

ASSESSMENT OF HEAVY METALS AND THEIR ESTIMATED DAILY INTAKES FROM TWO COMMONLY CONSUMED FOODS (KULIKULI AND ROBO) FOUND IN NIGERIA

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ABSTRACT

Most foodstuffs sold in Nigerian outdoor markets are often susceptible to pollution due to poor packaging. As a case study, this work was aimed at the evaluation of heavy metal (Cd, Cu, Zn, As, Pb and Ni) content of two widely consumed snack foods in the country, namely melon (*robo*) and groundnut (*kulikuli*). The *Robo* and *kulikuli* used in this study were purchased from Abeokuta. The products procured directly from the source of preparation served as control samples. All together, a total of two hundred and ninety-four samples were collected for both (*kulikuli* and *robo*) from seven different motor parks and forty-two samples of both (50% for each) formed the control. Samples were ground to powdered form and subjected to acid digestion. The resulting digests were analyzed for the heavy metal concentrations using calibrated atomic absorption spectrophotometer. Field survey was conducted to assess the average consumption of the two food types by an adult of 70 kg body weight and the daily intake of each was then calculated using standard procedures. Results showed that *kulikuli*; *robo* metal concentrations (mg/kg) were 0.23 to 1.25; 0.018 to 0.069; 6.73 to 9.23; 0.07 to 0.47; 13.83 to 33.13 and 16.15 to 53.91 for As, Cd, Cu, Ni, Pb and Zn respectively. Estimated daily dietary intake (mg/kg body weight) from the respective *robo* and *kulikuli*, for a 70 kg body weight, were 5.71×10^{-5} ; 8.57×10^{-5} , 9.57×10^{-3} ; 1.1×10^{-2} , 1.57×10^{-4} ; 4.14×10^{-4} , 8.86×10^{-4} ; 1.2×10^{-3} , 2.33×10^{-2} ; 3.5×10^{-2} and 2.76×10^{-2} ; 6.5×10^{-2} for Cd, Cu, Ni, As, Pb and Zn, respectively. Only Pb was above permissible level and based on estimated daily intake, risk factor decreased as $Pb > As > Zn > Cu > Cd > Ni$.

Key words: Foods, metal, contamination, environment, Nigeria

INTRODUCTION

Nigeria is popularly referred to as the most populous country in Africa, with over 130 million inhabitants [1]. One of the aftermaths of the increased human population is environmental pollution. It is possible to establish relationships between overpopulation, poverty and urban air pollution. Over population for a country of low gross domestic product spells poverty for the majority of the citizens and poverty prevents proper maintenance of internal combustion, resulting in the use of rickety, old, smoke – belching cars, two-stroke engine motorcycles (“Okada”) as means of public transport in the cities. Road traffic is identified to be a major source of air pollution in most Nigerian cities [2]. Air pollution in turn could be a correlate of food contamination. Most food items sold in the Nigerian outdoor markets are not adequately packaged. A great majority of foods such as local snacks, staple foods (cassava foods, rice, beans, grains, oil, fish, vegetable and meat) are displayed close to roadsides.

Although different foodstuffs have been assayed for heavy metal content in Nigeria, there are still a lot more that have not been assessed. Examples include some snack foods such as melon and groundnut cakes locally called *robo* for melon product and *kulikuli* for groundnut formulation. *Robo* is commonly consumed in the southwest region of the country while *kulikuli* is widely consumed across the nation. These snack foods are packed in containers such as basin, bowls, without any covering and displayed by the roadside. Alternatively, food vendors hawk them at motor parks as fast snack food, for commuters.

Food safety is an important aspect of a nation’s economic stability and due to previous reports on the degree of pollution of some other food items [3, 4, 5, 6], this study was aimed at assessing some heavy metal (As, Cd, Cu, Ni, Pb and Zn) levels of the two common food snacks; *kulikuli* and *robo*, using the products sold in Abeokuta, south-west Nigeria as a case study. In addition, estimated dietary intakes of the metals were also calculated.

Heavy metals, if present even in very low concentrations in foods, have the capability to cause human health problems. Information about the dietary intake of such metals is important to assess risks to consumers. Dietary intake could account for some fractions of the toxic metals found in the blood and urine of many Nigerians [7, 8, 9, 10]. Arsenic toxicity depends on the valence state, physical and chemical properties of the compound in which it occurs. Trivalent arsenic interacts with sulfhydryl group of proteins and enzymes. Pentavalent arsenic substitutes phosphate groups in oxidative phosphorylation. Arsenic, because of chemical similarities to phosphorus (P), is able to replace P in many plant cell reactions and shows much harmful toxicity to plants and animals. On absorption of the metal, it initially accumulates in the liver, kidney, lung, spleen, aorta and skin [11].

General symptoms of chronic arsenic exposure include weakness, general debility and lassitude, loss of appetite and energy, hair loss, hoarseness of the voice, weight loss and mental abnormalities. Related health problems include skin and vascular

disorders (acrocyanosis, angina pectoris, hypertension, myocardial infarction, mesenteric thrombosis, systemic occlusive arterial disease, bronchiectasis and recurrent bronchi-pneumonia), neuropathy, gastroenteritis, hepatotoxicity and hematological abnormalities such as anemia and leucopenia [11].

Cadmium has no known biological functions. It interferes with some essential function of Zn, thereby inhibiting enzyme reactions and nutrient utilization. It catalyzes oxidation reactions, generating free-radical tissue damage [12]. Zinc, an essential trace element is more toxic in salt form than in elemental form. Its ingestion causes gastrointestinal toxicity, pulmonary toxicity, nephrotoxicity and neurotoxicity [13, 14, 15].

Copper is an essential trace metal, vitally important for both physical and mental development in human, usually found in many food types particularly vegetarian foods such as nuts, seeds and grains. It is important for energy production in cells and is required for women's fertility in relation to estrogen metabolism amongst others. However, Cu accumulates easily in the body, hence, chronic low level intakes of heavy metals have damaging effects on human beings and other animals, since there is no good mechanism for their elimination. Conditions associated with increased copper body burden are arthritis, fatigue, insomnia, scoliosis, osteoporosis, heart disease, cancer, migraine, heart seizures, gum diseases, skin and hair problems. Reported also are mental and emotional disorders such as depression mood swings, fears, anxiety, panic attacks, violence and memory loss [14, 15].

Nickel is also an essential trace element whose role in the body is yet fully known. It is contained in many body tissues. Ordinarily, nickel is not known to be toxic to the body as the body does not readily absorb it [16]. However, nickel can combine with carbon monoxide (CO) to form a complex, nickel tetracarbonyl ($\text{Ni}(\text{CO})_4$), which is extremely poisonous, even more than CO, which is one of its precursor. Elevated dietary intake of the metal is associated with increased thyroid problems, cancer and heart disease [17].

Lead serves no useful purpose in the body and its toxicity affects virtually every organ in the human body. Its ability to mimic or inhibit calcium affects the actions of calcium-dependent or related processes. Pb also interacts with proteins such as sulfhydryl, amine, phosphate and carboxyl groups. The toxic metal primarily affects the peripheral and central nervous systems, renal functions, blood cells, metabolism of vitamins D. It is associated with hypertension, reproductive toxicity, developmental effects and neurological disorders, some of which may be irreversible [16, 18].

MATERIALS AND METHODS

Study area

Abeokuta is the capital of Ogun State in the southwestern region of the country, inhabited primarily by the Yoruba ethnic group. The motor parks, like in any other Nigerian city are located randomly near major outdoor markets. Stationary shops are

constructed within the parks and mobile traders and hawkers display their goods for commuters and drivers to buy.

Ethics

Permissions were obtained from the scientific committees of the Moshood Abiola Polytechnic and University of Agriculture, Abeokuta and the research was conducted following ethical procedures.

Sample collection

A challenge to the collection of *kulikuli* and *robo* samples was that most of the vendors were mobile, therefore not restricted to a particular location, moving from one end of a park to the other. Effort was therefore made to reduce the incidence of procuring products from the same vendor. It is a common practice for a vendor to sell either *kulikuli* or *robo* in multiples to customers. The quantity of each product in a pack varies with price. In line with this, at a particular motor park, three packs of a given product were randomly purchased per week for seven weeks from different vendors. In the laboratory, one sample was then removed from each product pack per week and stored for metal analysis.

Hence, twenty-one samples of groundnut cake (*kulikuli*) were collected from each of the seven motor parks in the city namely Asero, Adatan, Sapon, Ita-oshin, Lafenwa, Itoku and Kuto. Similarly, twenty-one samples of melon cake (*robo*) were procured from each of the stations. In addition, twenty-one samples of each food product were collected from the production centers, to serve as controls. All together, a total of two hundred and ninety four (21 x 7 x 2) samples were collected for both *kulikuli* and *robo* from the seven different motor parks and forty-two (21 x 2) samples of both food types served as controls. Samples were stored in transparent polythene bags, segregated according to food type and transported to the laboratory for metal analysis.

Analytical precision and quality assurance

Samples were cautiously collected to avoid contamination. All the glassware used were washed clean with distilled water after soaking for 24 h in 1% HNO₃, and analytical grade reagents purchased from Aldrich Chemical Company Limited, England were used. Reagent blank determinations were used to correct errors. Multiplicity of samples (n = 21) for each determination ensured reproducibility of data.

Metal determination

The samples were oven dried at 105°C to constant weight for 90 minutes, cooled to room temperature of 28 ± 1°C and ground to fine powder in a porcelain mortar and exactly 1 g of the ground sample was quantitatively transferred into a well-glazed porcelain crucible, placed in a muffle furnace and ashed at 450°C for 12 hours. The resultant ash was cooled to room temperature and digested to a clear solution with 5 ml of 5M HNO₃. The residue was then filtered into a calibrated 50 ml volumetric flask using Whatman No. 41 filter paper, and the solution was made up to mark with deionised water. The total concentrations of the metals in the digests were determined by aspirating the solution into Buck Model 210A atomic absorption

spectrophotometer after the necessary standardization procedures and the respective spectral lines (nm) were 213.9, 283.3, 324.7, 228.8, 232.0 and 193.7 for Zn, Pb, Cu, Cd, Ni and As respectively from hollow cathode lamps.

Estimation of daily dietary intake

Field survey for estimation of average consumption of the two food types

Individual or household consumption data for various food types such as vegetables, cereals, pulses, fruits, fish, meat, eggs, milk, dairy products, fats, oils, legumes, nuts, grains, cakes and staple foods are not available in Nigeria in comparison to the developed countries [19]. Field survey was conducted, using the procedures described in Adekunle *et al.* [6]. The weight of products consumed by adult on daily basis was evaluated and the value obtained was 100g on the average. The daily intake of each was calculated by multiplying the respective concentration in each food (melon or groundnut cake) by the food weight (100 g) and dividing the product by the body weight of a typical adult of 70kg body weight.

Statistical analysis

Results were generally expressed as mean \pm standard deviation. In order to ascertain if there was significant variations at $p \leq 0.05$ for a particular metal level in each product in relation to the different motor parks, data were subjected to Analysis of Variance (ANOVA) and Duncan Multiple Range Test (DMRT) to separate the means.

RESULTS

Trace metal level and their daily human intake

Results showed that *kulikuli*; *robo* metal concentrations (mg/kg) were 0.23 to 1.25; 0.018 to 0.069; 6.73 to 9.23; 0.07 to 0.47; 13.83 to 33.13 and 16.15 to 53.91 for As, Cd, Cu, Ni, Pb and Zn respectively and the summary of the pooled data are also presented ((Tables 1-3). The relative abundance of the metals decreased in the order Zn > Pb > Cu > As > Ni > Cd for both groundnut and melon cakes. Metal concentrations in all the samples from the motor parks were higher than those found in the control samples and the level of a particular metal was higher in groundnut cake than in melon cake food. In comparison with the control, the primary contaminant in the cakes, obtained from all the study sites (motor parks and production centres), was Pb.

The overall contributions of the snack foods to consumer metal daily intake (Fig.1) were 5.71×10^{-5} ; 8.57×10^{-5} mg of Cd, 9.57×10^{-3} ; 1.1×10^{-2} mg of Cu, 1.57×10^{-4} , 4.14×10^{-4} mg of Ni, 8.86×10^{-4} ; 1.2×10^{-3} mg of As, 2.33×10^{-2} ; 3.5×10^{-2} mg of Pb and 2.76×10^{-2} ; 6.5×10^{-2} mg of Zn per kg body weight respectively. Only exposure to Pb and As exceeded the established maximum acceptable daily dietary intake levels in mg/kg body weight [13, 17, 20, 21]. Results indicated that risk of toxic metal intake from both food types above the acceptable daily dose decreased in the order Pb > As > Zn > Cu > Cd > Ni.

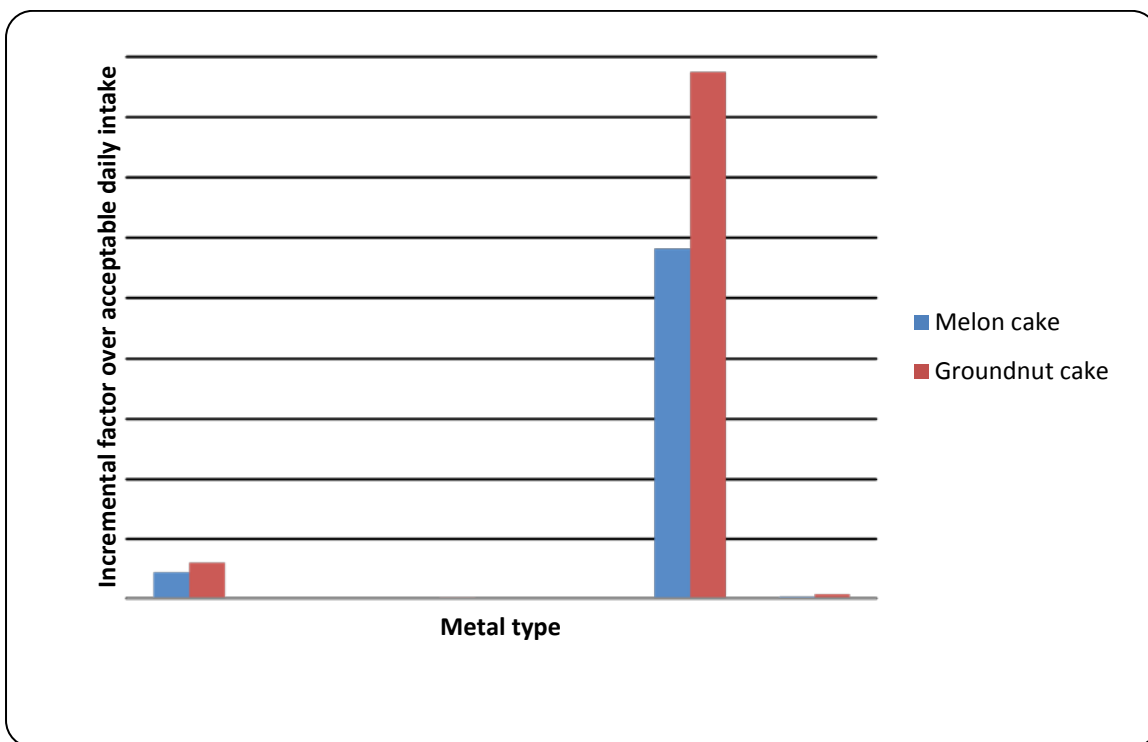


Figure1: Incremental factor of estimated daily intake of metals from melon and groundnut cakes over the acceptable daily intake

DISCUSSION

Excess metal concentrations in all the samples from the motor parks, in comparison to those found in the control samples, was attributed to atmospheric contamination. Elevated metal in groundnut cake relative to melon cake was probably due to the fact that melon cake was prepared from melon seeds, which are usually above the soil surface, unlike groundnut in which the reverse is the case [22]. Predominance of Pb over the other metals in all the samples, suggests that Pb is still the primary pollutant in the Nigerian environment, which is attributed to vehicular emissions and related automobile activities such as auto mobile repairs, battery waste disposal on land amongst others. Leaded gasoline is still utilized in Nigeria with estimated annual release of gaseous Pb in urban areas put at 2800 metric tonnes. The other metals (Zn, Cd, Cu, and Ni) are often used as minor additives to gasoline and different auto-lubricants [23, 24, 25,26].

Other sources of metals in the food products include; indiscriminate combustion of solid wastes and cigarette smokes released by smoking drivers and commuter could also be a contributory factor to metal in the foods [7, 27, 28], which could contribute to atmospheric pollution, contaminated process water and the soil – root transfer mechanisms in the soils, where the parent plant materials were grown via fertilizers (inorganic and manure fertilizer) in addition to sprays and dusts used as insecticides and pesticides for crop protection during cultivation [22]. A strong relationship

between soil heavy metals and farm produce was reported [6, 29] in Nigeria, suggesting that soil pollution is a contributory factor to food metal contamination in Nigeria.

Metals have been reported by Nigerian authors in a variety of foodstuffs in the country. These include vegetables, dry fish, smoked fish, meat preparations, spices, cocoa and cocoa products among many [3, 5, 6, 29, 30]. Trace metal in foods such as cereals, wheat, maize, rice, biscuit, legumes and beans have also been reported in different parts of the world [19, 31]. However, with the advent of the use of lead – free gasoline in the developed countries, Pb levels in foods are very much below the threshold of 0.2 mg/kg [20].

When compared with the results (1.11×10^{-2} to 2.02×10^{-2} mg/kg body weight) obtained on Pb in green leafy vegetables, commonly consumed in Nigeria, the value obtained in this study for Pb (2.33×10^{-2} ; 3.5×10^{-2} mg/kg body weight) is higher, suggesting that the risk of metal (such as Pb) entry into the human system may be higher via consumption of these exposed food snacks relative to vegetable consumption [6]. Such commonly consumed contaminated food snacks could play a significant role in elevated blood Pb levels reported in some Nigerians [7, 8, 9].

This phenomenon is not peculiar to Nigeria alone. Santos et al. [32] reported daily intake of eight elements via foodstuffs as 3.4×10^{-4} mg of Uranium (U) 1.8×10^{-3} mg of Cd, 2.8×10^{-3} mg of Pb, 2.3×10^{-2} mg of Cr, 8.9×10^{-2} mg of Ni, 1.12 mg of Cu, 2.5 mg of Mn, 3.5 mg of Al and 4.8 mg of Zn from meat, cow milk, flours, wheat and manioc consumed by the adult inhabitants of Rio de Janeiro. Similarly, for adult male population of Catalonia [19], metal intakes (mg/kg body weight) from vegetables, pulses, cereals, fruits, fish foods, meat, eggs, dairy products, milk, fats and oils were in the range of 4.86×10^{-3} to 2.90 of As, 1.43×10^{-2} to 4.72×10^{-2} of Cd, and 2.57×10^{-3} to 7.06×10^{-2} .

CONCLUSION

Trace metals (Pb, Cd, Ni, Cu, Zn and As) were detected in the foodstuffs (*kulikuli* and *robo*). Lead appeared to be the predominant metal contaminant and was the only element that exceeded the recommended safe level of dietary exposure. The risk - factors of dietary exposures to the metals for the consumers decreased in the order Pb > As > Zn > Cu > Cd > Ni.

RECOMMENDATION

It is recommended that regular monitoring of these food categories be conducted, to avoid metal build up in the body, whose detrimental impact becomes apparent only after several years of exposure.

Table 1: Trace metal concentrations (mg/kg) in melon cakes sold at different motor parks in Abeokuta

Location	Trace metals					
	Cd	Cu	Pb	Zn	Ni	As
Asero (n = 21)	0.048 ±0.001 ^a	6.79 ±0.25 ^b	19.88 ±0.71 ^b	16.15 ±1.90 ^c	0.12 ±0.02 ^b	0.68 ±0.11 ^b
Adatan (n = 21)	0.049 ±0.008 ^a	7.07 ±0.13 ^b	18.30 ±3.11 ^b	21.78 ±1.53	0.12 ±0.02 ^b	0.84 ±0.11 ^b
Sapon (n = 21)	0.052 ±0.005 ^a	6.77 ±0.13 ^b	13.83 ±0.88 ^d	18.43 ±0.73 ^b	0.08 ±0.01 ^c	0.38 ±0.17 ^c
Ita – oshin (n = 21)	0.018 ±0.009 ^b	8.03 ±0.26 ^a	14.88 ±2.23 ^c	19.95 ±0.70 ^a	0.15 ±0.03 ^a	0.23 ±0.03 ^c
Lafenwa (n = 21)	0.057 ±0.006 ^a	7.93 ±0.26 ^a	17.90 ±0.92 ^b	19.63 ±2.93 ^b	0.15 ^a ±0.03 ^a	1.18 ±0.06 ^a
Itoku (n = 21)	0.028 ±0.010 ^b	6.73 ±0.13 ^b	19.60 ±2.48 ^a	20.73 ±0.67 ^a	0.07 ±0.02 ^c	0.89 ±0.04 ^b
Kuto (n = 21)	0.045 ±0.008 ^a	7.83 ±0.29 ^a	15.75 ±0.57 ^c	18.55 ±0.15 ^b	0.13 ±0.02 ^a	0.79 ±0.11 ^b
Control (n = 21)	0.005 ±0.001 ^b	2.53 ±0.25 ^c	10.23 ±0.35 ^a	16.70 ±1.25 ^c	0.04 ±0.01 ^d	ND

Sample population is denoted by n, values in the same column with different superscripts are significantly different from each other ($P \leq 0.05$). ND = not detected. Permissible limits for Cd in all foods = 0.05 mg/kg, permissible limits for Cu in all foods = 10 mg/kg, permissible limits for Pb in non-leafy foods such as cereals, nuts, legumes = 0.2 mg/kg, permissible limits for Zn in grains = 50 mg/kg., permissible limits for Ni = 0.5 mg/kg.

Table 2: Trace metal concentrations (mgKg⁻¹) in groundnut cakes (Kulikuli) sold at different motor parks in Abeokuta

Location	Trace metal					
	Cd	Cu	Pb	Zn	Ni	As
Asero (n = 21)	0.052 ±0.006 ^a	7.29±0.23 ^c	25.79±0.25 ^c	43.99±0.44 ^c	0.40±0.03 ^a	1.00±0.25 ^b
Adatan (n = 21)	0.057 ±0.001 ^a	8.23±0.17 ^b	40.63±7.25 ^a	53.91±3.33 ^a	0.17±0.04 ^b	1.25 ^a ±0.50 ^a
Sapon (n = 21)	0.058 ±0.002 ^a	7.10±0.08 ^c	17.10±1.84	43.07±3.58 ^d	0.13±0.04	0.62±0.13 ^c
Ita – oshin (n = 21)	0.069 ±0.008 ^a	8.97±0.49 ^a	15.03±3.08	42.87±0.44 ^d	0.33 ±0.04 ^{ab}	0.25±0.02 ^d
Lafenwa (n = 21)	0.062 ±0.005 ^a	9.23 ±0.21 ^{ab}	33.13±1.41 ^b	43.15±0.70 ^d	0.46±0.03 ^a	1.50±0.01 ^a
Itoku (n = 21)	0.059 ±0.008 ^a	8.13 ±0.13 ^b	27.03±2.09	48.27±0.81 ^b	0.33 ±0.02 ^{ab}	0.98±0.15 ^b
Kuto (n = 21)	0.067 ±0.002 ^a	9.20±0.08 ^a	26.68±0.74 ^c	44.67±1.77 ^c	0.47±0.02 ^a	1.13 ^b ±0.38 ^b
Control (n = 21)	0.057 ±0.002 ^a	3.07±0.17 ^d	10.52±1.28 ^e	43.92±1.58 ^c	0.06±0.01 ^b	ND

Sample population is denoted by n, values in the same column with different superscripts are significantly different from each other ($P \leq 0.05$). ND = not detected Permissible limits for Cd in all foods = 0.05 mg/kg, permissible limits for Cu in all foods = 10 mg/kg, permissible limits for Pb in non-leafy foods such as cereals, nuts, legumes = 0.2 mg/kg, permissible limits for Zn in grains = 50 mg/kg., permissible limits for Ni = 0.5 mg/kg.

Table 3: Summary of pooled data from the seven stations, for metal concentrations in *kulikuli* and *robo* found in Abeokuta, Nigeria

Parameter	Melon cake (mg/kg) (n = 147)	Groundnut cake (mg/kg) (n = 147)
<i>Metal</i>		
<i>Concentration in food (mg/Kg)</i>		
As	0.62± 0.36 (0.23 – 1.18)	0.84± 0.48 (0.25 – 1.25)
Cd	0.04 ± 0.01 (0.018 – 0.057)	0.06± 0.01 (0.052 – 0.069)
Cu	6.7± 1.7 (6.73 – 8.03)	7.7± 1.9 (7.10 – 9.23)
Ni	0.11 ± 0.04 (0.07 – 0.13)	0.29± 0.15 (0.13 – 0.47)
Pb	16.3± 3.1 (13.83 – 19.88)	24.5± 9.3 (15.03 – 33.13)
Zn	19.3±1.7 (16.15 – 21.78)	45.5± 3.8 (42.87 – 53.91)
<i>Dietary intake (mg/kg/bw)</i>		
As	8.86 x 10 ⁻⁴	1.20 x 10 ⁻³
Cd	5.71 x 10 ⁻⁵	8.57 x 10 ⁻⁵
Cu	9.57 x 10 ⁻³	1.10 x 10 ⁻²
Ni	1.57 x 10 ⁻⁴	4.14 x 10 ⁻⁴
Pb	2.33 x 10 ⁻²	3.50 x 10 ⁻²
Zn	2.76 x 10 ⁻³	6.50 x 10 ⁻²

Values in parenthesis = range for trace metal level for metal concentration, acceptable daily intake (ADI) established by WHO (1982) for a 70 kg person: Cd = 0.06, Cu = 0.05 – 0.5, Pb = 0.003 – 0.004, Zn = 0.3 – 1.0, Ni = 1.3 and As = 0.002, unit in mg/kg/body weight, n = total number of test samples excluding controls

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