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# Quality control by the determination of heavy metals in new variety of cocoa (*cocoa mercedes*) Côte d'Ivoire.

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**Abstract** : Three heavy metals Cadmium (Cd), Chromium (Cr) and Lead (Pb) were investigated in samples (almonds, teguments, fresh juice and fermented juices) of cocoa (*cocoa mercedes*). The *Cocoa "Mercedes"* is promoted in Côte d'Ivoire to substitute the old plants in order to increase the productivity. The cocoa samples were collected from two (2) experiment stations (Abengourou (East) and Divo (Southwest)) and two (2) extension stations (Adzope (Southeast) and Yamoussoukro (Central)) of Côte d' Ivoire. Each sample was mineralized by digestion (3:1 HF: $HNO_3$) and purified. The purified liquid extract was analyzed by Atomic Absorption Spectrometry (AAS) with graphic furnace according to Quality Control /Quality Assurance QC / QA procedures. The results revealed the bioavailability of the tree heavy metals with variable concentration in different parts of the cocoa. The lowest concentrations were observed in Cr (mean: 4.50 - max: 8.90). The study brought up the concentrations (in µg / kg) higher for Pb (mean = 454.17 and max = 1690. 00) and Cd (mean = 126. 08 and max = 644.00).

Keywords: Heavy metals, Cacao Mercedes, *Theobroma cacao* , Quality control, Bioavailability.

# Contrôle de la qualité par la détermination de métaux lourds dans une nouvelle variété de cacao (*cacao mercedes*) en Côte d'Ivoire.

**Résumé** : Les métaux lourds Cadmium (Cd), Chrome (Cr) et Plomb (Pb) ont été recherchés dans les échantillons (amandes, téguments, jus frais et jus fermentés) de cacao (*cacao mercedes*). Le *cacao mercedes* est en vulgarisation en Côte d'Ivoire pour le renouvellement du verger cacaoyer ivoirien. Les échantillons de cacao ont été prélevés sur deux (2) stations d'expérimentations (Abengourou à l'Est et Divo au Sud-ouest) et deux (2) stations de vulgarisation (Adzopé au Sud-est et Yamoussoukro au Centre) de la Côte d'Ivoire. Chaque échantillon a été minéralisé par digestion (3:1 HF:$HNO_3$) et purifié. L'extrait liquide purifié est analysé par la Spectrométrie d'Absorption Atomique (AAS) au four de graphite conformément aux procédures de Contrôle Qualité /Assurance Qualité (CQ/AQ). Les résultats ont permis de montrer une bioaccumulation dans les différentes parties du cacao des trois métaux lourds avec des teneurs variables. L'étude fait apparaitre les concentrations (en µg / kg) relativement faibles pour le Cr (moy : 4.50 - max : 8.90) plus élevées pour le Pb (moy= 454.17 et max=1690.00) et pour le Cd (moy =126.08 et max= 644.00).

Mots clés: Métaux lourds, Cacao Mercédès, *Theobroma cacao,* Contrôle qualité, Bioaccumulation.

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## 1. Introduction

Cocoa (*Theobroma cacao* L.) is known in the world for its derived products. Among them, chocolates are well appreciated and used in all ages. Côte d'Ivoire was in the 90s the first producer of cocoa's beans. Actually, it represents 35-40 % of world cocoa beans production. However, the *Forastero*, *Trinitario* and *Criollo* which are the three main cocoa varieties planted in Côte d'Ivoire have more than 40 years of age. This leads to a decline in cocoa production performance. To maintain its position as world leader in cocoa beans production, the "Centre National de Recherche Agronomique (CNRA)" of Côte d' Ivoire has been entrusted to renew the orchard with a new hybrid. This new hybrid is called "*cocoa Mercedes"* and it is selected because of its main characteristics: the precocity of its production (18 months instead of 5 years for the traditional cocoa) and the productivity (3 tons per hectare per year instead of 0.3 tons for traditional cocoa). It had been massively introduced over the last five (5) years in the fields by farmers because the seeds were free.

The plants of cocoa *mercedes* were grown under tropical conditions at the experimental farm (Station) of the "*Centre National de Recherche Agronomique* (CNRA)" of Côte d'Ivoire. We selected four (4) regions located in Abengourou (East): Station 1 (St1), Divo (South-west): Station 2 (St2), Adzope (South): Station 3 (St3) and Yamoussoukro (Center): Station 4 (St4), (Figure 1).

Past research has increased productivity and improved more the knowledge of the physico-chemical and biological composition of cocoa [1-3]. Most of the studies highlighted and showed that cocoa's chemical and molecular composition have therapeutic and nutritional interest [4].

Despite these results, the scientific committee of the Developed Countries imposed quality control of food products. Now, more regulatory measures and warning systems have been developed to control food at the frontiers of Europe and United States of America. In 2010 the European commission in Rapid Alert For Food and Feed (RASFF) has notified that 52% of products from Third World Countries contained microorganisms, pesticides and heavy metals[5].The RASFF is based on alert notifications, information and rejection of food containing high level of concentration of contaminants (pesticides, heavy metals, pathogens and mycotoxins). It is necessary to know the baselines of residual contaminants in food under the normal conditions of production. As there are more than thousands chemical contaminants listed in accordance with international regulations, it would be difficult to analyze all of them in this present study. We are interested in three heavy metals because of their natural and artificial origin[6]. The aim of the present study is to determine the bioavailability of Cadmium (Cd), Lead (Pb) and Chromium (Cr) in new cocoa hybrid "*cocoa Mercedes"* of Côte d'Ivoire. There are exhaustive lists of analytical methods. The Methods used was the standard and classic methods of analysis. It has been approved by Food and Agriculture Organisation (FAO) and the International Agencies of Atomic Energy (IAAE)[7, 8]. It consisted of the mineralisation by acid solution and analysis by Atomic Absorption Spectrometry with graphite furnace.

## 2. Materials and methods

### 2.1. Sampling

Four (4) experimentation farms of CNRA's corresponding to four (4) stations of sampling were selected and located in Côte d'Ivoire (Figure I). Cocoa sample were randomly collected from the four (4) stations St1, St2, St3 and St4. For each station farm, 1000 kg of pods of cocoa were weighed. The harvested pods were broken to extract the beans. To create representative for each station farm, we made tree (3) homogenate composite samples.

### 2.2. Samples preparation

The fresh juice resulting from cocoa beans was collected and lyophilized. The samples were stocked in small glass bottles and stored in a cryogenic condition at -20°C until used for the different analysis.

The beans were fermented for a period of four (4) days. After fermentation, the beans were sun dried on mats made from palm leaves. The dry cocoa beans were sieved to remove dirt. Once the cocoa beans were dry, teguments were separated from the almonds. Samples were ground and transformed in a homogeneous powder after sieving on a stainless steel sieve (63µm of Porosity). The powder was then stocked in small glass bottles.

### 2.3. Mineralization of sample

For each sample, 0.2 g of freeze-dried cocoa sample were weighed (P), in a Teflon flask. 1 ml of Acid solution (3:$HNO_3$ conc. and 1: HCl conc.) mixed during 1 hour at +20°C.

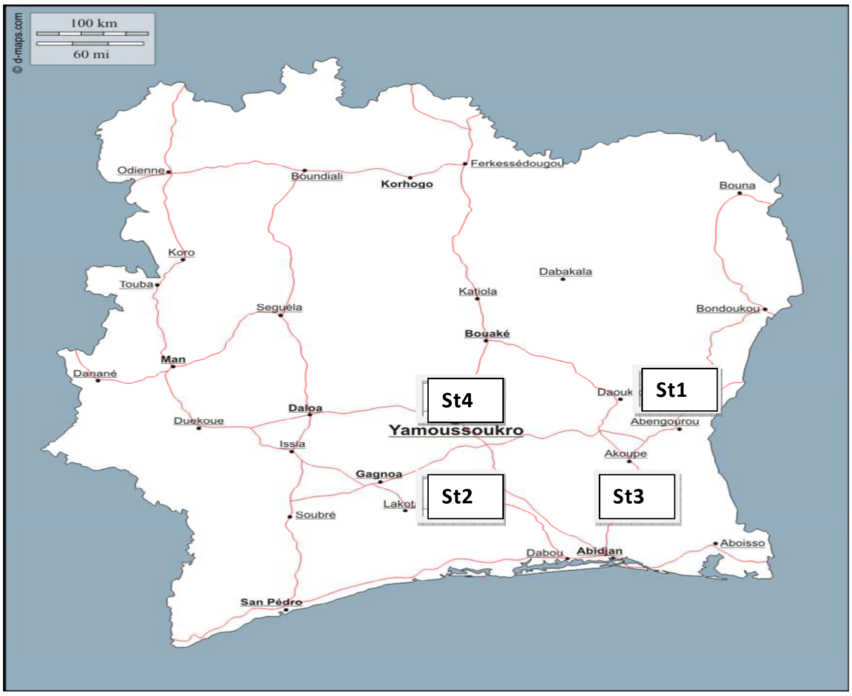


**Figure 1**: Location of the four stations on the map of Côte d'Ivoire

After, fill with 6 ml of conc. boric Acid in the Teflon flask. The mixture was heated at 100 ± 5°C in water bath for 3 hours. Finally, the mineralised residue was cooled to 20°C and 6 ml of conc. fluoridric acid HF was added. We diluted the solution (residue + HF) with deionised water to obtain 100ml, the final volume (Vf) of mineralised liquid [9].

## 2.4. Analysis

The mineralised liquid (Vf) was analysed by Atomic Absorption Spectrometry- Graphite furnace (AAS) calibrated with PERKIN ELMER GF AAS mixed standard 5% $HNO_3$/ HF/ HCl. Certify NIST. The accuracy was 0.5% and the precision was 10% for each element. All measurements were performed in triplicate using Control Quality solution (QC) of Cd, Cr and Pb[10, 11]. **Table I** shows the conditions of calibration and the program fixed on the AAS for each element before analyzing the blanks, the standard solutions of calibration and the natural sample.

**Table I:** Calibration data and conditions of analysis by Atomic Absorption Spectrometry- Graphite furnace Atomic Absorption Spectrometry (AAS).

| **Elements** | **Cd** | **Cr** | **Pb** |
|---|---|---|---|
| Instrument type | Zeeman | Zeeman | Zeeman |
| Conc. unit | µg/l | µg/l | µg/l |
| Instrument Mode | Absorbance | Auto normal | Auto normal |
| Sampling Mode | Auto normal | Auto normal | Auto normal |
| Calibration Mode | Concentration | Concentration | Concentration |
| Measurement mode | Peak Area | Peak Area | Peak Area |
| Replicates' standards | 3 | 3 | 3 |
| Replicate samples | 3 | 3 | 3 |
| wavelength | 1800 nm | 2300 nm | 2100 nm |
| slit with | 0.5nm | 0.5nm | 0.5nm |
| gains | 71% | 56% | 34% |
| Lamp current | 4.0mA | 7.0 mA | 8.0mA |
| Temperature | 1800 °C | 2300°C | 2100 °C |
| Total volume | 20 µg/l | 20 µg/l | 20 µg/l |

**Table II:** Concentration of six calibrations solution

| | Cd (µg/l) | Cr (µg/l) | Pb (µg/l) |
|---|---|---|---|
| Standard 1 | 0.0 | 0 | 0 |
| Standard 2 | 0.5 | 4 | 10 |
| Standard 3 | 1.0 | 8 | 20 |
| Standard 4 | 1.5 | 12 | 30 |
| Standard 5 | 2.0 | 16 | 40 |
| Standard 6 | 2.5 | 20 | 50 |

## 2.5. Statistical analysis

All results have been summit to excel Microsoft. For each sample, three analyses have been performed and then an average value has been calculated for the standard deviation (σ) and the Coefficient of Variation (CV)[12].

## 3. Results and discussion

The Calibration curves of each element (**figures. 2 - 4**): Abs (nm) = $f$ ( $C_{\mu g/l}$ ) were automatically built with six (6) standard solutions with different concentrations (**Table II**). The ranges of calibration concentration of the solution for the elements were Cd (0-2.5 µg/l)), Cr (0-20 µg/l) and Pb (0- 50 µg/l)). The regression equation coefficients and correlation coefficient $R^2$ were also displayed for Cd [ y = 0,031x + 0,010, $R^2$ = 0,988] **(1)**, Pb [ y = 0. 000x + 0,003 $R^2$ = 0.996] **(2)**, and Cr [y = 0,01x + 0,007, $R^2$ = 0,995] **(3)**. The $R^2$ of the linear regression of the curves were superior to 0.99. That was a good linear correlation between the absorbance (nm) and concentration (µg/l). Also, the linearity was satisfactory for measurement of the level of concentration.

Using the calibration curve for each element, the device gave directly the results (µg/l) for each sample. The limit of quantification (LQM) was respectively: Cd (0.5 µg/l), Pb (10 µg/l) and Cr (5 µg/l). Only the values superior or equal to the LQM were considered. The calibration verified and performed by the solution of control (NIST): Cd (2,0 µg/l ±10%), Cr (16 µg/l ±10 ) and Pb (40 µg/l ±10%).

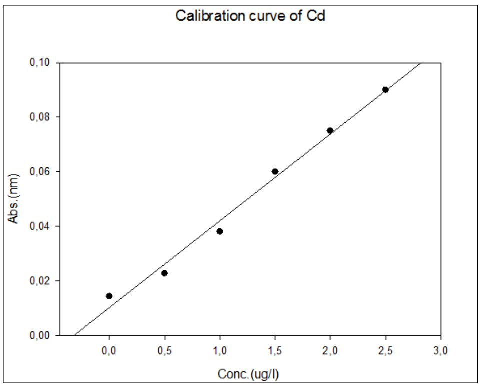


**Figure 2**: Calibration's curve of Cd

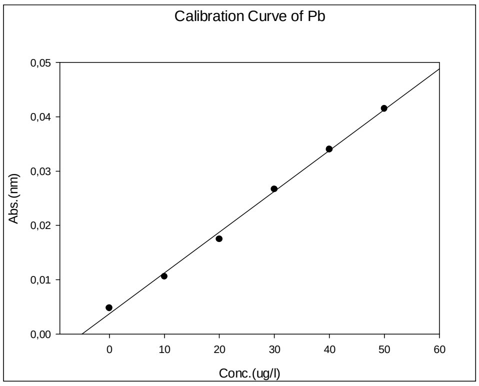


**Figure 3**: Calibration's curve of Pb

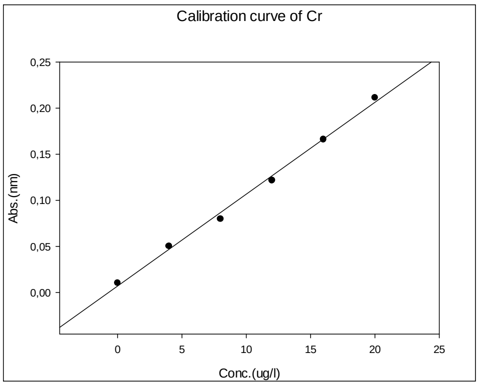


**Figure 4**: Calibration curve for Cr

### 3.1. Quantitative analysis

Tables III, IV and V show the concentrations of the cadmium (Cd), chromium (Cr) and lead (Pb). The concentrations (µg/kg) of dry weigh were calculated by the following formula (4) from the recommended method of IAAE [8].

$$C\ (\mu g/kg\ ) = \ C1(\mu g/l) \times \ 1000 \times \frac{Vf(l)}{P(kg)} \times \frac{1}{fD} \qquad \textbf{(4)}$$

*C* = Concentration of the element µg/kg
*C1* = Concentration (µg/l) read automatically by the Calibration Curve
*Vf* = Final volum (100ml) mineralised liquid
*P* = Sample's weight (2g = 0.002kg)
*fD* = Factor of Dilution :

$$fD = \frac{Vp(ml)}{VfD\ (ml)} \qquad \textbf{(5)}$$

*Vp* = Volume (ml) sampled from the mineralised liquid
*VfD* = Total volum of dilution (ml)

**Tables III, IV** and **V** also show the average the standard deviation and the coefficient of variation (CV). The CV was the ratio of the standard deviation to the mean. The higher the value of the coefficient of variation, the greater the dispersion around the average is large. The results showed that all the CV were under 10 % and ranged between 4-9.6 % for the Cd, 7-10,5 % for Cr and 2.5-7.9 % for Pb.

- Cadmium (Cd) is a disturbing metallic element. Its main components are solid. The different forms are cadmium chloride ($CdCl_2$), cadmium sulfate ($CdSO_4$), cadmium sulfide CdS. Industrial activities are the main source of air emissions [13, 14].

The **Table III** shows the results of analysis. The concentrations are between 0.5 and 644.0 µg/kg. The average concentration is 126.08 µg/kg. The high values are observed in the tegument of the cocoa (344.0 - 644.0 µg/kg). The lowest values are obtained in the juice (0.5 - 86.7) and almonds (0.5-88.8 µg/kg). The average values could be comparable with the concentration of Cadmium met in the food (0.05 - 0.1 mg/kg)[13]. We notice that the highest value (644.0 µg/kg) is observed on the teguments' samples. This level of value was determined in cocoa powders. The concentrations reported by the authors on the cocoa from different geographical origins were ranged from 94-1833 µg/kg[15]. The highest concentration is indicative of contamination. In this assumption we have to know if the soils of area did or not contain the traces elements. In the absence of results of soil collected during the sampling of this study, we used the data provided from the studies of soil diagnosis based on the geochemistry of the regions[16]. The soils contain Cd with average concentration ranged from 0.1-1.9 mg/kg. Relatively low concentrations in the soil can be seen. Despite this, we found relatively high levels in cocoa. The presence of Cd in the plants can be explained by the properties of bioaccumulation from the soil. The authors also highlighted that cadmium accumulates in the root of the plant. Therefore atmospheric deposition is negligible[14,17]. The concentrations of the phosphate fertilizer and application of soil could represent significant sources of cadmium.

- Chromium (Cr), exists in various oxides of chromium such as Chromium oxide II (CrO); Chromium oxide (III), $Cr_2O_3$; Chromium oxide (IV) or chromium dioxide $CrO_2$; Chromium oxide (VI) or chromium trioxide or chromic acid $CrO_3$. Chromium was present in the environment in the form (III)[18].

The **Table IV** displays the concentrations of chromium that vary between 1.03 and 8.93 µg/kg. The average value is 4.5 µg/kg. The lowest values are obtained in the juice (1.03 - 5.00 µg/kg). The higher values are observed in the tegument of the cocoa (7.48 - 8.93 µg/kg). The highest value of concentration is inferior to the limit generally observed (0.1 mg/kg)[13]. The level of concentration is low and comparable with those found in similar studies, according to the geochemistry results of the regions[16]. The Cr appeared in the soil with significant concentrations (10 - 48 mg/kg). The low concentration in cocoa can be explained by the factor of bioaccumulation which is low in comparison to that of other heavy metals. Some authors have shown that the chromium is abundantly present in the soil[18]. But it is mainly in organic form and hard to be assimilated by the roots of plants. It accumulates more in the soil. That why its bioavailability is low.

- Lead (Pb) is a natural product. In the environment, lead could be found in different forms: metallic form (Pb metal), ionized form (Pb II), under the form of organic salt and the inorganic form. Generally Pb and its derivated compounds were in several uses. The principal chemical forms were Pb (element), $PbCl_2$ (lead Chloride), $PbCrO_4$ (lead chromate), $PbCO_3$ (lead Carbonate), $PbO_2$ (lead

Dioxide), PbO (lead Oxide), $Pb(NO_3)_2$ (lead Nitrate, $PbSO_4$ (lead sulfate ), PbS (lead Sulfur ), $Pb_3O_4$ (lead Tetra oxide)[19, 20].

The results of lead are shown in **Table V**. The concentrations of Pb are between 10.0 and 1690.0 µg/kg. The high concentrations are obtained in the tegument of the cocoa (905.0-1690.0 µg/kg). The minimum concentrations are observed in the juice (10.0-365.0 µg/kg). The average concentration is 454.7 µg/kg and superior than 0.1 mg/kg[13].

The average concentration is also comparable with the high concentration reported by the studies on biovailability of lead in cocoa powder and related products. The concentration ranged from 11-769 mg/kg. In the soil of the area of our study, the average concentration measured by authors was 13-49 mg/kg[16]. These values could be comparable with the level of chromium. So the Pb appears in the soil with significant concentration [20]. The possible origin of contamination of lead in cocoa is the soil. The lead can be leached in the soil solution and thus promote the accumulation of lead by roots of the plant. Lead is absorbed passively by the roots and quickly transferred on the vacuoles of the plants.

**Table III:** Results of Cadmium (Cd) analysis on Almonds, Teguments and the Juices of cocoa Mercedes

| Samples | Type | Stations | Location | ESSAI 1 | ESSAI 2 | ESSAI 3 | Average | Max. | Min. | Standards déviation | C.V % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | µg/kg | µg/kg | µg/kg | µg/kg | µg/kg | µg/kg | µg/kg | % |
| AmAB | ALMONDS | St1 | ABENGOUROU | 52.0 | 60.0 | 62.7 | 58.2 | 62.7 | 52.0 | 5.6 | 9.6 |
| TeAB | TEGUMENTS | St1 | ABENGOUROU | 328.0 | 349.0 | 354.0 | 343.7 | 354.0 | 328.0 | 13.8 | 4.0 |
| JnfAB | JUICES | St1 | ABENGOUROU | 76.9 | 89.2 | 90.7 | 85.6 | 90.7 | 76.9 | 7.6 | 8.9 |
| AmDI | ALMONDS | St2 | DIVO | 80.8 | 92.5 | 93.1 | 88.8 | 93.1 | 80.8 | 6.9 | 7.8 |
| TeDI | TEGUMENTS | St2 | DIVO | 344.4 | 368.9 | 373.7 | 362.3 | 373.7 | 344.4 | 15.7 | 4.3 |
| JfDI | JUICES | St2 | DIVO | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.0 | 7.9 |
| JnfDI | JUICES | St2 | DIVO | 25.3 | 28.6 | 29.5 | 27.8 | 29.5 | 25.3 | 2.2 | 7.9 |
| AmAD | ALMONDS | St3 | ADZOPE | 17.3 | 19.0 | 19.8 | 18.7 | 19.8 | 17.3 | 1.3 | 6.8 |
| TeAD | TEGUMENTS | St3 | ADZOPE | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.0 | 7.9 |
| JfAD | JUICES | St3 | ADZOPE | 16.7 | 17.8 | 18.3 | 17.6 | 18.3 | 16.7 | 0.8 | 4.6 |
| JnfAD | JUICES | St3 | ADZOPE | 72.1 | 80.4 | 81.8 | 78.1 | 81.8 | 72.1 | 5.3 | 6.7 |
| AmYA | ALMONDS | St4 | YAMOUSSOUKRO | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.0 | 7.9 |
| TeYA | TEGUMENTS | St4 | YAMOUSSOUKRO | 630.0 | 649.3 | 652.7 | 644.0 | 652.7 | 630.0 | 12.2 | 1.9 |
| JfYA | JUICES | St4 | YAMOUSSOUKRO | 79.9 | 89.3 | 90.9 | 86.7 | 90.9 | 79.9 | 5.9 | 6.9 |
| JnfYA | JUICES | St4 | YAMOUSSOUKRO | 70.4 | 79.9 | 85.2 | 78.5 | 85.2 | 70.4 | 7.5 | 9.6 |

Max. : Maximum ; Min. : Minimum ; C.V. : Coefficient of Variation

**Table IV:** Results of Chromium (Cr) analysis on Almonds, Teguments and the Juices of cocoa Mercedes

| Samples | Type | Stations | Location | ESSAI 1 | ESSAI 2 | ESSAI 3 | Average | Max. | Min. | Standards déviation | C.V % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | µg/kg | µg/kg | µg/kg | µg/kg | µg/kg | µg/kg | µg/kg | % |
| AmAB | ALMONDS | St1 | ABENGOUROU | 3.70 | 4.26 | 4.31 | 4.10 | 4.31 | 3.70 | 0.30 | 8.30 |
| TeAB | TEGUMENTS | St1 | ABENGOUROU | 6.71 | 7.80 | 8.00 | 7.50 | 8.00 | 6.71 | 0.70 | 9.30 |
| JnfAB | JUICES | St1 | ABENGOUROU | 3.29 | 3.53 | 4.00 | 3.60 | 4.00 | 3.29 | 0.40 | 10.00 |
| AmDI | ALMONDS | St2 | DIVO | 1.97 | 2.34 | 2.30 | 2.20 | 2.34 | 1.97 | 0.20 | 9.00 |
| TeDI | TEGUMENTS | St2 | DIVO | 8.13 | 9.20 | 9.37 | 8.90 | 9.37 | 8.13 | 0.70 | 7.60 |
| JfDI | JUICES | St2 | DIVO | 4.50 | 5.15 | 5.30 | 5.00 | 5.30 | 4.50 | 0.40 | 8.50 |
| JnfDI | JUICES | St2 | DIVO | 0.96 | 1.08 | 1.01 | 1.00 | 1.08 | 0.96 | 0.10 | 6.20 |
| AmAD | ALMONDS | St3 | ADZOPE | 6.00 | 6.93 | 7.13 | 6.70 | 7.13 | 6.00 | 0.60 | 9.00 |
| TeAD | TEGUMENTS | St3 | ADZOPE | 4.45 | 5.15 | 5.40 | 5.00 | 5.40 | 4.45 | 0.50 | 9.80 |
| JfAD | JUICES | St3 | ADZOPE | 1.07 | 1.06 | 1.09 | 1.10 | 1.09 | 1.06 | 0.00 | 1.40 |
| JnfAD | JUICES | St3 | ADZOPE | 2.33 | 2.64 | 2.71 | 2.60 | 2.71 | 2.33 | 0.20 | 7.90 |
| AmYA | ALMONDS | St4 | YAMOUSSOUKRO | 5.00 | 5.15 | 5.20 | 5.10 | 5.20 | 5.00 | 0.10 | 2.00 |
| TeYA | TEGUMENTS | St4 | YAMOUSSOUKRO | 8.08 | 9.00 | 9.41 | 8.80 | 9.41 | 8.08 | 0.70 | 7.70 |
| JfYA | JUICES | St4 | YAMOUSSOUKRO | 2.79 | 3.16 | 3.33 | 3.10 | 3.33 | 2.79 | 0.30 | 8.80 |
| JnfYA | JUICES | St4 | YAMOUSSOUKRO | 2.51 | 2.84 | 3.1 | 2.8 | 3.1 | 2.51 | 0.3 | 10.5 |

Max. : Maximum ; Min. : Minimum ; C.V. : Coefficient of Variation

**Table V**: Results of lead (Pb) analysis on Almonds, Teguments and the Juices of cocoa Mercedes

| Samples | Type | Stations | Location | ESSAI 1 | ESSAI 2 | ESSAI 3 | Average | Max. | Min. | Standards déviation | C.V % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | µg/kg | µg/kg | µg/kg | µg/kg | µg/kg | µg/kg | µg/kg | % |
| AmAB | ALMONDS | St1 | ABENGOUROU | 259.3 | 277.2 | 285.4 | 274.0 | 285.4 | 259.3 | 13.3 | 4.9 |
| TeAB | TEGUMENTS | St1 | ABENGOUROU | 863.6 | 917.2 | 934.3 | 905.0 | 934.3 | 863.6 | 36.9 | 4.1 |
| JnfAB | JUICES | St1 | ABENGOUROU | 299.4 | 338.9 | 348.7 | 329.0 | 348.7 | 299.4 | 26.1 | 7.9 |
| AmDI | ALMONDS | St2 | DIVO | 330.8 | 352.4 | 357.8 | 347.0 | 357.8 | 330.8 | 14.3 | 4.1 |
| TeDI | TEGUMENTS | St2 | DIVO | 1517.8 | 1600.0 | 1621.0 | 1579.6 | 1621.0 | 1517.8 | 54.5 | 3.5 |
| JfDI | JUICES | St2 | DIVO | 10.0 | 10.3 | 10.5 | 10.3 | 10.5 | 10.0 | 0.3 | 2.5 |
| JnfDI | JUICES | St2 | DIVO | 10.0 | 10.0 | 10.6 | 10.2 | 10.6 | 10.0 | 0.3 | 3.4 |
| AmAD | ALMONDS | St3 | ADZOPE | 90.7 | 98.4 | 103.4 | 97.5 | 103.4 | 90.7 | 6.4 | 6.5 |
| TeAD | TEGUMENTS | St3 | ADZOPE | 10.0 | 10.3 | 10.6 | 10.3 | 10.6 | 10.0 | 0.3 | 2.9 |
| JfAD | JUICES | St3 | ADZOPE | 10.4 | 10.3 | 10.6 | 10.4 | 10.6 | 10.3 | 0.2 | 1.5 |
| JUICES | JUICES | St3 | ADZOPE | 266.2 | 290.6 | 304.2 | 287.0 | 304.2 | 266.2 | 19.3 | 6.7 |
| AmYA | ALMONDS | St4 | YAMOUSSOUKRO | 562.4 | 590.0 | 603.0 | 585.1 | 603.0 | 562.4 | 20.8 | 3.5 |
| TeYA | TEGUMENTS | St4 | YAMOUSSOUKRO | 1640.9 | 1700.0 | 1730.0 | 1690.3 | 1730.0 | 1640.9 | 45.3 | 2.7 |
| JfYA | JUICES | St4 | YAMOUSSOUKRO | 342.2 | 366.0 | 386.9 | 365.0 | 386.9 | 342.2 | 22.4 | 6.1 |
| JnfYA | JUICES | St4 | YAMOUSSOUKRO | 294.8 | 317.4 | 326.8 | 313.0 | 326.8 | 294.8 | 16.4 | 5.2 |

Max. : Maximum ; Min. : Minimum ; C.V. : Coefficient of Variatio

**3.2. Spatial analysis**

Qualitative analysis was done comparing concentrations of the parameters in the different parts of samples. The **Figures 5** to **8** give amounts (µg/kg) of the three heavy metals.

- *Station of Abengourou (St1):* In the experimental station of Abengourou, the level of lead and cadmium are the highest. The measured concentrations are practically in the form of trace. These different metals are present in different parts of studied cocoa.

- *Station of Divo (St2):* The **Figure 6** shows high peaks of concentration of Pb and Cd in the part of tegument and almonds.

- *Station of Adzope (St3):* The Adzope station presents spatial distribution metals. But their presence is more amplified in fines and the non fermented juice with a high concentration lead.

- *Station of Yamoussoukro (St4):* At the station of Yamoussoukro, the highest concentrations are also observed for lead and cadmium.

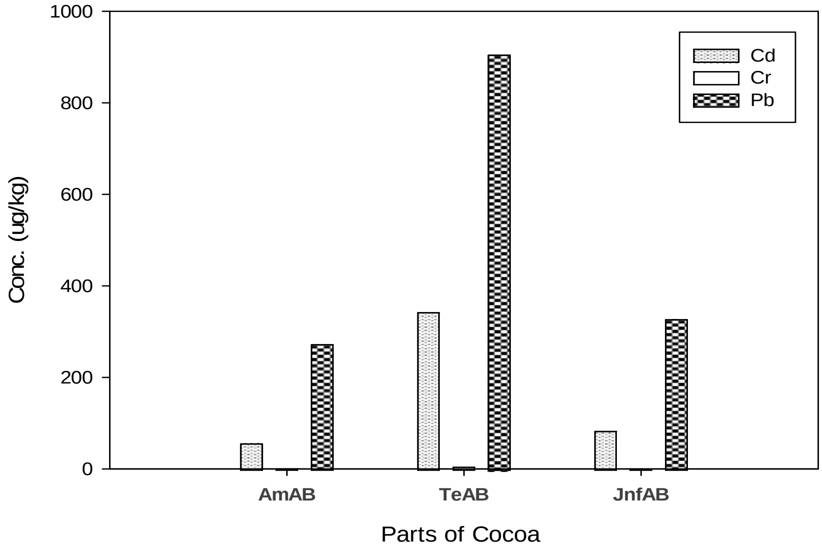


**Figure 5:** Concentration of heavy metals in Station of Abengourou

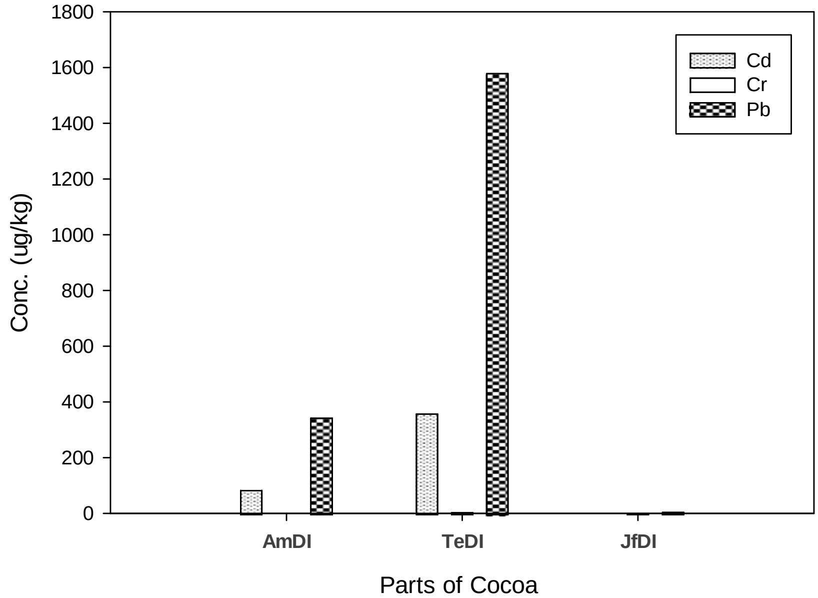


**Figure 6:** Concentration of heavy metals in Station of Divo

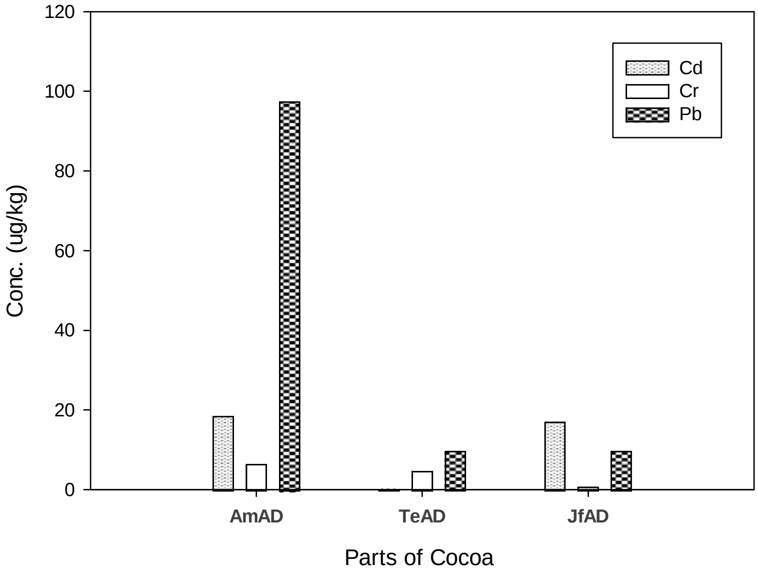


**Figure 7:** Concentration of heavy metals in Station of Adzopé

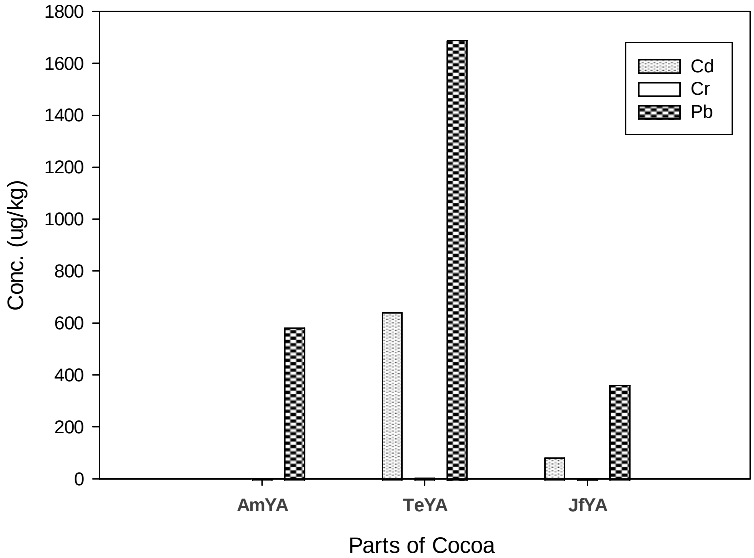


**Figure 8:** Concentration of heavy metals in Station of Yamoussoukro

### 3.3. Bioavailability of the three metals

Many studies have shown that the heavy metals in general were not very bioavailable in plants. The results of these studies showed the presence of the three metals simultaneously. In the result shown in **Table VI**, the Lead ratio of integument and almonds is ranged between 2.5 and 9. According to these results, the levels of concentration of the metals on integument samples appeared greater than that in almonds and juice samples. The probable source of transfer of these elements was the environmental impacts and human activities. The mains vectors of transport are the atmospheric particles and the soil. For example chromates of lead, $PbCrO_4$ were used as pigments in plastics, paints and printing industries. The residues could be transported by the water. In water solution (basic), the lead chromate, was partial dissolved and could form a complex.

$$PbCrO_4 + 4OH^- \longrightarrow \underbrace{Pb(OH)_4^{2-}}_{\text{Complex of lead}} + (CrO_4)^2 \quad (6)$$

The complex $Pb(OH)_4^{2-}$ in natural condition may absorb onto colloidal particles, suspended sediments and the soil. Concerning the Cd, various minerals and chemical forms were used in chemical pesticides for plant protection.

**Table VI:** Comparison of lead ratio $Pb_{Te}/Pb_{Am}$ for the four stations

| | Abengourou | Divo | Adzopé | Yamoussoukro |
|---|---|---|---|---|
| $Pb_{Te}/Pb_{Am}$ | 3.3 | 4,5 | 9.7 | 2.5 |

## 4. Conclusion

This study was to implement the analysis of traces metal in the context of quality control of the *cocoa mercedes*. The three heavy metals were present in the different part of the cocoa. This study has highlighted the higher presence of Pb and Cd in the samples. In the field of the health control and the export trade, it was important to take action of good agricultural practices and the traceability. The external factors such as environment, water spray, treatment products, the composts, and the waste management should be controlled. Apart from comparison guides or food safety standard values, it was important to notice the simultaneous presence of three metals. These metals were characterized by their physical and chemical affinity to bind. The trend of contamination was dominated by Pb and Cd. Further analysis should be conducted in order to understand the bioavailability of these three metals in cocoa.

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