Uncorrected Proof

Levels of Selected Heavy Metals in Varieties of Vegetable oils Consumed in Kingdom of Saudi Arabia and Health Risk Assessment of Local Population

Muhammad Waqar Ashraf
Department of Natural Sciences & Mathematics, Prince Mohammad Bin Fahd University, Al Khobar 31952, Kingdom of Saudi Arabia.
mashraf@pmu.edu.sa*

Summary: Selected heavy metals, namely Cu, Zn, Fe, Mn, Cd, Pb and As, in seven popular varieties of edible vegetable oils collected from Saudi Arabia, were determined by graphite furnace atomic absorption spectrometry (GF-AAS) using microwave digestion. The accuracy of procedure was confirmed by certified reference materials (NIST 1577b). The concentrations for copper, zinc, iron, manganese, lead and arsenic were observed in the range of 0.035 - 0.286, 0.955 – 3.10, 17.3 – 57.8, 0.178 - 0.586, 0.011 - 0.017 and 0.011 - 0.018 µg/g, respectively. Cadmium was found to be in the range of 2.36 – 6.34 ng/g. The results are compared internationally and with standards laid down by world health agencies. A risk assessment study has been carried out to assess exposure to these metals via consumption of vegetable oils. A comparison has been made with safety intake levels for these heavy metals recommended by Institute of Medicine of the National Academies (IOM), US Environmental Protection Agency (US EPA) and Joint FAO/WHO Expert Committee on Food Additives (JECFA). The results indicated that the dietary intakes of the selected heavy metals from daily consumption of 25 g of edible vegetable oils for a 70 kg individual should pose no significant health risk to local population.

Key Words: Vegetable oils; Heavy metals; Contamination; Health Risk Assessment; Human Exposure

Introduction

Vegetable oils are widely used in cooking, food processing, cosmetic, pharmaceutical and chemical industries. The presence of essential fatty acids, fitosterols and a tocopherol, enhances the nutritional value of vegetable oils. Vegetable oils are beneficial and popular due to their cholesterol-lowering effect. This is largely a result of the high levels of antioxidative substances and monosaturated fatty acids found in most pure vegetable oils. In contrast, animal fats are predominantly saturated and do not react readily with oxygen [1].

The quality of edible oils can be evaluated by the determination of several trace metals. Trace metals find their way into vegetable oils, both by endogenous and exogenous sources. Levels of trace metals like Fe, Zn, Cu, Mn, Cd, Pb and As are known to have adverse effects on oxidative stability of vegetable oils. Copper and iron catalyze the decomposition of hydroperoxides which lead to formation of undesirable substances in oils [2]. The presence of trace metals in vegetable oils depends on many factors: they might originate from the soil, fertilizers, and presence of industry or highways near the plantations [3]. The metals may also be introduced during the production process, packaging material or by contamination from the metal processing equipment and thus, be suspended in the oil [4]. Toxic elements can be very harmful even at low concentration when ingested over a long time period [5]. The essential metals can also produce toxic effects when the metal intake is excessively elevated [6]. The trace metals enhance the rate of oxidation of edible oils by increasing the generation of free radicals from fatty acids or hydroperoxides.It is necessary to assess the levels of heavy metals in edible vegetable oils and to report possible contamination that would represent a health hazard. Researchers from different parts of the world have determined heavy metals in vegetable oils [2-3,7-8]. Food consumption had been identified as the major pathway of human exposure to toxic metals, compared with other ways of exposure such as inhalation and dermal contact. Taking into account the metabolic role of some metals and the large use of vegetable oils, it is of great significance to evaluate the presence of heavy metals in commercially available vegetable oils [9-10].

Saudi consumers increasingly sought to adopt a healthier diet with widening awareness of the health problems caused by excessive weight. There is a big turn over from animal fat based cooking oils to vegetable oils. However, there has been no report, to our knowledge, on the heavy metal levels in edible vegetable oils in Saudi Arabia. The main objective of this study were to determine the concentrations of seven heavy metals (copper, zinc iron, manganese, cadmium, lead and arsenic) in edible vegetable oils consumed in KSA and estimate the potential human health risks from consumption of these vegetable oils.

Results and Discussion

Average concentration levels along with standard deviation and range of the elements analyzed (As, Cd, Cu, Fe, Mn, Pb & Zn) are given in Table-1. The zinc content of the samples ranged from 0.955 to3.1µg/g; soybean oil had the lowest zinc concentration whereas corn oil had the highest. Zinc is known to be involved in most metabolic pathways in humans and is regarded as cofactor for many enzymes. Zinc deficiency can lead to growth retardation and immunological abnormalities. The zinc levels in the oil samples were lower than those in previous reports [3,7,8], but the levels were higher than these literature values 0.04-0.70 µg/g [11] and 0.0484-0.2870 mg/kg [2].

Copper is essential for human body but very high intake can cause adverse health problems. Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea [12]. Chronic copper poisoning results in Wilson's disease, characterized by a hepatic cirrhosis, brain damage, demyelination, renal disease, and copper deposition in the cornea. Copper deficiency leads to hypochromic anemia, leucopenia and osteoporosis in children [13]. Minimum and maximum values of copper in our samples were 0.035 and 0.286 µg/g in corn oil and olive oil. In the literature copper levels in edible oil samples have been reported in the range of 0.021-0.265µg/g [3], 12.71-50.5 µg/g, 21.0-31.0 µg/g [14], 0.0184-0.2870µg/g [2] and 0-130 ng/g [15,16]. Our copper values in the investigated oil samples were in agreement with those reported in the literature [7,8,17].

The minimum and maximum iron levels observed were17.3µg/g in corn oil and 57.8µg/g in olive oil. The reported iron values for oil samples were 16.2-56.3µg/g [3], 52.0-291.0 µg/g [7], 0.0039-0.0352 mg/kg [2], 0-800 ng/g [15-16] respectively. Our iron levels were in agreement with those reported in the literature [3]. Iron deficiency is frequently associated with anemia and, thus, reduces working capacity and impaired intellectual development [18]. It is known that adequate iron in diet is very important for decreasing the incidence of anemia.

The lowest manganese content was 0.178µg/g in rapeseed oil while the highest manganese content was 0.586µg/g in peanut oil. Manganese deficiency can produce severe skeletal and reproductive abnormalities in mammals. High doses of manganese produce adverse effects primarily on the lungs and on the brain. The US National Academy of Sciences recommended 2.5-5 mg per day manganese (National Academy of Sciences 1980) and, the WHO (World Health Organization) recommended 2-9 mg per day for an adult [19].

Cadmium is a highly toxic metal with a natural occurrence in soil, but it is also spread in the environment due to human activities. After ingestion, Cadmium is first transported to the liver through the blood. There, it is bond to proteins to form complexes that are transported to the kidneys. Cadmium accumulates in kidneys, where it damages filtering mechanisms. Excessive cadmium exposure may give rise to renal, pulmonary, hepatic, skeletal, reproductive effects and cancer. The JECFA provisional tolerable weekly intake (PTWI) for cadmium is 7 µg/kg body weight. The highest cadmium content in our oil samples was 6.34ng/g in corn oil, whereas the lowest cadmium content was 2.36 ng/g in olive oil.

Arsenic is a known carcinogen in humans, causing lung, liver, skin and bladder cancer [20]. In its most recent evaluation of arsenic, the Joint FAO/WHO Expert Committee on Food Additives [21] established a provisional tolerable weekly intake (PTWI) of 15 µg/kg body weight for inorganic arsenic. The arsenic content of samples ranged from 0.011to 0.018µg/g; corn oil had the lowest arsenic concentration whereas sesame oil had the highest. Our values for arsenic were above the Spanish values [15-16] but similar to Chinese values [3].

The minimum and maximum lead levels were 0.011µg/g in rapeseed oil and 0.017µg/g in sesame oil. The lead levels in all investigated edible oils were found to be lower than legal limits [9]. Lead is similar to cadmium that has no beneficial role in human metabolism, producing progressive toxicity. Lead serves no useful purpose in the human body, but its presence in the body can lead to toxic effects, regardless of exposure pathway. Some researchers have suggested that lead continues to contribute significantly to socio-behavioral problems such as juvenile delinquency and violent crime [22]. WHO has established a provisional tolerable weekly intake (PTWI) for lead of 0.025 mg/kg of body weight [23].

Table 1: Heavy metal concentrations in vegetable oils (µg/g)

Oil Type		As	Cd*	Cu	Fe	Mn	Pb	Zn
Corn Oil	X±SD	0.011 ± 0.002	6.34 ± 0.51	0.035 ± 0.001	17.3 ± 0.8	0.297 ± 0.23	BDL	3.1 ± 0.290
	Range	0.005 - 0.017	3.77 - 7.16	0.019 - 0.041	16.4 - 18.9	0.211 - 0.304		2.25 - 3.78
Sunflower Oil	X±SD	0.013 ± 0.001	2.88 ± 0.34	0.062 ± 0.004	33.4 ± 2.1	0.347 ± 0.037	0.011 ± 0.001	1.54 ± 0.05
	Range	0.006 - 0.013	1.98 - 2.97	0.029 - 0.071	27.8 - 36.1	0.311-0.386	0.007-0.014	1.13-1.86
Soybean Oil	X±SD	0.016 ± 0.001	4.58 ± 0.25	0.052 ± 0.001	24.3 ± 1.3	0.130 ± 0.012	0.014 ± 0.001	1.36 ± 0.02
	Range	0.009 - 0.017	4.10 - 4.98	0.042 - 0.061	23.1 - 25.7	0.172 - 0.138	0.012 - 0.16	1.12 - 1.53
Peanut Oil	X±SD	0.017 ± 0.001	3.66 ± 0.20	0.178 ± 0.013	37.8 ± 2.7	0.586 ± 0.033	0.013 ± 0.001	1.78 ± 0.08
	Range	0.008 - 0.018	3.09 - 3.98	0.144 - 0.183	34.3 - 39.7	0.543 - 0.618	0.006 - 0.018	1.12 - 1.93
Sesame Oil	X±SD	0.018 ± 0.001	5.78 ± 0.21	0.049 ± 0.003	43.8 ± 4.7	0.269 ± 0.002	0.017 ± 0.002	0.955 ± 0.071
	Range	0.014 - 0.021	5.11 - 5.86	0.037 - 0.061	39.8 - 46.3	0.183 - 0.289	0.013 - 0.023	0.633 - 1.12
Olive Oil	X±SD	0.013 ± 0.001	2.36 ± 0.11	0.286 ± 0.016	57.8 ± 3.8	0.186 ± 0.006	BDL	1.88 ± 0.07
	Range	0.007 - 0.014	2.17 - 2.86	0.211 - 0.312	38.8 - 68.3	0.096 - 0.210		1.36 - 2.11
Rapeseed Oil	X±SD	0.018 ± 0.001	5.71 ± 0.11	0.193 ± 0.012	26.8 ± 1.6	0.178 ± 0.009	0.011 ± 0.001	1.67 ± 0.12
	Range	0.013 - 0.023	5.30 - 5.91	0.176 - 0.219	23.3 - 28.2	0.113 - 0.204	0.007 - 0.015	0.48 - 0.180
			* ng/g				BDL Below Detection Limit	

Intake of elements from food consumption is dependent on the element concentrations in food and the quantity of food consumed by individual. World renowned agencies like US Environmental Protection Agency (US EPA), Joint FAO/WHO Expert Committee on Food Additives [21] and Institute of Medicine of the National Academies (IOM) have provided guidelines on the intake of trace elements by humans. The IOM of the National Academies recommended the adequate intake (AI) and the tolerable upper intake level (UL) values for some essential elements [23-24]; the JECFA recommended permissible tolerable weekly intakes (PTWIs) and acceptable daily intakes as guidelines for food additives and certain contaminants in foods [21]. Also, the US EPA provided reference dose (R_fDo) values in ug/kg body weight/day for some elements [25]. The data obtained in the present work was used to evaluate the possible health hazards from the consumption of edible vegetable oils by local population.

According to a maximum dietary intake of 25 g of a single type of fat or oil for an adult per day recommended by World Health Organization [26], the estimated daily dietary intakes (EDDIs) of heavy metals from edible oils analyzed were calculated with mean concentration values, *(X) µg/g* x *25g/day* x *1/70Kgbw* (Table-2). The estimated weekly dietary intake (EWDI) were also calculated from average concentration values, *(X) µg/g* x *175g/week* x *1/70Kgbw* (Table-3).

The UL, AI, guideline and PTWI values were used to compare the estimated dietary intakes of trace elements (Tables-2 and 3). The results in Table-4 suggest that the EDDI of Cu, Zn, Fe and Mn by a 70 kg adult consuming 25 g of edible vegetable oils per day were all far below the respective AI and UL recommended by IOM. As shown in Table-5, the EWDI of Cu, Zn, Fe, Mn, Cd, Pb and As by a 70 kg adult consuming 175 g of edible vegetable oils per week were all less than the derived guideline values and PTWI served by JECFA, therefore, weekly consumption of 175 g of edible vegetable oils in KSA generally did not pose any serious health risks to local population. Presented data compares well with internationally reported values (Table-4).

Experimental

A total of 161 edible vegetable oil samples (32 corn oil, 21 soybean oil, 19 sesame oil, 17 rapeseed oil, 17 peanut oil, 27 olive oil, and 28 sunflower oil samples) were purchased from Saudi hypermarkets during 2011-2012. The most widely and frequently consumed brands were selected. The collected oil samples were packed in polyethylene bags and kept refrigerated till analyzed. In all cases, analyses were completed before mentioned expiry dates.

All reagents were of analytical reagent (AR) grade unless otherwise stated. Double deionized water was used for all dilutions. HNO_3 and H_2O_2 were of suprapure quality (E.Merck, Dermsdat, Germany). All the plastic and glassware were cleaned by soaking in a 10% nitric acid solution and then rinsed with double deionized water. A Shimadzu AA-6200 equipped with ASC 6100 autosampler atomic absorption spectrometer equipped with HGA graphite furnace (GF-AAS) was used to determine Cu, Zn, Fe, Mn, Cd, Pb and As. For graphite furnace measurements, argon was used as inert gas. The operating conditions for GF-AAS analyses were same as mentioned elsewhere [7].

Microwave digestion method was preferred because of its proven accuracy both with respect to time and recovery. Approximately one gram samples were digested with 5.0 mL HNO_3, 3.0 mL of H_2O_2 in microwave digestion system and diluted to 10.0mL with doubly distilled water. Digestion conditions for microwave system were applied as 2min for 250W, 2min for 0W, 6min for 250W, 5min for 400W, 8min for 550W, vent: 8min, respectively. One blank sample was subjected to same procedure.

Appropriate quality assurance and quality control procedures were followed to ensure the reliability of obtained data. Recovery experiments were performed to assure the reliability of data. Certain quantities of each element of interest were added to sample matrix. The experiments were performed in triplicate. Table-5 shows the recovery data. The accuracy of the results was >95% for all elements. The accuracy of the method was evaluated by means of trace element determination in a standard reference material (NIST-SRM 1577b bovine liver). The achieved results were in good agreement with certified values. All metal concentrations were determined on a wet weight basis (µg/g). The results along with detection limits are given in Table-6.

Table-2: Estimated daily dietary intake (EDDI)s and contribution of essential elements to UL and RDA/AL from consumption of 25g edible oils per day

	Corn Oil	Sunflower Oil	Soybean Oil	Peanut Oil	Sesame Oil	Olive Oil	Rapeseed Oil	IOM RDA/AL (µg/d)*	IOM UL (µg/d)**
Cu	0.88[1]	1.55	1.3	4.45	1.23	7.15	4.83	990	10000
Zn	77.5	38.5	34	44.5	23.9	47	41.8	11000	40000
Fe	432.5	835	607.5	945	1095	1407.5	675	8000	45000
Mn	7.42	8.67	3.25	14.7	6.72	4.65	4.45	2300	11000

[1]EDDI values calculated from element mean value (µg/day/70kg bw)
*Adequate Intake (AI) for individuals 19-70years old, Food & Nutrition board of IOM, 2002
**Upper tolerable intake level for individuals 19-70years old, IOM, 2003

Table-3: Estimated weekly dietary intakes (EWDI) and contribution of heavy metals to PTWI from consumption of 175g edible oils per week.

.	Corn Oil	Sunflower Oil	Soybean Oil	Peanut Oil	Sesame Oil	Olive Oil	Rapeseed Oil	Guideline* (µg/kg/week)	PTWI (JECFA)** (µg/kg/bw)
Cu	0.08[1]	0.155	0.13	0.445	0.123	0.715	0.483	280	3500
Zn	7.75	3.85	3.4	4.45	2.39	4.7	4.18	2100	7000
Fe	43.25	83.5	60.75	94.5	109.5	140.75	67.5	4900	5600
Mn	0.742	0.867	0.325	1.47	0.672	0.465	0.445	1680	NA
Cd	0.016	0.007	0.011	0.009	0.014	0.006	0.014	7	7
Pb	NA	0.035	0.035	0.033	0.043	NA	0.028	NA	25
As	0.028	0.033	0.040	0.043	0.045	0.045	0.045	2.1	15

*RfDo values for body weight 70kg & oil consumption duration 7days (US EPA,2007a)
**PTWI values (FAO/WHO, 1999)
[1]Weekly dietary intake values calculated from elements mean value (µg/kg bw/day). Average body weight 70kg

Table-4: Comparison with international values.

	Corn	Sunflower	Soybean	Peanut	Sesame	Olive	Rapeseed	Reference
As	0.011	0.013	0.016	0.017	0.018	0.013	0.018	This work
	0.012	0.011	0.015	0.013	0.019	0.012	0.015	[3]
*Cd	6.34	2.88	4.58	3.66	5.78	2.36	5.71	This work
	8.43	3.51	4.36	3.81	5.44	2.64	6.33	[3]
Cu	0.035	0.062	0.052	0.178	0.049	0.286	0.193	This work
	0.0138	0.0226	0.073			0.0155		[2]
Fe	17.3	33.4	24.3	37.8	43.8	57.8	26.8	This work
	52	105.3				139		[7]
	0.0195	0.0107	0.0129			0.0295		[2]
Mn	0.297	0.347	0.13	0.586	0.269	0.186	0.178	This work
	1.64	0.12				0.04		[7]
	0.0017	0.0026	0.022			0.0065		[2]
Pb	BDL	0.011	0.014	0.013	0.017	BDL	0.011	This work
	0.009	0.01	0.015	0.012	0.018	0.013	0.012	[3]
	BDL	0.0016	BDL			0.0074		[2]
Zn	3.1	1.54	1.36	1.78	0.955	1.88	1.67	This work
	2.56	1.23	0.742	1.3	0.883	1.41	1.57	[3]
	3.08	1.10				1.03		[7]

*Cd ng/g

Table-5: Data pertaining to average standard addition recoveries.

Metal	Cu		Zn		Fe		Mn		Cd		Pb		As	
µg/g added	5	10	10	20	10	20	5	10	5	10	5	10	5	10
µg/g recovered	4±2	9±2	8±3	19±2	9±2	18±2	4±2	8±3	4±2	8±2	4±2	9±2	4±2	8±2

Table-6: Trace metal levels in SRM NIST 1577b, recoveries and detection limits.

Metal	Certified Value (µg/g)	Our Value (µg/g)	Recovery (%)	DL(ug/g)
Fe	184	182±14	99	0.017
Zn	127	126±7	99	0.01
Mn	10.5	10.3±0.7	98	0.019
Pb	0.129	0.126±0.02	97.6	0.098
Cd	0.5	0.48±0.04	96	0.092
Cu	160	157±9	98	0.011
As	0.05	0.05±0.01	99	0.121

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