0.16	0.11	0.09	407	1020	11.33	137.33	< QL	1.25	3.60	1.32	0.03
CHA	6	2.51	<QL	0.01	3509	1107	4.80	182.30	< QL	4.21	9.34	0.86	0.06
FRE	5	0.60	0.06	0.02	3288	1289	3.79	633	< QL	3.14	4.22	0.34	0.07
FRU	6	1.40	<QL	< QL	4481	867	0.00	123.30	6.67	5.14	4.32	<QL	< QL
INN	2	0.92	0.49	0.10	137	1024	5.07	279.50	< QL	0.42	0.28	2.63	0.04
JAF	2	0.82	0.30	0.10	5290	789	8.44	253.30	< QL	0.30	0.17	1.09	0.03
JUA	6	3.70	0.06	0.03	571	623	8.09	186.83	5.76	9.52	4.16	1.27	0.04
JUD	3	2.57	0.15	0.46	18212	1593	10.07	171	< QL	1.61	14.50	14.03	0.47
JUS	3	1.34	0.39	0.08	10971	898	21.10	164	< QL	1.46	37.43	0.40	0.06
JUV	6	0.81	<QL	0.16	921	750	8.37	114	< QL	0.69	14.73	4.93	0.05
LAS	1	<QL	<QL	0.08	30199	1112	6.73	119	< QL	1.51	22.70	1.53	0.07
OJA	5	28.22	< QL	< QL	3121	969	22.14	1423	5.20	8.62	260	< QL	< QL
PAS	6	1.29	< QL	0.19	179.30	784	8.56	199	< QL	2.05	7.80	6.21	0.04
SAN	9	0.22	0.46	0.12	13714	1268	12.06	240	< QL	1.08	6.89	2.25	0.06
SIR	1	< QL	0.47	< QL	162	317	10.30	233	< QL	0.21	1.36	2.21	0.05
TRO	2	< QL	0.16	0.09	1182	918	9.16	115	< QL	0.66	24.95	1.40	0.03
VIB	2	0.47	0.22	0.08	133.30	769	5.30	279	< QL	0.23	0.95	2.10	0.04
VIP	7	2.79	0.10	0.03	228	640	5.61	111	4.14	2.79	3.03	0.80	0.07

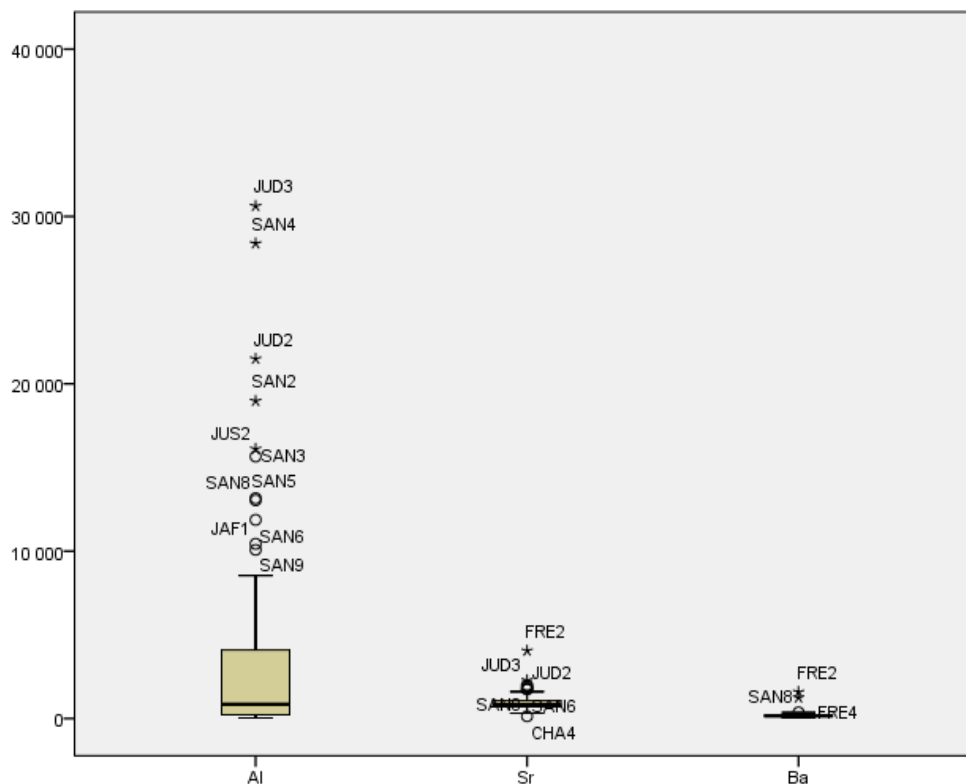


Figure 2. Whisker box distribution diagram for Al, Sr and Ba concentrations in ppb

### 3.5.2 Intra-Unit Variability of Trace Element Concentrations (Hg and Pb)

#### Case of mercury (Hg)

Of all the trace elements, only Hg and lead have sufficiently high levels that can exceed the standard (Figures 3 and 4) as indicated in the previous paragraph.

As for Hg, the units FRU, JUA, OJA and VIP presented values higher than the different existing standards which fix a concentration limit of 1 ppb (Table 4), if the JUA<sub>4</sub> unit has a concentration at the limit of the standards (0.99 ppb), the concentrations of JUA<sub>2</sub> and more particularly of JUA<sub>6</sub> are above the norms with values of 1.86 ppb and 31.70 ppb respectively; the same is true of OJA<sub>3</sub> and VIP<sub>3</sub> with concentrations of 26.00 ppb and 28.20 ppb respectively. The FRU

unit is also concerned by the contamination with Hg, in particular with FRU<sub>4</sub> and FRU<sub>5</sub> the Hg concentrations of which are respectively 14.6 ppm and 25.40 ppm. These values are higher than that in literature literature review (Tables 1 & 2).

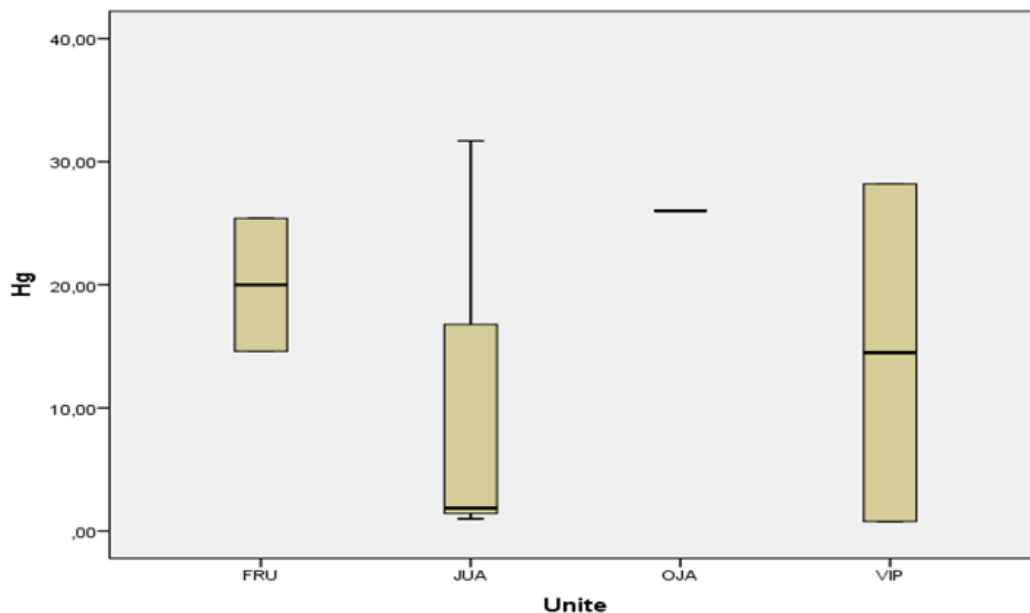


Figure 3. Whisker box distribution diagram for Hg concentrations in ppb according to the production units

**Case of lead (Pb)**

With regard to Pb, the units OJA, VIT, JUS and TRO are shown by the graph of Figure 4. They have concentrations exceeding the standards which are 50 ppb.

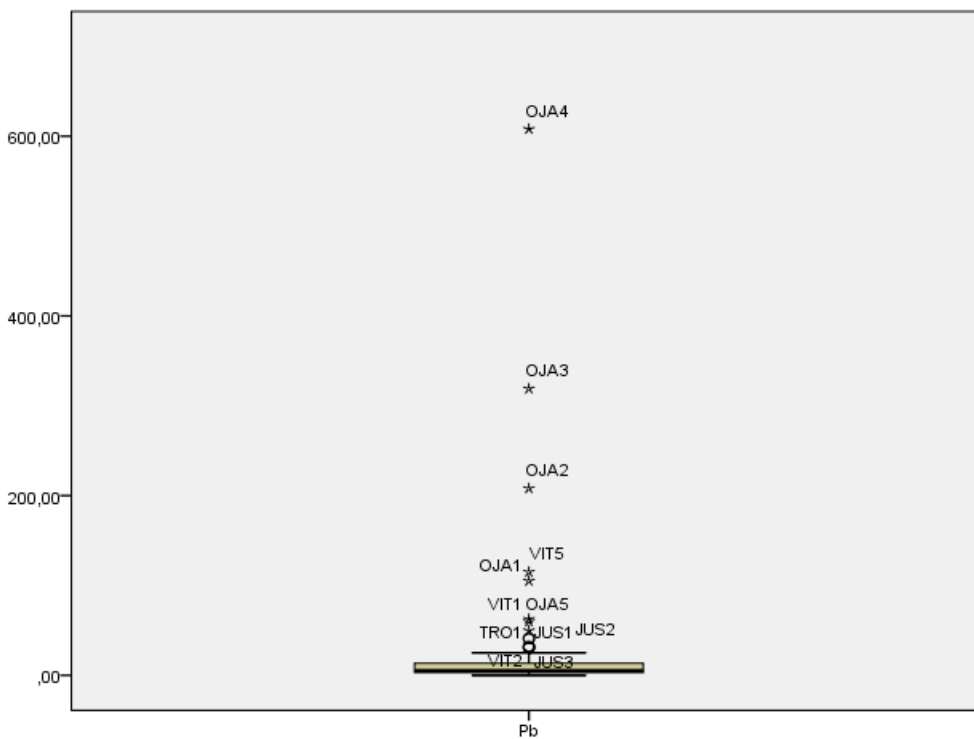


Figure 4. Whisker box distribution diagram for Pb concentrations in ppb

All juices from OJA unit production contain more than twice the reference value of Benin (Table 11) and Codex (50 ppb) but JUS approaches with a concentration of 49.80 ppm for JUS<sub>2</sub> (Table 10). The VIT1 juice sample from the VIT unit also crossed the threshold with a concentration of 62.60 ppb. These values are slightly above the results of the literature.

Finding substantial amounts of contaminants in the various juice samples cited above raises the issue of food control. These studies should be appraised in order to determine precisely the source of contamination and to consider source elimination strategies for bringing products up to standard.

#### 4. Discussion

According to Anna Szymczycha-Madeja and al. (2013), the concentrations of Al, Cd, Pb determined in pineapple juices by ICP-MS are below the limit of quantification, except for Ba for which they obtained 38 ppb, while reviews of the literature on pineapple juices (Adetola and al. 199; Szymczycha-Madeja and al. 2014) revealed concentrations in the following ranges (in ppb): Al (ND-4200 ppb) (Braganca et al. 2011; Szymczycha-Madeja and al. 2013; Arruda and al. 1993; Bao and al. 1999; Lopez and al. 2002; Santos Froes and al. 2009), Ba (40-110 ppb) (Szymczycha-Madeja and al. 2013; Santos Froes and al. 2009), Cd (ND-12 ppb) (Tormen and al. 2011; Szymczycha-Madeja and al. 2013; Williams and al. 2010; Santos Froes and al. 2009), Pb (ND-240 ppb) (Tormen and al. 2011; Szymczycha-Madeja and al. 2013; Santos Froes and al. 2009), Se (14-15 ppb) (Arruda and al. 1994), Sn (ND-450 ppb) (Hotegni and al. 2016; Szymczycha-Madeja and al. 2014) and Sr (88-620 ppb) (Williams and al. 2010; Camara and al. 1995). These values are lower than the extreme values obtained during this work for Al, Ba, Pb and Sr (Table 2). On the other hand, these concentrations are higher for Cd, Se and Sn than those presented in this study.

In addition, Lai and al. (2016) have obtained the following concentrations: Al (88 ppb), Ba (114 ppb), Cd (12 ppb), Pb (236 ppb), and Sr (621 ppb). These concentrations are lower than those obtained during the present study except for the lower Pb and the Cd, which is consistent with our results (Table 2).

Paula and al. (2015) have made a rapid assessment of the metallic contamination in commercial fruit juices by inductively coupled mass spectrometry after simple dilution. The mean values obtained for pineapple juice are 880 ppb for Sr, 1.1 ppb for Cd and 1.6 ppb for Pb. If the mean values obtained in our work are consistent with these results for Sr, this is not the case for the mean Cd concentrations which is higher and Pb which is lower than our results (Table 3). But the average grades of Pb are similar to those of (Paula and al. 2015) and al. who obtained (20.75 µg/l) for Pb concentration (Table 1 and 2).

Pineapple is the main source of Al and Sr in juices. Ba would be provided by ferralitic soils characteristic of the study area (Figure 3). These results are in agreement with those of (Paula and al. 2015) who established that pre- and post-harvest factors determine the levels of the selected risk elements in 100% fruit juices.

However, there is no standard for classifying the Al and Sr elements despite their preponderance (Figure 2). Some values of Ba (three samples) are higher than those obtained in the literature (Codex Alimentarius 1999; Miele and al. 2014; Szymczycha-Madeja and al. 2014; Szymczycha-Madeja and al. 2013).

Overall, the syrup contains fewer pollutants than the entire juices combined. Would it be an average of eliminating these elements? If this is the case, a deepening of the phenomenon would make it possible to find a definitive solution to the decontamination of juices.

Finding substantial amounts of contaminants in the various juice samples cited above raises the issue of food control. These studies should be appraised in order to determine precisely the source of contamination and to consider source elimination strategies for bringing products up to standard.

#### 5. Conclusion

The concentration averages are consistent with that of the literature. These averages show juices, for the most part, in compliance with quality standards of food and drinking water. However, some juice samples are heavily contaminated, especially in Pb, Hg and Ba, which sometimes exceeds the reference standards. Al and Sr showed the highest levels of contamination, although Sr is not regulated by individual countries and World Health Organization (WHO). This study opens perspectives of deepening allowing to understand the mechanism of migration of the contaminants in the human food chain and to propose strategies of bringing back to norm of the products manufactured in the units concerned by the high levels of contaminants.

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