

Cadmium , nickel and lead in chocolates and candies from Baghdad markets in Iraq.

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Abstract:

Background:Foods and food related products are imported or entered to the country by illegal ways , these foods may contain potential contaminants such as heavy metals . Among the most imported foods are chocolates and candies which consumed frequently by children.

Objective:In this study, selected heavy metals; Cadmium (Cd) , Nickel (Ni) and Lead (Pb) were evaluated in commercial candies and chocolates products that are commonly consumed by children in Iraq. The chocolates which studied were Twix (Germany) , Mars and Galaxy (Emirates)and the candies were Melody Pops (Iraq), Caretos and Lip-Top (India) .

Methods:Prospective study was done in Baghdad from January to April 2017. 60 samples of three brands of chocolates and three brands of candies (10 samples for each brand) were analyzed for their content of Cd , Ni and Pb. Electrothermal Atomic Absorption Spectrometry (ETAAS) was used for determination of metals under study .

Results:Mean levels of Cd in three types of chocolates were $0.3282 \pm 0.0203 \mu\text{g/g}$ in Twix chocolate , $0.323 \pm 0.03199 \mu\text{g/g}$ in Mars chocolate and $0.329 \pm 0.01912 \mu\text{g/g}$ in Galaxy chocolate whereas mean levels of Cd in three types of candies were $0.0947 \pm 0.00386 \mu\text{g/g}$ in Lip-Top candy , $0.093 \pm 0.00368 \mu\text{g/g}$ in Melody – Pops candy and $0.0935 \pm 0.003837 \mu\text{g/g}$ in Caretose candy, while mean levels of Ni in same types of chocolates were $4.38 \pm 0.1109 \mu\text{g/g}$, $4.23 \pm 0.2111 \mu\text{g/g}$ and $4.24 \pm 0.2675 \mu\text{g/g}$ respectively whereas mean levels of Ni in same types of candies were $1.417 \pm 0.1 \mu\text{g/g}$, $1.376 \pm 0.05461 \mu\text{g/g}$ and $1.422 \pm 0.0968 \mu\text{g/g}$ respectively , in addition , mean levels of Pb in three types of chocolates were $2.212 \pm 0.1398 \mu\text{g/g}$, $2.185 \pm 0.200 \mu\text{g/g}$ and $2.305 \pm 0.2166 \mu\text{g/g}$ respectively , whereas mean levels of Pb in three types of candies were $1.17 \pm 0.1149 \mu\text{g/g}$, $1.138 \pm 0.08626 \mu\text{g/g}$ and $1.159 \pm 0.07156 \mu\text{g/g}$ respectively Conclusion:Contamination of chocolates and candies with these elements leads to health problems for citizens, especially children, and may lead to cancerous tumors. Therefore, children should be reduced to eating these foods. The government must strictly control the importation and entry of these foods.

Key words: , Cadmium , Lead , Chocolates , Candies.

الخلاصة:

بعض المنتجات الغذائية تستورد او تدخل الى البلاد بطرق غير قانونية ، هذه المواد قد تحتوي بعض الملوثات مثل عناصر الفلزات الثقيلة . من بين تلك الاطعمة الشوكولاتة والحلويات والتي تستهلك اغلب الاحيان من قبل الاطفال. في هذه الدراسة اختبر عدد من عناصر الفلزات الثقيلة مثل الكاديوم والنيكل والرصاص والتي قيست مستويات تراكيزها في بعض انواع الشوكولاته والحلويات والمرغوبة من قبل اطفال العراق . انواع الشوكولاتة التي استخدمت في هذه الدراسة هي توكيس (صناعة المانيا) و شوكولاتة مارس وشوكولاتة كالاكسي (صناعة الامارات) اما انواع الحلويات التي استخدمت كانت حلوى بوبس (صناعة العراق) وحلوى كريتوس وحلوى لب – توب (صناعة الهند) . الدراسة الحالية اجريت في بغداد من شهر كانون الثاني الى شهر نيسان من عام 2017. حلل 60 نموذج من الشوكولاتة والحلوى (10 نماذج من كل نوع من انواع الشوكولاتة والحلوى المذكورة) الى محتوياتها من عناصر الفلزات الثقيلة الكاديوم والنيكل والرصاص بواسطة جهاز مطياف الامتصاص الذري . وكانت معدلات مستويات تراكيز الكاديوم في الانواع الثلاثة من الشوكولاتة (0.3282 ± 0.0203) مايكروغرام/غم في شوكولاتة توكيس و (0.323 ± 0.03199) مايكروغرام/غم في شوكولاتة مارس و (0.329 ± 0.01912) مايكروغرام/غم في شوكولاتة كالاكسي ، بينما معدلات تراكيز الكاديوم في الانواع الثلاثة من الحلوى هي (0.0947 ± 0.00386) مايكروغرام/غم في حلوى لب – توب و (0.093 ± 0.00368) مايكروغرام/غم في حلوى ميلودي – بوبس و (0.0935 ± 0.003837) مايكروغرام/غم في حلوى كريتوس. معدلات تركيز النيكل في نفس الانواع الثلاثة من الشوكولاتة كانت (4.38 ± 0.1109) مايكروغرام/غم و (4.23 ± 0.2111) مايكروغرام/غم و (4.24 ± 0.2675) مايكروغرام/غم.

مايكروغرام/غم و (4.24 ± 0.2675) مايكروغرام/غم على التوالي ، وكانت معدلات تراكيز النيكل في الانواع الثلاثة من الحلوى هي (0.1 ± 1.417) مايكروغرام/غم و (0.05461 ± 1.376) مايكروغرام/غم و (0.0968 ± 1.422) مايكروغرام/غم على التوالي . اما معدلات تراكيز الرصاص في الانواع الثلاثة من الشوكولاتة كانت (0.1398 ± 2.212) مايكروغرام/غم و (0.200 ± 2.185) مايكروغرام/غم و (0.2166 ± 2.305) مايكروغرام/غم على التوالي وكذلك تركيز عنصر الرصاص في الانواع الثلاثة من الحلوى كانت (0.1149 ± 1.17) مايكروغرام/غم و (0.0862 ± 1.138) مايكروغرام/غم و (0.07156 ± 1.159) مايكروغرام/غم على التوالي ايضا . لذلك ارتأينا ان تلوث الشوكولاتة والحلوى بهذه العناصر قد يؤدي الى مشاكل صحية لدى المواطنين وخصوصا الاطفال ، وقد يؤدي الى اورام سرطانية ، لذلك يجب ان يحث الاطفال على التقليل من تناول هذه الاطعمة ، والحكومة يجب ان تراقب وتنظم بصرامة استيراد ودخول هذه الاطعمة الى البلد

مفاتيح الكلمات: النيكل ، الكاديوم ، الرصاص ، شوكولاتة ، حلوى

Introduction:

There is great interest in various parts of the world about the quality of imported food products especially coming across borders^[1] due to the abundance of these materials and the huge influx into the country . The variety of imported foodstuffs and the multiplicity of different ways of entering the country and the size of the pollution it carries makes it difficult to impose a ban to prevent the entry of these contaminated foods. In addition, many food items are brought to the plumber before the incoming tourists,. Among the common food products imported are biscuits, bean curd, chocolates, bean paste , teas, candies and various spices and nuts ^[2]. It is worth mentioning that food products undergo a number of industrial processes and are packaged as a means of successful marketing and to protect them when loading. In addition, the outer envelope of these products is decorated with colored inks^[3]. One of the most prominent food products, sweets and chocolates, which are often eaten by children are wrapped in colorful wrappers in order to attract them to buy food product. Heavy metals such as lead (Pb) , Nickel (Ni) and Cadmium (Cd) can be transferred from the colored casing to the food material by four mechanisms : peeling , blocking , rubbing and diffusion (4). Therefore, its necessary to observe human exposure to toxic metals present in the food^[5] .

Human uptake of Cd happens mainly through foods , foods that are rich in Cd especially cocoa powder . An exposure to significantly higher Cd levels takes place

during smoking which can increase effects by activating Cd that is previously present from cadmium-rich food .The absorption of cadmium in large quantities may lead to symptoms of poisoning such as stomach agonies and severe vomiting , damage to the immune system and central nervous system , bone fracture and possibly DNA damage or cancer development.(6-7).

It is normal for food to contain a small amount of Ni But it is known about fat and chocolate that it contains large amounts above normal .Nickel occurs naturally in plants more than in animal flesh ^[8] . The absorption of nickel in small amounts is very necessary for the human body, but uptake it in very large quantities may lead to damage to the body and induces toxicity symptoms like nose cancer , prostate cancer , respiratory failure , birth defects and heart disorders^[9] Nickel may be transferred to food due to industrial processes such as canning, heating and drying in vessels containing nickel^[10]

Lead exposure has been a significant public health issue for decades. The problem of contamination of candy and chocolate with lead is not new but has evolved over time. Scientific studies have shown that continuous exposure to lead leads to increased concentration in the blood,

blood lead levels (BLL) as low as 10 $\mu\text{g}/\text{dL}$ in adults are associated with high blood pressure, impaired kidney function nervous system and neurobehavioral effects, cognitive impairment that appears in advanced age, and subtle cognitive effects attributed to prenatal exposure^[11].

Materials and methods:

Sample collection:- Sixty samples of six different foreign and domestic brands of chocolates and candies (10 samples for each brand were obtained) : Twix chocolate (Germany) , Mars chocolate and Galaxy chocolate (Emirates) and Melody pops candy (Iraq) , Lip-top candy and Caretos candy (India) were analyzed for their content of Pb , Cd and Ni . These 60 candies and chocolates samples were procured from main food distribution networks , supermarkets and markets in Baghdad from January to March 2017.

Chemical analysis:- Distilled water (ultrapure water) was further deionized (SKU:D4521).The reagents used concentrated nitric acid (65%) and hydrogen peroxide(30%) were high purity spectroscopic Ultrex (Merck,Germany) grades. Working standards of Pb , Cd and Ni (1000 ppm) were obtained from Fluka (Buchs SG Switzerland). Chemical solutions , Palladium (Pd) stock standard solution 3 g/L was prepared from Pd 99.9% Sigma Aldrich (USA) and Mg(NO₃)₂

Statistical analysis:-

statistical analysis of data was obtained by using Microsoft Excel (2007) software and the Statistical Package for Social Science (SPSS) version (10). Descriptive statistics for all data of each set were expressed as Mean \pm SD , student's t-test was used to evaluate the significance of differences between concentration levels of each metal in every three types of chocolates and candies.

Stock standard solution 2g/L was prepared from Mg(NO₃)₂ (Merck).

All glasswares were cleaned by kept overnight in 10% (v/v) nitric acid , followed by rinsing with distilled water and finally washed with ultrapure water before use.

Procedure:- About 0.2 g of duplicate samples of each chocolates and candies were taken in digestion flasks, added 2 mL of mixture of (65% HNO₃ and 30 %H₂O₂) in ratio of (1:1, v/v) for decomposition of organic matter , and kept for 10 min at room temperature, then the flasks were placed in a Polytetrafluoroethylene(PTFE)container.

This was then heated following a one-stage digestion program at 80% of total power (900 W) for 3 - 5 min. After cooling the digestion flask, the resulting solutions were evaporated to semidried mass to remove excess acid, and then diluted to 10 mL in volumetric flasks with 0.2 M HNO₃, for the determination of Cd , Ni and Pb by Electrothermal Atomic Absorption Spectrometry (ETAAS)(12).

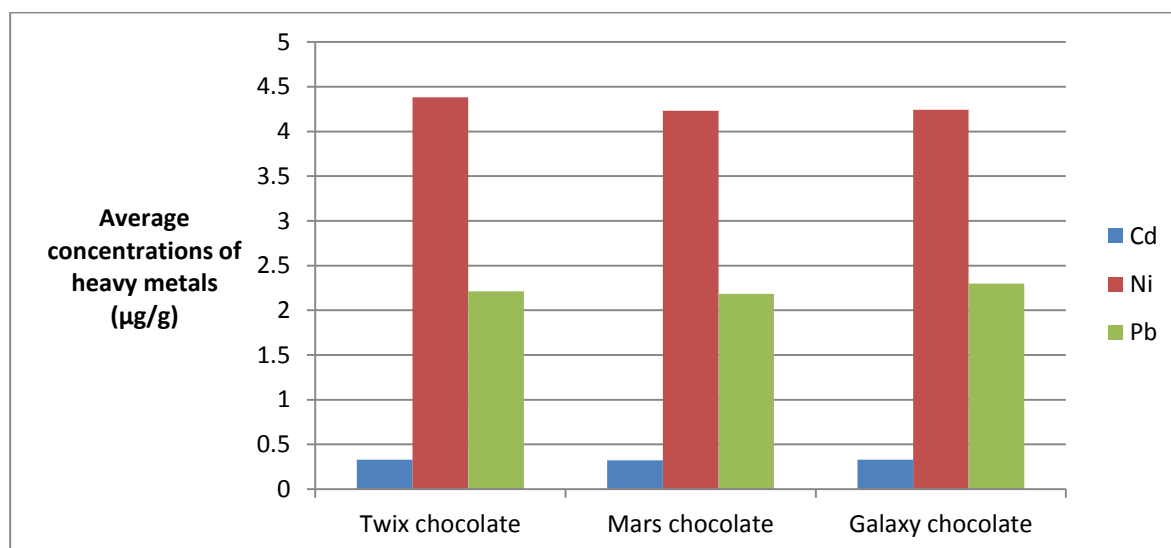
Result and Discussion:

The concentrations of Cd , Ni and Pb in three types of chocolates and three types of candies are presented in Table 1 , Table 2 , Table 3, Table 4 , Figure 1 and Figure 2 along with the statistical parameters . ten samples for each type of chocolates and candies were analyzed to assess the amounts of these metals.

Table 1: Metal contents ($\mu\text{g/g}$) in three types of chocolates.

Chocolate	Heavy metals	S1 $\mu\text{g/g}$	S2 $\mu\text{g/g}$	S3 $\mu\text{g/g}$	S4 $\mu\text{g/g}$	S5 $\mu\text{g/g}$	S6 $\mu\text{g/g}$	S7 $\mu\text{g/g}$	S8 $\mu\text{g/g}$	S9 $\mu\text{g/g}$	S10 $\mu\text{g/g}$	Mean \pm SD $\mu\text{g/g}$
Twix	Cd	0.357	0.35	0.345	0.34	0.31	0.33	0.33	0.32	0.30	0.30	0.3282 \pm 0.0203
	Ni	4.25	4.3	4.27	4.29	4.3	4.45	4.5	4.55	4.49	4.4	4.38 \pm 0.1109
	Pb	2.55	2.15	2.15	2.13	2.11	2.01	2.25	2.2	2.2	2.3	2.212 \pm 0.1398
Mars	Cd	0.34	0.39	0.35	0.30	0.29	0.31	0.34	0.39	0.30	0.32	0.323 \pm 0.03199
	Ni	4.1	4.2	4.3	4.0	4.0	4.1	4.1	4.4	4.6	4.5	4.23 \pm 0.21108
	Pb	2.1	2.2	2.0	2.45	2.5	1.9	2.1	2.0	2.3	2.3	2.185 \pm 0.20007
Galaxy	Cd	0.36	0.31	0.33	0.33	0.30	0.34	0.34	0.32	0.35	0.31	0.329 \pm 0.01912
	Ni	4.3	4.5	4.6	3.9	3.9	4.0	4.0	4.5	4.4	4.3	4.24 \pm 0.26750
	Pb	2.5	2.3	2.1	2.5	2.4	2.0	2.2	2.5	2.0	2.55	2.3050 \pm 0.2166

S1 , S2 = Sample1 , Sample2

**Figure 1: Comparative levels of selected heavy metals in three types of chocolates.****Table 2: averages of concentration means of every metal in three types of chocolates**

Heavy metals	chocolates			Average ($\mu\text{g/g}$)
	Twix	Mars	Galaxy	
Cdconc. $\mu\text{g/g}$	0.3282	0.323	0.329	0.3267
Niconc. $\mu\text{g/g}$	4.38	4.23	4.24	4.283
Pbconc. $\mu\text{g/g}$	2.212	2.185	2.305	2.234

Data analysis in Table 1 showed there were no significant differences in concentration means of Cd in three types of chocolates evaluated in this study, that also regarding the concentration means of the two other metals Ni and Pb. There were significant differences between concentration means of three metals in

each type of chocolates, it can be seen from Table 2 that the concentration means average of Ni in three types of chocolates are nearly 2 times higher than Pb concentration means average and more than 13 times higher than Cd concentrations average.

Table 3: Metal contents ($\mu\text{g/g}$) in three types of candies.

Candy	Heavy metals	S1 $\mu\text{g/g}$	S2 $\mu\text{g/g}$	S3 $\mu\text{g/g}$	S4 $\mu\text{g/g}$	S5 $\mu\text{g/g}$	S6 $\mu\text{g/g}$	S7 $\mu\text{g/g}$	S8 $\mu\text{g/g}$	S9 $\mu\text{g/g}$	S10 $\mu\text{g/g}$	Mean \pm SD $\mu\text{g/g}$
Lip-top	Cd	0.098	0.090	0.092	0.100	0.100	0.090	0.095	0.096	0.091	0.095	0.0947 \pm 0.00386
	Ni	1.42	1.35	1.25	1.30	1.55	1.40	1.45	1.40	1.50	1.55	1.417 \pm 0.10
	Pb	1.28	1.00	1.30	1.12	1.20	1.10	1.30	1.00	1.25	1.15	1.17 \pm 0.1149
Melody - Pops	Cd	0.092	0.089	0.090	0.096	0.091	0.090	0.090	0.098	0.099	0.095	0.093 \pm 0.00368
	Ni	1.35	1.31	1.35	1.33	1.30	1.40	1.41	1.45	1.42	1.44	1.376 \pm 0.05461
	Pb	1.20	1.14	1.12	1.15	1.25	1.10	1.20	1.00	1.00	1.22	1.138 \pm 0.08626
Caretos	Cd	0.090	0.097	0.091	0.090	0.099	0.095	0.091	0.094	0.099	0.089	0.0935 \pm 0.003837
	Ni	1.50	1.25	1.30	1.35	1.42	1.45	1.50	1.52	1.40	1.53	1.422 \pm 0.09682
	Pb	1.14	1.00	1.25	1.20	1.18	1.23	1.15	1.11	1.13	1.20	1.159 \pm 0.07156

#S1, S2= Sample1, Sample2

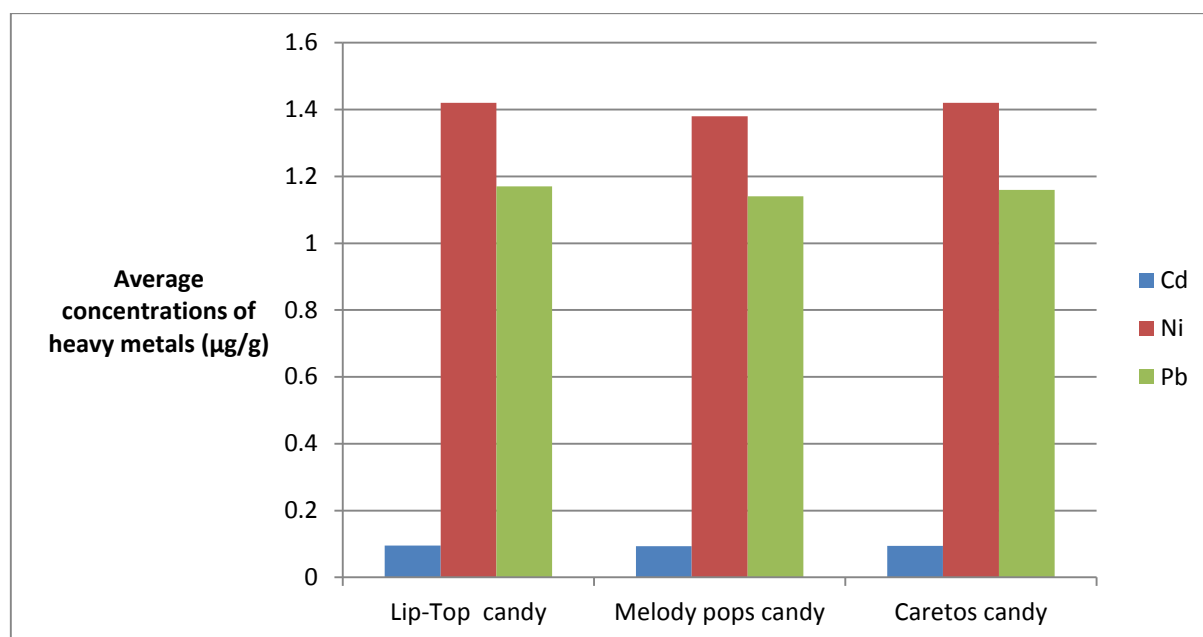


Figure 2: Comparative levels of selected heavy metals in three types of candies.

Table 4: averages of concentration means of every metal in three types of candies.

Heavy metals	Candies			Averages(µg/g)
	Lip-top	Melody pops	Caretos	
Cdconc.µg/g	0.0947	0.093	0.0935	0.0937
Niconc.µg/g	1.417	1.376	1.422	1.405
Pbconc.µg/g	1.17	1.138	1.159	1.15567

Data analysis in Table 3 showed there were no significant differences between concentration means of each one of three metals (Cd , Ni and Pb) in three types of candies evaluated in this study, while there were significant differences between concentration means of three metals in each brand of candies, it can be seen from Table 4, that the concentration means average of Ni in candies is nearly 20% higher than Pb concentration means

Discussion:

The presence of heavy metals in foodstuffs, sweets and chocolates varies in importance. For example, lead, cadmium and mercury are classified as toxic, while iron, zinc, copper, chromium, cobalt, nickel and manganese are classified as necessary⁽¹³⁾. In present study, analytical results indicated that Ni content in candies and chocolates samples was higher than Ni Which is low in a number of food

average and 15 times higher than Cd concentration means average.

Data analysis in Table 2 and Table 4 showed that concentrations average of Cd in chocolates is 3.5 times higher than its concentrations average of candies , concentrations average of Ni in chocolates is 3 times higher than its concentrations average of candies and concentrations average of Pb in chocolates is nearly 2 times higher than its concentrations average of candies products (0.001- 0.01 µg/g) and With very high concentrations in some other food products such as cocoa (up to 0.8 µg/g) by National Food Agency of Denmark , 1995⁽¹⁴⁾ and higher than Nickel content In different types of candy and chocolates which were announced by Sarala Devi and Selavpathy , 1995 with mean of (0.88 µg/g)^[15] . Consumption of nickel by eating food does not cause health risks for a large number of consumers. There is a small

percentage of people (app.10%, mainly women) are allergic tonickel. The sensitivity of nickel occurs only when absorbed by the skin⁽¹⁶⁾.Currently, nickel compounds are not considered carcinogenic compounds for humans or animals (WHO, 1984) ^[17], but the probability that the element of nickel as a catalyst has been proven(WHO , 1991) ^[18]. The level of concentration of cadmium in chocolate officially approved in Poland is 0.05 µg/g (FAO/WHO,2001)^[19] According to the levels set by the Polish regulatory agency, chocolates and candies samples in present study contained concentrations higher than the authorized limits. The International Agency for Research on Cancer (IARC) announced that cadmium is classified as a carcinogen of humans and has been associated with an increased risk of cancer Cadmium can accumulate in the liver and kidney and may cause many cancer effects, including prostate cancer⁽¹²⁰⁾. The maximum level of lead in chocolate defined by FAO/WHO (2001) is 1µg/g .and by the polish national standard for lead in chocolates is 0.30 µg/g ^[19] . According to these limits ,candies samples in our study contained concentration level higher than the authorized limits by FAO/WHO and more than three times the authorized limits by Poland regulatory agency, while the chocolate samples containedmore than 2 times the prescribed concentration level by FAO/WHO and more than 7 times prescribed concentration level by Poland regulatory agency. Cocoa beans contain a large amount of insoluble dietary fiber and soluble starch. This chemical mixture of cocoa helps to link lead and cadmium so strongly that this can be considered the potential source of lead and cadmium^[21]. The lead found in chocolate and candies can interact with chromium (VI) to form an inorganic (PbCrO4) saltwhich is malign to health, as Cr(VI) is known to be associated with cancer induction , especially bronchial carcinoma and lung

cancer ^[20].The presence ofPb and Cd in chocolate products could be natural or due to processing , these can be introduced during the preparation process or result from contamination via utensils, environmental pollution or storage and transportation ^[22]. Pb even at low levels may cause learning disabilities and behavioral problems . Children underage six years are mor at risk because it is the age when the brain is developing ^[23].Generically , children can absorb lead more easily than adults. The proportion of Pb absorbed from gastrointestinal tract have been reported for infant 40 – 50% whereas is about 10% in adults ⁽¹²⁾.

Conclusion:

The results of the present study indicate that the levels of the heavy metals under study (Ni , Pb and Cd) were found highest in the chocolates followed by candies.Regardless of the source of pollution of these metals, The continued consumption of these contaminated food products may lead to health damage . Candies and chocolates are favorites food items of children. Hence, children are the most attackable to contamination, thus , the daily dietary intake of chocolates and candies must be reduced . The Iraqi government must also take strict measures to control imported foodstuffs as well as illegally entering the country to protect citizens, especially children, from the risk of contamination with carcinogens.

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