LEAD AND SOME TRACE ELEMENTS CONCENTRATION IN COCOA CANDIES

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ABSTRACT

The distribution of lead, zinc, lithium, aluminum, cerium, vanadium, antimony and arsenic was investigated in cocoa candy samples collected from Basra local markets. The samples were analyzed by inductively coupled plasma-mass spectrometer (ICP-MS). Concentration of these trace elements (µg/g fresh weight) ranged between 0.1065 – 0.4371 for pb, 0.1791 – 1.289 for Li, 8.460 – 52.0728 for Al, and from not detected to 0. 2923, 0.0091 and 0.0272 for Ce, V and Sb respectively, while As was not detected in all samples.

The average amount of trace elements present in samples in general, below the maximum permitted concentration. These data indicate that the consumption of candies are safe in moderate quantities.

KEYWORDS. Trace Elements, Lead, Cocoa, Contamination

1. INTRODUCTION

Trace elements are an important source of food contamination. The main menaces to human health are associated with exposure to lead, arsenic cadmium and copper (Jarup, 2003). Normally the food chain is exposure to pollution by trace elements in industrial sluge and sediment (Islam et al., 2009). All the vegetables commonly consumed in diets contain dangerously high concentrations of trace elements (Alam, 2003). Chocolate is a complex sample with a high content of organic compounds (Leggli *et al.,* 2011). It contains essential trace elements and nutrients like iron, calcium and potassium and some vitamins on the other hand it has highest natural source for magnesium where as lead is very harmful element to human body. Most studies were determinate trace elements in food such as Hashim and Hamid (1995) they were focusing in evaluation of trace elements in the diet of female university students. Hamurcu *et al.* (2010) showed that pb and Zn has high levels in the fruit samples. The French food safety agency (AFSSA) estimated dietary exposures to the main minerals and trace elements from 1319 samples of food typically consumed by the French population, one of them was dark chocolate have the highest levels of Cr, Mn, Co, Ni and Cu (Noel *et al.,* 2012). While minor studies focus in candy, Onianwa *et al.*(1999) found the average lead content of cocoa powder in Nigeria to be 310 ng/g with a range of 80 – 880 ng/g while the Dahiya *et al.* (2005) found the range of lead concentrations in cocoa-based chocolates in India between 0.05 – 8.3 µg/g. Chocolate products and the manufactured cocoa contain relatively high levels of lead contaminant compared with baseline value for Nigerian cocoa beans used in making those products indicate most lead contamination in those products occurs after the beans harvested and dried, during the shipping of beans and / or the manufacturing of cocoa , chocolate bonbons and the other source of contamination of the finished products is tentatively attributed to atmospheric emissions of leaded gasoline during fermentation and sun drying of beans (Rankin *et al.*, 2005). Kim *et al.* (2010) indicate that harmful metals such as pb and cr could migrate from the printed outer packages to food, lead was detected at concentrations of 110.3 – 1429.3 mg / kg in candy. In addition to Leggli *et al.* (2011) study some trace element in chocolate samples. For these reasons above this study focus to determinant lead and other elements perhaps available in candy due to contamination for protection public health against the hazardous of elements toxicity.

2. MATERIALS AND METHODS

Candies were collected from Iraqi markets (Basra), in two orders of same type, the period between first and second order one month. All these candies cover with cocoa, available, cheap and likely for kids; on the other hand, it was differ in originator. Cocoa was isolated from 5 pieces by plastic knife than, homogenized by porcelain mortar. About 1g of cocoa (triplicate) was then put in digestive tubes, mixed with 10 ml HNO_3 and 5ml $HCLO_4$, incubated for 6 hours in laboratory temperature, the mixture was heated up to 150 c for 1 hour. The tubes were removed and allowed to cool after that 2 ml of H_2O_2 were added (the addition of H_2O_2 can increase the solubilizing power of acids and decomposition of organic matter), tubes were heated again for five hours until the HNO_3 boils off and $HCLO_4$ white fumes begin to appear digestion was complete. Samples were filtrated through Whatman No. 1 filter paper and th en diluted to 25 ml volume with deionized water according to Twyman (2005).

A blank digest were carried out in the same way. The mineral contents of the samples were quantified against standard solutions of know concentrations which were analyzed concurrently (skujins, 1998). The samples were run on an inductively coupled plasma mas spectrometer (ICP-MS). All reagents were of analytical grade, deionised water was used throughout, glassware were washed in diluted HNO_3 and rinsed with deionised water.

Statistical analysis

Data from concentration of 8 elements in cocoa were compared for both orders by independent samples T- test and correlations. Data analysis was carried out using the soft ware program SPSS 16. Differences were considered significant at P< 0.01 by one way ANOVA between trace elements.

3. RESULTS

In this study, a total number of 120 candy pieces were collected from Iraqi market. About 66.67 % from candies were Turkish, 16.67 Syrian, 8.33 Iranian and 8.33 Iraqis as available in markets. Concentrations of trace elements (pb, Zn, Li, Al, Ce, V, Sb and As) in candies between two orders and each other were compared. The overall concentrations in this studied cocoa were provide in tables 1 to 7 and presented in µg/g wet weight. The order of mean elements concentration in cocoa samples was Zn> Al > pb > Li > Ce > Sb > V > As. Approximate average in both orders were found for pb, the values range between 0.1065 – 0.4317 µg/g fresh weight was observed in Turkish sample (tab. 1) pb concentrations were detected in all samples as well as Zn, Al and Li. The highest values of zinc was 50.743 µg/g fresh wt. and lowest values was 0.3065 µg/g fresh wt. The levels of Li in cocoa are shown in Tab 3, highest and lowest values were 1.266 and 0.1791 µg/g fresh wt. found in same product. Sample no.2 was has highest concentration of Al in both orders while the lowest concentration was in sample no. 4 reach to 9.2046 µg/g fresh wt. as showed in Tab. 4. on the other hand, the Ce, V and Sb concentrations were showed in Tab. (5,6 and 7) and found to be present in some samples only especially for Sb that available in one sample only while As was not detected in all samples.

Significant differences to all elements were not found between orders (p>0.01) while Significant differences found (p<0.01) between Zn and pb, Li, Ce, V, Sb and (p<0.01) between al and pb, Li, Ce, V, Sb.

Table (1): lead concentrations and SD in cocoa by µg/g fresh wt.

Pb		*first order*		*second order*	
no.	country	con.	SD	con.	SD
1	Turkey	0.2091	0.0061	0.2091	0.0577
2	Turkey	0.3188	0.0683	0.4371	0.0656
3	Turkey	0.3474	0.0817	0.2059	0.0993
4	Turkey	0.1065	0.0117	0.1065	0.0521
5	Turkey	0.1125	0.0384	0.179	0.0333
6	Turkey	0.2729	0.0563	0.1753	0.0708
7	Turkey	0.2792	0.0858	0.1306	0.0956
8	Turkey	0.1669	0.0410	0.238	0.0515
9	Iraq	0.2458	0.0135	0.2692	0.0523
10	Iran	0.1885	0.0139	0.1644	0.0175
11	Syria	0.3583	0.0624	0.1502	0.0711
12	Syria	0.2042	0.0086	0.1893	0.0540
correlation 0.313447				p> 0.01	

Table (2): Zinc concentrations and SD in cocoa by µg/g fresh wt.

Zn		*first order*		*second order*	
no.	country	con.	SD	con.	SD
1	Turkey	0.3065	0.0577	3.2727	0.0585
2	Turkey	20.0021	0.9504	50.743	0.5011
3	Turkey	43.7327	0.5000	23.3597	0.8083
4	Turkey	14.5723	0.9517	13.7175	0.1166
5	Turkey	14.194	1.4422	21.521	0.7071
6	Turkey	29.4661	1.0149	18.0682	0.5980
7	Turkey	20.2819	0.4448	24.1161	0.5469
8	Turkey	19.2519	0.5132	30.5422	0.6017
9	Iraq	26.5543	0.5774	21.4934	0.7211
10	Iran	27.5352	1.0786	19.4057	1.5275
11	Syria	23.5258	0.7211	8.3398	0.2150
12	Syria	6.7809	0.4041	8.8963	0.5179
correlation 0.340574			p> 0.01		

Table (3): Lithium concentrations and SD in cocoa by µg/g fresh wt.

Li		*first order*		*second order*	
no.	country	con.	SD	con.	SD
1	Turkey	0.8253	0.0344	0.7658	0.0361
2	Turkey	0.5211	0.0169	0.4918	0.0169
3	Turkey	0.4958	0.0818	0.3541	0.0818
4	Turkey	0.3321	0.0577	0.3321	0.0064
5	Turkey	0.2650	0.0111	0.2843	0.0108
6	Turkey	0.2937	0.0285	0.2443	0.0285
7	Turkey	1.2669	0.6280	0.1791	0.0476
8	Turkey	0.9972	0.1017	1.1734	0.3847
9	Iraq	0.4772	0.0489	0.3925	0.0763
10	Iran	0.2597	0.0438	0.1839	0.0438
11	Syria	0.7049	0.0729	0.5787	0.0706
12	Syria	0.6080	0.0778	0.4732	0.0778
correlation 0.455854			p> 0.01		

Table (4): Aluminum concentrations and SD in cocoa by µg/g fresh wt.

Al		*first order*		*second order*	
no.	country	con.	SD	con.	SD
1	Turkey	9.4984	0.4028	13.196	1.0151
2	Turkey	35.4954	1.9760	52.0728	1.9760
3	Turkey	20.4124	0.6333	19.3155	0.6333
4	Turkey	9.6402	0.5774	9.2046	0.5884
5	Turkey	9.3012	0.7294	10.5646	0.7294
6	Turkey	18.1138	0.8845	13.3501	0.8845
7	Turkey	18.8718	0.7654	21.497	1.5386
8	Turkey	18.4527	0.7308	25.7184	1.1354
9	Iraq	18.2401	1.3858	15.8398	0.5035
10	Iran	18.0675	1.0396	13.5596	0.2932
11	Syria	17.593	1.2315	8.460	0.2672
12	Syria	21.9592	0.4718	8.6264	0.7071
correlation 0.796741			p> 0.01		

Table (5): Cerium concentrations and SD in cocoa by µg/g fresh wt.

Ce		*first order*		*second order*	
no.	country	con.	SD	con.	SD
1	Turkey	0.0002	0.0001	ND	0
2	Turkey	ND	0	0.0796	0.0230
3	Turkey	0.0215	0.0027	ND	0
4	Turkey	ND	0	ND	0
5	Turkey	ND	0	0.0333	0.0120
6	Turkey	0.2923	0.0574	0.0364	0.0034
7	Turkey	0.0126	0.0034	ND	0
8	Turkey	0.0152	0.0030	0.0156	0.0040
9	Iraq	0.0030	0.0009	ND	0
10	Iran	0.1454	0.0442	0.0334	0.0034
11	Syria	ND	0	ND	0
12	Syria	ND	0	ND	0
correlation 0.311866			p> 0.01 ND= not detected		

Table (6): Vanadium concentrations and SD in cocoa by µg/g fresh wt.

Zn		*first order*		**second order**	
no.	country	con.	SD	con.	SD
1	Turkey	ND	0	ND	0
2	Turkey	ND	0	ND	0
3	Turkey	ND	0	ND	0
4	Turkey	ND	0	ND	0
5	Turkey	ND	0	ND	0
6	Turkey	ND	0	ND	0
7	Turkey	ND	0	0.034	0.0091
8	Turkey	0.0040	0.0015	ND	0
9	Iraq	ND	0	ND	0
10	Iran	ND	0	ND	0
11	Syria	0.0044	0.0013	ND	0
12	Syria	ND	0	ND	0
correlation -0.13466			p> 0.01 ND= not detected		

Table (7): Antimony concentrations and SD in cocoa by µg/g fresh wt.

Sb		*first order*		**second order**	
no.	country	con.	SD	con.	SD
1	Turkey	ND	0	ND	0
2	Turkey	ND	0	ND	0
3	Turkey	0.0272	0.0084	ND	0
4	Turkey	ND	0	ND	0
5	Turkey	ND	0	ND	0
6	Turkey	ND	0	ND	0
7	Turkey	ND	0	ND	0
8	Turkey	ND	0	ND	0
9	Iraq	ND	0	ND	0
10	Iran	ND	0	ND	0
11	Syria	ND	0	ND	0
12	Syria	ND	0	ND	0
p> 0.01			***ND= not detected***		

4. DISCUSSION

Trace elements are of high ecology significance since they are not removed from soil as a result of self purification, but accumulated in reservoirs and enter the food chain (Loska and Wiechu, 2003). All the cocoa plantations in Nigeria were polluted with some trace elements (Aikpokpodion *et al.,* 2010). The concentration of Zn and pb in soil may be derived from various sources including anthropogenic pollution, weathering of natural high background rocks and metal deposits (Senesi *et al.,* 1999). According to Howe, *et al.* (2005) all the study results for As and Ce were below the respective sample detection limits but even among these, some of the maximum values observed indicated that the source of cocoa powder was different in origin or industrial contamination take place. Some pb (0.3583 – 0.4371 µg/g) occur at concentration levels above these reported from the other countries but it seems unlikely that most of these will contribute significantly to public health risks as reported in Howe *et al.*(2005). Some trace element were detected at high concentration may be due to migration of element from the printed outer packages to candy (Kim *et al.,* 2008)

Zinc is distributed widely in plant and animal tissues and presents in all living cells. It is essential for plants in lipid and carbohydrate metabolism and is required at levels of 10 – 20 ppm (Kabata-pendias and Pendias, 1992). Therefore, it was normally available in cocoa and it was not harmful for children if they take up with the current reference daily intake 15 mg/day (Acholonu, 2005) but over load of Zn > 100 mg/ day also can be dangerous. It can depress the immune system and cause anemia (Akhter *et al.,* 2002) therefore Zn levels in cocoa was conceder normal and cocoa not contamination even at high concentration like 50.743 µg/g wet weigh.

The aluminum concentration in this study lowest than Leggli *et al.*(2011) of (27.2 – 92.1 µg/g) for dark chocolate. The FAO/WHO Expert Committee on food additives (1989) has established a provisional tolerable daily intake of 1 mg/kg of body weigh, which equates to a tolerable daily intake of 70 mg for a 70 kg adult. The amount of Al resulting in this study does not pose a hazard for a healthy population (Leggli *et al.*,2011)

Lithium concentration was high (0.1839 – 1.2669 µg/g fresh wt.) compared with Noel *et al.* (2012) was 0.008 µg/g fresh wt. (max 0.013) in dark chocolate, due to differences in origin or industrial contamination occurrence (Rankin *et al.,* 2005)

Vanadium concentration was below (0.034 µg/g) and available in three samples only, Hepkins and Mohr (1974) clarify essentiality of V in man has been hypothesized but not demonstrated. V was believed to be involved in N_2 fixation but it has not been proved to be essential for plants, it is essential for some animal but it not required by humans, levels required by animal for optimum growth are 0.05 – 0.5 ppm in food and toxic in large amounts (Van Zinderen Bakker and Jaworski, 1980). Plants may be required vanadium at low levels (0.002 ppm) (Tisdale *et al.,* 1985). Thus we can consider cocoa candy in this study without contamination by vanadium. Howe *et al.*(2005) reported that As concentration in crops (ginger) were generally low (0.001 – 0.016 µg/g dry wt.) as well as Demirozu and Saldaml (2002) reported arsenic values varying between 21.87 and 29.00 ng/g and 42.63 and 57.02 ng/g in the semolina and Wheat respectively while in this study was not available in all cocoa samples.

This result will compliment available baseline data on food composition in Iraq and will be useful in estimating dietary intake of these metals in the general Iraqi children.

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الخلاصة

شخص توزيع الرصاص والليثيوم والالمنيوم والسيروم والفاناديوم والانتيمون والزرنيخ في عينات كاكاو الحلويات المجموعة من اسواق البصرة. حللت العينات بجهاز inductively coupled plasma-mass spectrometer تراوح تركيز العناصر النزرة (مايكوغرام / غرام وزن رطب) من 0.1065 – 0.4371 للرصاص و 0.1791– 1.289 لليثيوم و8.460 – 52.0728 للالمنيوم وتراوح التركيز من غير المحسوس الى 0.2923 و0.0091 و0.0272 لعناصر السيروم والفاناديوم والانتيمون على التوالي بينما الزرنيخ ليس له تركيز محسوس في جميع العينات.

معدل تركيز العناصر في العينات كان اقل من الحد الاعلى المسموح به وهذا يشير الى الاستهلاك الأمن لتلك الحلويات.