Determination Of Cadmium, Lead, And Copper In Bread Sold In Street From Different Governorates In Egypt

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ABSTRACT

Forty one white bread samples were collected from street in different Egyptian local markets located in six governorates in Egypt during 2005. The samples were subjected to heavy metals analysis to determine lead (Pb), cadmium (Cd), and copper (Cu) levels. The bread samples were digested by wet digestion method, using conc. nitric acid (65 %) and measured by Atomic Absorption Spectrometer (AAS). The results revealed that all tested samples were contaminated with at least one element of the three investigated elements. Data showed that Cd and Cu were the most frequently detected elements, where the contamination percentage was 100%. However, Pb detected in 73.2% of the total number of samples analyzed. The highest mean concentration values of Pb and Cu were detected in bread samples collected from Qaluobiya governorate. However, the lowest mean values of Pb and Cu were detected in the samples collected from Miufiya and El Sharkiya governorates, respectively. The highest concentration level of Cd detected in bread samples collected from Cairo governorate; while, the lowest mean value recorded in samples collected from El Sharkiya governorate. Also, dietary exposures to Pb, Cd, and Cu elements were mathematically estimated to evaluate the risk to consumer due to their dietary intakes. The estimated weekly intakes (EWI s) of Pb, Cd and Cu for a 60 kg adult consuming 1507.1 g of white bread per week were 1.34, 0.3, and 42.7 (µg/kg body weight /week), respectively, which contribute 5.4%, 4.3%, and 1.22% from their respective provisional tolerable weekly intake values (PTWIs) (Pb: 25; Cd:7; Cu:3500 ug/kg body weight/week).

INTRODUCTION

Heavy metals are among the most frequently encountered contaminants in the environment. Several reports have focused on the residues of numerous heavy metals in foodstuffs (Cabrera et al., 1995; Llobet et al., 1998). Other reports have delineated on the contamination of the cereal products, including bread with heavy metals. (Hubbard and Lindsay, 1979) reported that the major route of man's exposure to heavy metal was ingestion. Even in the case of lead where the use of leaded petrol products ambient lead levels higher than other heavy metals pollutants, direct inhalation contributes less to the total body burden than

ingested lead. The main contributors, therefore, to heavy metals in the body were the foods consumed.

In Egypt, bread is a major component of people's diets. The per Capita consumption of bread is among the highest in the world, and bread is one of the few commodities still on the government's subsidy list (Ahmed et al., 2000). Local bread is produced in a number of different types of bakeries. In cities, most of the bakeries are either fully or partially automated. Solar and natural gas are main sources of energy used to operate these bakeries, although a considerable number of bakeries are using mazout, a heavy fraction of petroleum product (fuel no. 6). Electricity operated bakeries are also available, though in relatively small numbers. On the other hand, bakeries in the country side are less well equipped and many of them are fueled with agricultural and municipal solid waste. The levels of some heavy metals in bread and cereal have been studied in different parts of the world because of the paramount importance of these food materials and the heavy reliance of some societies on them (Devos et al., 1990; Lodovici et al., 1995). On the other hand and despite the high magnitude of bread consumption in Egypt, meager attempts were conducted to mape out the concentration levels of these contaminants in bread (Youssof, 1999)

The aim of this study was to determine the levels of Cu, Pb, and Cd in white bread collected from streets where bread is sold in the open and exposed to various air borne contaminants from different governorates in Egypt. Moreover, the daily intake of three investigated elements based on consumption was ascertained.

MATERIAL AND METHODS

A total of forty one white bread samples collected from streets in different local markets located in six governorates in Egypt (Cairo, Giza, Minufiya, Ismalia, Sharkyia, and Qalyubiya) during 2005.

Sampling:

Ten loaves of each bread samples were cut into small pieces and mixed thoroughly to determine the cadmium, lead, and copper levels in the different bread samples.

Apparatus and Equipments:

Atomic absorption spectrometer (AAS) (Analytical technology, INC. Unicam 929) equipped with graphite furnace with autosampler and flame atomic absorption.

Method of analysis:

An analytical method of **(NMKL, 1991)** was selected for determination of Pb, Cd, and Cu, where it is suitable for all kinds of food

types. Wet digestion is recommended for samples from which easily volatizing like Pb, and Cd.

1. Digestions:

Three gram of homogenized bread samples were transferred to glass digestion flasks with 10 ml of conc. HNO3. The solutions were boiled for 72 hours, depending on the sample matrix. The nitric acid solution was evaporated, and the residue was transferred with 0.3 N HNO3 into 25 ml volumetric flasks. The reagent blank was prepared as sample stating from the wet digestion step.

2. Determinations:

Lead and cadmium were determined by Electro thermal (AAS), using Deuterium lamp for background correction, cuvette atomization and argon gas. A mixture of NH4H2PO4 and Mg (NO3)2 were used as matrix modification. However, Cu was determined by flame atomic absorption using Deuterium lamp for background correction and air -acetylene gas.

Typical furnace parameters for lead and cadmium in AAS are given in the following table.

Step	Temp. (°C)	Time (sec.)	Ramp (°C/sec)	*Gas flow (ml/min)*
Drying	**120**	**40**	**30 (Cd), 10 (Pb)**	**2**
Ashing	**800**	**20**	**50**	**2**
Atomization	**1800**	**3**	**0**	**0**
Cleaning	**2500**	**3**	**0**	**2**
Cooling	**20**	**5**	**0**	**2**

3. Quality Assurance procedures:

The criteria of quality assurance of Codex Committee are followed to determine the performance of the analytical method. Recovery percentages, accuracy, limit of determination and coefficient of variation (CV %) were determined for the tested elements using bread samples. Blank samples were fortified individually with 0.1, 0.03 and 4 mg/kg of Pb, Cd, and Cu, respectively and analyzed with every set of samples. The average recoveries of Cd, Pb, and Cu from bread samples are 85%, 102% and 86%, respectively. The relative standard deviation (CV %) of Cd, Pb, and Cu are 10%, 6.9% and 14.5%, respectively. The limit of determination is 0.002 mg/kg for Cd, 0.04 mg/kg for Pb and 0.1 mg/kg for Cu. The measurement uncertainty including random and systemic error (on 95% confidence level) for all three elements is less than $\pm$20%.

RESULTS AND DISCUSSION

Table (1) shows the minimum, maximum, mean of Cd, Pb, and Cu, contaminated samples with each element monitored in 41 samples of bread collected from different Egyptian local markets located in six governorates during 2005.

The results revealed that all analyzed samples, collected from different governorates, contaminated with at least one of the three investigated elements, and contamination percentage was 100%. Cadmium and copper were the most frequently detected elements in analyzed samples, where the contamination percentage was 100%. However, lead (Pb) detected in only 73.2% of the total samples analyzed.

Lead (Pb) was present in the environment because of air, soil, and water pollution. Major sources of lead are exhaust fumes from cars, industrial gases and liquid effluents, some phosphate fertilizers and pesticides. Today, foodstuff and water are the basic sources for daily lead intake for adults and children. As from table (1), the mean lead values in bread samples, collected from six governorates, were ranged from 0.04 to 0.23 mg/kg. The highest mean concentration recorded in the samples collected from Qaluobiya governorate (0.17 mg/kg). However, the lowest mean value (0.04 mg/kg) detected in samples collected from Minufiya governorate. The highest contamination percentage of Pb detected in the bread samples collected from Cairo governorate, where 90.5% of all samples collected from Cairo were contaminated with Pb. The most probable sources of contamination for lead transferred to bread structure may be the wheat flour and tap water used in bread production or may be due to the environmental pollution with lead. The main sources of the lead pollution in the environment may be industrial production processes and their emissions, road traffic with leaded petrol, the smoke and dust emissions of coal and gas fired power stations.

Cadmium is a metal as toxic as lead. It is such a cumulative poison, and mainly accumulated in kidney and liver in human beings. Food and especially bread are the major source for cadmium intake of human body (Tati et al. 1976; Biddle, 1982; Dunnick and Fowler; 1988; Robards and Worsfold, 1991). The minimum, maximum, and the mean concentrations of Cd in bread samples collected from different governorates are summarized in table (1). Data showed that all bread samples collected from all six governorates were contaminated with Cd contaminant, and the mean cadmium values were varied between 0.006 and 0.015 mg/kg. The highest mean cadmium value was found as 0.015 mg/kg in bread samples obtained from Cairo governorate. However, the lowest mean value was recorded in

samples collected from El Sharkiya governorate. The contamination with Cd may be due to the biosphere contamination due to its emission in the industrial processes such as batteries, metal melting and refining, coal and oil-fired power stations, electroplating plants, etc.

Copper (Cu) has been recognized as an essential element for many years, due to its presence in important proteins and enzymes. High levels of Cu can cause acute toxicity. Human deaths have been known to occur from deliberate ingestion of large quantities of copper sulfate. As shown in the table (1), all bread samples collected from six governorates were contaminated with Cu, and the mean copper levels were ranged between 1.13 and 2.3 mg/kg. The highest mean value of the samples was detected in samples collected from Qaluobiya governorate. While, the lowest mean concentration recorded in the samples collected from El Sharkiya governorate. The copper came mainly from the erosion of overhead cables by railway traffic. In addition, as for the other heavy metals, ferrous and non ferrous metal production processes, the treatment of waste, sand combustion are all, to varying degrees, major sources of copper in the environment.

Numbers of studies were carried out to determine the lead, cadmium, and copper contents in bread samples. In Finland, the lead, cadmium, and copper contents were found as 8-16 µg/kg, 14-30 µg/kg, and 1.5-3.2 mg/kg in different bread types (Tahvonen and Kumpulaninen 1994a; Tahvonen and Kumpulaninen 1994b). In case of comparison of these values with those obtained from our study, it was determined that mean lead value is 53.3 (µg/kg) higher than Finland and the mean cadmium value (12 µg/kg) was lower than those obtained in Finland, In addition, the mean copper value (1.7 mg/kg) of this study is in the range that of Finland The lead and cadmium contents were found as 64.6±18.8 µg/kg, 49.4±14.1 µg/kg in white bread samples in Greece (Tsoumbaris and Tosukali, 1994), which is less from the present data. In Turkey, the lead, cadmium and copper contents were found as 28.6 µg/kg, 4 µg/kg, and 0.7 mg/kg (Demirözüt, et. al. 2003), which were less than the present data. The lead content was found as 257.3 µg/kg, in Egypt, (Iskander et. al., 1992; murcottj@who.int.Ahmed et al., 2000). In case of comparison of these values with those obtained from our study, it was determined that mean lead value is less than the previous studies conducted in Egypt. However, the mean cadmium value was higher than that of Egypt

Dietary exposure to Cd, Pb, and Cu:

The daily intake of an element from food consumption is dependent on the element concentration in food and an amount of food consumed. The Global Environment Monitoring System / Program (GEMS/Food, 2003)

recommended daily consumption of 215.3 g of white bread per day in the Middle Eastern. The estimated weekly intakes (EWI) values shown in table (2) were calculated by assuming that a 60 kg individual will consume 215.3 g of bread per day. Thus, the EWI values table (2) of trace elements by an adult (µg/kg body weight) consuming of 1507.1 g of bread /week equal to mean concentration of element (µg/kg) multiplied by the amount of bread consumed per week (Kg) and divided by the average weight of an individual (60 Kg). The results in table (2) showed that the estimated weekly intakes (EWI s) of Pb, Cd and Cu were 1.34, 0.3, and 42.7 (µg/kg body weight /week), respectively, which contribute 5.4%, 4.3%, and 1.22% from their respective provisional tolerable weekly intake values (PTWI) recommended by the expert committee on food additives (Joint FAO /WHO Expert Committee on Food Additives, 2004). The PTWIs in µg/kg body weight are as follows: Cd: 7; Pb : 25, and Cu: 3500.

The provisional tolerable daily intake values established from (Joint FAO/WHO Expert Committee on Food Additives, 2004) for the adults that have 60 kg, body weight is 214 ug for Pb, 60 ug for Cd, and 30 mg for Cu. In calculations made by taking the mean, median, and maximum of each metal obtained in our study and the weight values, give the following results for each metal (table 2). The table showed that all the estimated daily intakes values (EDIs) and rate percentage (%) in mean, median, and maximum metal levels basis were below their respective provisional tolerable daily intakes values, So there is no health risk from the consumption of white bread and bread has no significant role in the dietary intakes of heavy metals

Conclusion:

The levels of trace metals in 41 samples of white bread collected from different local markets located in six governorates in Egypt were determined the results from this study suggested that:

- All bread samples analyzed were contaminated with at least one element of the three investigated elements.
- Cadmium and copper were the most frequently detected elements, where the contamination percentage was 100%. However, Pb detected in 73.2% of the total number of samples analyzed.
- The highest mean concentration value of Pb and Cu detected in bread samples collected from Qaluobiya governorate. While, the lowest mean

values of Pb and Cu were recorded in samples collected from Miufiya and El Sharkiya governorates, respectively.

- The highest concentration level of Cd detected in bread samples collected from Cairo governorate; however the lowest mean value recorded in El Sharkiya governorate.
- The estimated weekly intakes values (EWI s) of Pb, Cd and Cu from weekly consumption of 1507.1 g of white bread pose no risk since they were lower than the respective established provisional tolerable weekly intakes of these elements. Also, the estimated daily intakes values (EDIs) and rate percentage (%) in mean, median, and maximum metal levels basis were below their respective provisional tolerable daily intakes values, So there is no health risk from the consumption of white bread and bread has no significant role in the dietary intakes of heavy metals.

Table (1): Minimum, Maximum, Mean in (mg/kg), number and percentages of Contaminated samples and the analyzed metals residues in bread samples collected from different governorates in Egypt during 2005.

Commodity	governorates	Total no. of samples analyzed	Contaminated samples		Elements	Contaminated samples with each element		Min. In (mg/kg)	Max. In (mg/kg)	Mean. In (mg/kg)
			No.	%		No.	%			
Bread	Cairo	21	21	100	Pb	19	90.5	0.04	0.094	0.045
					Cd	21	100	0.004	0.11	0.015
					Cu	21	100	1.13	2.6	1.74
	Giza	9	9	100	Pb	5	55.6	0.04	0.084	0.055
					Cd	9	100	0.004	0.023	0.009
					Cu	9	100	1.3	3.41	1.97
	Minufiya	2	2	100	Pb	1	50	0.04	0.04	0.04
					Cd	2	100	0.008	0.01	0.009
					Cu	2	100	1.13	1.74	1.44
	Qalyubiya	3	3	100	Pb	2	66.7	0.1	0.23	0.17
					Cd	3	100	0.004	0.013	0.009
					Cu	3	100	1.4	3.6	2.3
	Ismalia	4	4	100	Pb	2	50	0.04	0.07	0.05
					Cd	3	100	0.002	0.013	0.008
					Cu	3	100	1	2.9	1.85
	Sharkiya	2	2	100	Pb	1	50	0. 11	0. 11	0. 11
					Cd	2	100	0.004	0.008	0.006
					Cu	2	100	1.1	1.15	1.13
	Total no. of samples	41	41	100	Pb	30	73.2			
					Cd	41	100			
					Cu	41	100			

Table (2): Estimated daily intakes (EDI) and estimated weekly intakes (EWI) by adults consuming bread

Metal	The estimated values in wet weight basis in (µg/kg)			Daily estimated intake values (EDI) ** in (µg/kg body weight)			The daily intake value established from JECFA in (µg/day/60kg body weight)	Rate percentage (%) ***			Provisional tolerable weekly intakes (PTWI) (µg/kg body weight)	Estimated weekly intakes in (µg/body weight) (EWI) calculated from mean	A % of PTWI
	Mean	Median	Maximum	Calculated value from mean	Calculated value from median	Calculated value from maximum		Calculated value from mean	Calculated value from median	Calculated value from maximum			
Pb	53.3	40	230	11.48	8.61	49.52	214	5.4	4	23.14	25	1.34	5.4
Cd	12	9	110	2.58	1.94	23.86	60	4.3	39.8	39.8	7	0.3	4.3
Cu	1800	1700	3600	387.54	366	778.1	30000	1.3	1.22	2.6	3500	42.7	1.22

** The dietary intake of each metal was calculated by multiplying the concentration of these metals in bread by the weights of that group Consumed per capita (215.3 g/person/day) (GEMS/Food Regional Diets, 2004). Food consumption of white bread in Middle Eastern is 215.3 (g/person/day).

*** The rate (%) of each metal was calculated by division the estimated intake to the daily intake value established from JECFA and by multiplying by 100.

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الملخص العربى

تقدير الكادميوم والرصاص والنحاس فى عينات من الخبز المعروض في الطرقات في بعض محافظات مصر

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*وزارة الزراعة – مركز البحوث الزراعية – المعمل المركزى لتحليل متبقيات المبيدات والعناصر الثقيلة فى الأغذية – الدقى-جمهورية مصر العربية

تم فى هذة الدراسة تجميع ٤١عينة من الخبز الأبيض من الطرقات في الأسواق المحلية لستة محافظات فى مصر وذلك خلال عام ٢٠٠٥ لتقدير عناصر الرصاص و الكادميوم والنحاس . خضعت جميع العينات لتحليل العناصر الثقيلة وذلك عن طريق هضمها بواسطة حامض النيتريك المركز (٦٥%)

والقياس بواسطة جهاز الامتصاص الذرى. أظهرت النتائج أن جميع العينات التى تم تحليلها كانت ملوثة بعنصر واحد على الأقل من العناصر الثلاثة التى تم تقديرها. كما أظهرت النتائج أن كلا من عنصرى الكادميوم و النحاس اكثر العناصر شيوعا فى هذة العينات حيث بلغت نسبة التلوث ١٠٠%.بينما كانت نسبة التلوث بعنصر الرصاص ٧٣,٢% من العدد الكلى للعينات التى تم تحليلها. ولقد لوحظ أن أعلى تركيزات لعنصرى للرصاص و النحاس فى العينات التى تم تجميعها من محافظة القليوبية . بينما وجد أن أقل تركيزات للرصاص و النحاس فى عينات الخبز التى تم تجميعها من محافظتى المنوفية و الشرقية على التوالى. كما وجد أن أعلى تركيزات لعنصر الكادميوم فى عينات الخبز التى تم تجميعها من محافظة القاهرة, بينما كانت أقل تركيزات للكادميوم فى العينات التى تم تجميعها من محافظة الشرقية. كما أشتملت الدراسة حساب مقدار المتناول اليومى و الأسبوعى للفرد من عناصر الرصاص و الكادميوم و النحاس و ذلك لتحديد مدى خطورة ذلك على صحة الأنسان نتيجة ما قد يتواجد من هذة العناصر فى عينات الخبز. ولقد أضحت النتائج أن مقدار المتناول الأسبوعى عناصر الرصاص و الكادميوم و النحاس للفرد (متوسط وزنة ٦٠ كجم) والذى يستهلك ١٥٠٧,١ جرام من الخبز الأبيض أسبوعيا" كان ١,٣٤ للرصاص و ٠,٣ للكادميوم و ٤٢,٧ للنحاس (ميكروجرام / وحدة وزن / أسبوع) والتى تمثل ٥,٤% و ٤,٣% و ١,٢٢%، على التوالى من النسب المسموح بها عالميا من مقدارالمتناول الأسبوعى للفرد لكل عنصر (ميكروجرام / وحدة وزن / أسبوع) (٢٥ للرصاص ؛ ٧ للكادميوم ؛ ٣٥٠٠ للنحاس).أي أن الخبز الأبيض عند عرضه للبيع في الطرقات يحدث به تلوث غير مرغوب وان كان مستوي هذا التلوث كما نتج من البحث لم يتعدي الحدود الخطرة والتي تسبب ضرر علي الصحة العامة .