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Trace elements determination by ICP-QMS in octopus edible samples from Mexico City markets

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Abstract. The purpose of this study was to evaluate the total concentration levels of trace elements (Cr, Cu, Mn, Pb, Rb and Sr) in octopus' mantle and tentacles samples from Mexico City markets, by using the Mexican regulation applied to food for human consumption. The determination of both essential (Cr, Cu, Mn) and non-essential (Pb, Rb and Sr) trace elements was made by inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS). The samples were collected from local markets and supermarkets from each of 16 delegations of Mexico City, Distrito Federal. The overall ranges of concentrations found were: 2.4-4.8, 5.1-95.3, 1-6, 0.1-1.6, 0.4-4.5 and 11-58 mg/kg for Cr, Cu, Mn, Pb, Rb and Sr, respectively. The maximum and mean concentration values obtained for Cu and Cr in mantle and tentacle samples from both kind of markets, are above of the NOM-051-SCFI/SSA1-2010 (closest Mexican standard), according to USDA National NDB for Standard Reference consumer exposure (100g/day) of octopus. It was observed that the maximum Pb concentration value found in mantle and tentacle samples from supermarkets origin exceeds the NOM-129-SSA1-1995 and NOM-242-SSA1-2009 reference values, while the maximum mean value is below the regulation. Similar Mexican regulation data for Mn, Rb and Sr were not found.
Keywords: Trace elements, octopus, cephalopods, ICP-QMS, Mexico City.

Resumen. El objetivo del presente estudio fue evaluar el nivel de concentración total de elementos traza (Cr, Cu, Mn, Pb, Rb y Sr) en muestras de manto y tentáculos de pulpo, recolectadas en mercados de la Ciudad de México, mediante la comparación con la normatividad mexicana aplicada en alimentos para consumo humano. La determinación de elementos traza esenciales (Cr, Cu y Mn) y no-esenciales (Pb, Rb y Sr) se llevó a cabo mediante espectrometría de masas con fuente de plasma de acoplamiento inductivo y analizador de masas cuadrupolo (ICP-QMS). Las muestras se recolectaron en mercados fijos y tiendas de supermercado, en cada una de las 16 delegaciones de la Cd. de México, Distrito Federal. Los rangos de concentraciones encontradas fueron: 2.4-4.8, 5.1-95.3, 1-6, 0.1-1.6, 0.4-4.5 y 11-58 mg/kg para Cr, Cu, Mn, Pb, Rb y Sr, respectivamente. Los valores máximo y mínimo de concentración obtenidos para Cu y Cr, en muestras de manto y tentáculo de pulpo recolectadas en ambas clases de mercados, fueron superiores a los correspondientes a la NOM-051-SCFI/SSA1-2010 (normatividad mexicana más relacionada). Esto, considerando el valor de referencia para exposición al consumidor de pulpo (100g/día) indicado por el USDA NDB. Las muestras de manto y tentáculo de pulpo, recolectadas en los supermercados, mostraron que el valor máximo de concentración de Pb excede los valores de referencia establecidos por las NOM-129-SSA1-1995 y NOM-242-SSA1-2009. Mientras que el valor promedio máximo es inferior a la normatividad mencionada. No se encontraron datos de normatividad mexicana para Mn, Rb y Sr.
Palabras clave: elementos traza, pulpo, cefalópodos, ICP-QMS, Ciudad de México.

Introduction

Metals that are nutritionally essential for humans are Co, Cr, Cu, Fe, Mg, Mn, Mo, Se and Zn. Fairbrother et al. [1] suggest that risk assessors should consider the essential elements as comprising three groups: those that are cations (Zn, Fe, Cu, Mn, Cr), those that are anions (Mo, Se), and those that are a bioinorganic complex (i.e., the Co complex, cobalamin). Excess amounts of essential metals can result in adverse effects to the homeostatic mechanisms of an organism. Specific biochemical functions have not been yet known for some elements, among them: Al, Br, Cd, Ge, Pb,. Li, Rb and Sn [2].

Recently, Guérin et al. [3] mentioned the attention paid to the study of essential and toxic trace elements content in foodstuffs because of the health benefits and risks of food consumption [4, 5, 6, 7]. Toxicologists tend to regard seafood as a major vector for toxic substances such as metal trace elements because many marine organisms have the potential to bioconcentrate high levels of metals from their environment [8, 9, 10, 11]. For example, Lourenço et al. [12], mentioned that little is known about the function of Sr and Rb in organisms, but the results of a few studies indicate that cephalopods may constitute a good source of Sr. Thus, there is an open research field in this area.

The pollution of the oceans or the continental waters, results from the spill of hundreds of million tons of residues and wastewaters coming from urban sites and farming lands. Besides, great amounts of chemical substances are found in preda-

tor species, as a result of the biomagnification (concentration of the chemical substances in the levels superiors of the trophic chain). These concentrations also are consequences of the bioaccumulation of chemical substances in tissues, throughout the life of the organism. For example, a large fish (representing older age) will have a higher content of a chemical substance than a small fish of the same species [13].

Mollusks have an important role to play in the ecosystem, varying from the herbivorous chitons feeding on microalgae and seaweeds attached to rocks, to the specialist carnivores like octopuses feeding on individual crab species. The mollusks have high nutritious value, since they contain vitamins A, B and D, carbohydrates and proteins in suitable amounts and of easy digestion [14]. Cephalopods are a highly nutritious, because of lack of bones, the average edible part of these organisms is between 80 and 85% of the total body [15]. The cephalopods reproduce once in their life and they are characterized by their small life cycle. They are active predators having a determining role in the trophic chain in the oceans and they are also an important fishing resource [16]. Several studies have evaluated the capacity of cephalopods to accumulate trace elements [12, 17, 18, 19, 20]. In general, feeding is considered the primary pathway for trace elements bioaccumulation in cephalopod [21]. Due to their rapid growth and market price, the culture of cephalopods has been an increasing area of interest [22]. Therefore, octopus can constitute a significant source of essential elements for man but also represents a source of exposure to toxic elements.

In Mexico, the fishing is an important resource to provide food for the inhabitants [23]. The octopus capture represents the fourth place in fishing activities at the coast of the Gulf of Mexico and the Caribbean (the capture of fish, shrimp and oyster are the most important). The capture of the octopus includes mainly two species: red octopus (*Mayan octopus*) and the common octopus (*Octopus vulgaris*). The 95 percentage of the octopus capture comes from the states of Yucatan, Campeche, Quintana Roo and Veracruz [24].

Thus, there is need to asses the trace elements concentrations in this food product, in order to evaluate the relationships between adverse effects observed in humans because of the dietary exposure. Martins et al. [25] have evaluated even the different cooking methods (grilling, frying and boiling) on selenium content of marine species commonly consumed in Portugal.

Methods used to trace elemental characterization of biological materials include: atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICPAES), inductively coupled plasma mass spectrometry (ICP-MS), particle induced x-ray emission (PIXE), neutron activation analysis (NAA) and energy dispersive x-ray fluorescence (EDXRF) [4, 26, 27]. In Mexico, different AAS techniques (flame, FAAS; graphite furnace, GFAAS; hydride generation, HGAAS and cold vapor, CVAAS) have been recommended by the Mexican Official Standards NOM-117- SSA1-1994 [28] and PROY-NOM-211-SSA1-2002 [29] for the analysis of As, Hg, Ag, Cd, Cr, Cu, Fe, Ni, Pb, Se, Sn and/or Zn in water, ice and food and additives for human consumption.

Nowadays, the use of ICP-MS is becoming more common in determination of essential and toxic elements concentration levels in consumed food products (3, 22, 27). Compared to graphite furnace atomic absorption spectrometry (GFAAS) or ICP-AES, this technique has some advantages: simultaneous multielement measurement capability, high sensitivity, linear dynamic range, characterized spectral interferences and rapid mass scanning [27].

The aim of the present study was to determine the total concentration levels of essential trace elements (Cr, Cu and Mn) and non-essential elements (Pb, Rb and Sr) by ICP-QMS in octopus edible tissues (mantle and tentacle) consumed in Mexico City, Distrito Federal. And to evaluate and to compare the results obtained with available Mexican reference values. Samples were collected from local markets and supermarkets from each of 16 delegations of the Distrito Federal, where the supermarkets represent the 52 percentage as the biggest local supplier of foodstuffs [30].

Experimental Procedure

The samples of octopus *Octopus vulgaris* (wet weight between 1.0-2.5 kg) were collected from one supermarket and one local market of each Mexico City delegation (see the sampling zone on Fig. 1). The samples were washed with deionized water, cutted off in small pieces and dried in oven to constant weight. About 0.11-0.14 g of dry weight of tentacle and mantle samples of each octopus were digested in a microwave oven (Provecto Analítica Jundiaí, model DGT 100 plus) using 2 mL concentrated HNO_3 and 1 mL H_20_2 30%. Digested samples were diluted to 10 mL in a volumetric flask. Analytical quantification of the isotopes ^{52}Cr, ^{63}Cu, ^{55}Mn, ^{208}Pb, ^{85}Rb and ^{88}Sr was performed by ICP-QMS (Perkin-Elmer, model Elan DRC-II). This instrument is equipped with Meinhard concentric nebulizer connected to a cyclonic spray chamber. A radiofrequency of 1100 W power was selected in pulse mode. Sample data were acquired by using 20 sweeps/reading, one reading/replicate, and a dwell time of 50 ms. High purity de-ionized water (resistivity 18.2 MΩ cm) used in sample and solution preparation was obtained using a Milli-Q water purification system (Millipore RiOs-DITM). All reagents used were of analytical-reagent grade except for nitric acid, which had been previously purified in a quartz sub-boiling still Kürner Analysentechnik) before use. The certified reference material (CRM) employed was IAEA V-10 (International Atomic Energy Agency), and ^{103}Rh was used as internal standard.

Results and Discussion

Table 1 shows the comparison of the measured values obtained for Cr, Cu, Mn, Pb, Rb and Sr with the certified values provided by the CRM IAEA V-10. Detection limit (LOD) is also presented for each analyzed element in this study. The relative error percentage values obtained were in descending order of

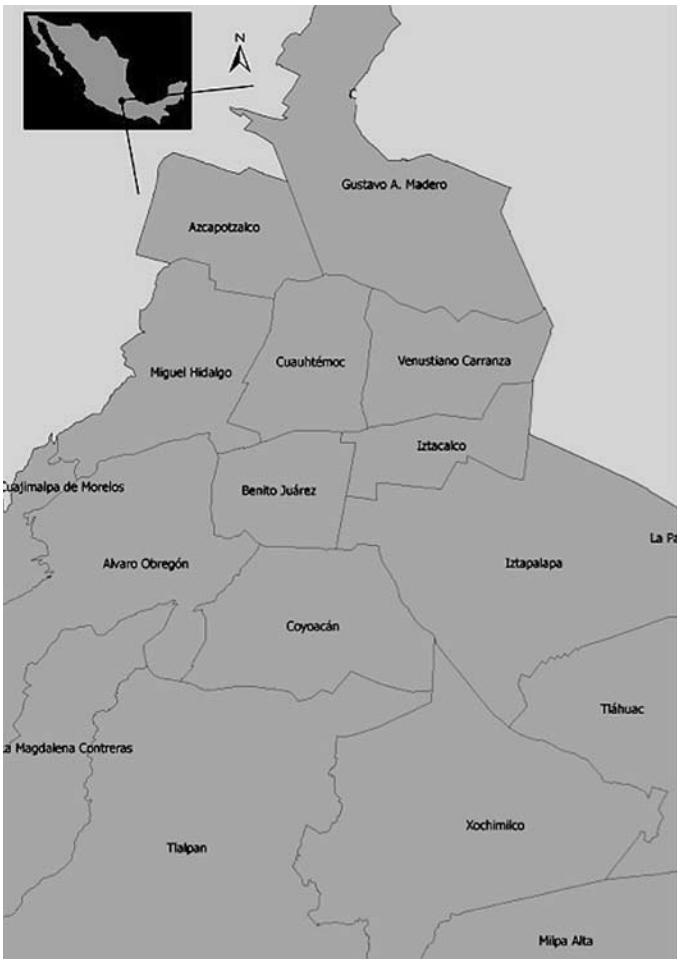

Fig. 1. Sampling zone. Mexico City, Distrito Federal and its sixteen delegations (Azcapotzalco, Alvaro Obregón, Benito Juárez, Coyoacán, Cuauhtémoc, Cuajimalpa de Morelos, Gustavo A. Madero, Iztacalco, Iztapalapa, Magdalena Contreras, Miguel Hidalgo, Milpa Alta, Tláhuac, Tlalpan, Venustiano Carranza and Xochimilco).

accuracy: 1.5, 1.9, -4.5, 6.6, -9.1. and –18.4 % for Sr, Mn, Cu, Cr, Rb and Pb, respectively. Likewise, the LOD values (in ng/g) observed in descending order of analytical sensitivity were: 0.2 for Cr and Pb; 0.4 for Rb and Sr; 0.5 for Mn and 1.2 ng/g for Cu. The analytical results were in good agreement with the certified values and below the acceptance criteria reported for elemental analysis in biological matrices [5, 31, 32]. The experimental procedure was reliable for analyzing the octopus samples.

Essential elements (Cr, Cu and Mn)

Chromium helps to maintain normal blood glucose levels, but its adverse effects of excessive consumption leads to chronic renal failure [33]. There are genetic diseases related to copper's metabolism: Menkes' kinky-hair disease related to copper deficiency, and Wilson's disease presented by copper in excess [34]. Symptoms of toxicity by manganese are the development of schizophrenia with nervous disorders similar to Parkinson's disease. Lower manganese blood levels have been observed in patients with osteoporosis, non-trauma epilepsy and Perthes' disease [35].

Table 2 presents the range and mean values for total concentrations (mg/kg) of essential elements (Cu, Cr and Mn) determined in mantle and tentacles octopus samples. This table also shows the closest Mexican regulation NOM-051-SCFI/SSA1-2010 [36] values for Cr and Cu. The range and mean calculated values obtained for Cr were similar in all kind of samples (mantle and tentacle from local and supermarkets). The minimum and maximum concentration values were: 2.4 mg/kg and 4.8 mg/kg, respectively. The maximum mean value obtained for Cr was 3.6 mg/kg. For Mn, a total concentration value of 1 mg/kg was obtained as a minimum and 6 mg/kg as the highest concentration observed, specially for mantle samples from supermarket origin. The maximum mean concentration value was 2 mg/kg (for all kind of samples, except for tentacle samples from local market). While for Cu it was observed appreciable differences in maximum range and mean values for mantle samples from both kind of markets. The minimum and maximum range concentration values were: 5.1 mg/kg (mantle samples from local market) and 95.3 mg/kg (mantle samples from supermarket), respectively. The maximum mean concentration value obtained was: 29.8 mg/kg (mantle samples from supermarket).

The experimental results of this research were compared with studies performed in Africa by Soldevilla [37]; in Monaco by Miramand and Guary [18]; and in Portugal by Lourenço et al. [12], Seixas et al. [21] and Napoleão et al. [38]. The mean concentration values reported for Cu in descending order were: 81, 36, 30 and 22.4 mg/kg for Seixas et al. [21], Soldevilla [37], Napoleão *et al.* [38] and Lourenço *et al.* [12]; and the maximum mean value for this work was 29.8 mg/kg. All values are similar, except for the highest mean concentration value from Seixas et al. [21]. It can be noted that a high value was also found in this study, in mantle from supermarket (95.3 mg/kg). The data reported for Mn mean concentration values were in descending order: 3, 2.39, 2.2, 1.82 and 1.8 mg/kg for Miramand and Guary [18], Seixas et al. [21], Soldevilla [37], Lourenço et al. [12] and Napoleão et al. [38]; while the maximum mean concentration result of this work was 2 mg/kg. No marked differences were noted among the country sampling and/or collection zones.

The results obtained for Cr and Cu determination were compared with the existing Mexican regulations related to the content of heavy metals in food for human consumption (Table 2). According to the NOM-051-SCFI/SSA1-2010 standard [36], the reference nutrition values are set as 0.022 mg/day for Cr and 0.65 mg/day for Cu, as daily intake suggested. The maximum total concentration values obtained for Cr and Cu in samples from supermarket are above of these regulations (0.48 mg/day for Cr in mantle and tentacle samples; and 9.53 mg/day for Cu in mantle samples), regarding the amount of consumption (100g/day) information from USDA National NDB for Standard Reference, NDB15166 [39]. There were not found Mexican regulation values for Mn.

Data from USDA NDB15166 [39] indicating the amount in 100g (amount of consumption per day) of edible portion of

Table 1. Results for certified reference material (CRM)[a] and limits of detection for trace elements analyzed by ICP-QMS.

Element	Certified value, mg/kg (95% C.I.[b])	Experimental value, mg/kg ± SD[c]	% Relative error [d]	LOD[e], ng/g
Cr	6.5 (5.6-7.1)	6.9 ± 0.2	6.6	0.2
Cu	9.4 (8.8-9.7)	9.0 ± 0.1	−4.5	1.2
Mn	47 (44-51)	48 ± 0.6	1.9	0.5
Pb	1.6 (0.8-1.9)	1.3 ± 0.02	−18.4	0.2
Rb	7.6 (7.3-7.8)	6.9 ± 0.1	− 9.1	0.4
Sr	40 (37-44)	39 ± 0.6	1.5	0.4

[a] CRM: IAEA V-10. [b] C.I.: Confidence Interval. [c] SD: Standard deviation. [d] % Relative error= ((mean experimental value - certified value) / certified value) 100. [e] LOD: Limit of detection.

Table 2. Range and mean values of total concentration for essential elements (Cu, Cr and Mn) in mantle and tentacle octopus samples from Mexico City markets. Data of Mexican regulation.

Element	Range (Mean ± SD[a]), mg/kg				Maximum concentration (maximum mean), mg/day[d]	Mexican regulation [36], SDI[e], mg/day
	Mantle[b]		Tentacle[c]			
	Supermarket	Local market	Supermarket	Local market		
Cr	2.4-4.8 (3.5 ± 0.7)	2.7-4.4 (3.5 ± 0.4)	2.7-4.8 (3.6 ± 0.5)	2.4-4.2 (3.4 ± 0.5)	0.48[f,g] (0.36)[g]	0.022
Cu	11.9-95.3 (29.8 ± 23.1)	5.1-92.0 (29.4 ± 26.6)	5.6-46.0 (14.3 ± 9.2)	5.8-17.1 (12.0 ± 3.5)	9.53[f] (2.98)[f]	0.65
Mn	1-6 (2 ± 1.2)	1-3 (2 ± 0.6)	1-3 (2 ± 0.6)	1-2 (1 ± 0.3)	0.60[f] (0.20)[f,g,h]	

[a] SD: Standard deviation. [b] Number of samples (n) = 16. [c] n = 15. [d] Regarding the consumer exposure (100g/day) for octopus edible samples, information from USDA National NDB for Standard Reference [39]. [e] SDI: Suggested daily intake. [f] Content found in octopus mantle samples from supermarket. [g] Content found in octopus tentacle samples from supermarket. [h] Content found in octopus mantle samples from local market.

octopus have established the values for Cu (0.435 mg/100g or 0.435 mg/day), and for Mn (0.025 mg/100g or 0.025mg/day). According to this, the maximum values obtained for the samples analyzed in this research exceeds the values established by the NDB15166 [39]. Values were: 9.53 mg/day for Cu, and 0.6 mg/day for Mn. Both values were obtained in the analysis of mantle samples from supermarket. Other reported regulations data for Cr, Cu and Mn are reported on Table 3. The values obtained were compared as mg/day unities. And, the comparison allowed to notice that the maximum experimental values obtained in this research, exceed the values recommended by the American Society Nutrition, ASN [40] and National Academies [41] for Cr and Cu.

Non-essential elements (Pb, Rb, Sr)

The main exposure route to lead in nonoccupationally exposed individuals is by food consumption [42]. Its toxicity results in anemia, kidney damage and central nervous abnormalities [2]. Rubidium is physiologically similar to potassium [2, 43] and it has been found in high levels in malignant and benign thyroid nodules [44]. The replacement of calcium by strontium because of their similar behaviors, originates osseous mineralization disorders [45, 46].

Table 4 displays the range and mean values for total concentrations (mg/kg) found for the analytical determination of non-essential elements (Pb, Rb, Sr), in mantle and tentacles octopus samples, consumed in the sampling zone. The range and mean calculated values obtained for Rb were similar in all kind of samples (mantle and tentacle from local and supermarkets). The minimum and maximum concentration values were: 0.4 mg/kg and 4.5 mg/kg, respectively. The maximum mean value obtained for Rb: 2.1 mg/kg. For Pb, a total concentration value of 0.1 mg/kg was obtained as a minimum and 1.6 mg/kg as the highest concentration observed, specially for tentacle samples from supermarket origin. The maximum mean concentration value was: 0.5 mg/kg (for mantle and tentacle samples from supermarket). While for Sr it was observed appreciable differences in maximum range value for mantle samples from supermarket. The minimum and maximum range concentration values were: 11 mg/kg (mantle and tentacle samples from local market) and 58 mg/kg (mantle samples from supermarket), respectively. The maximum mean concentration value obtained was: 21 mg/kg (mantle samples from local market).

The results obtained in this work were compared with data reported by Lourenço et al. [12], Raimundo et al. [47] and Seixas et al. [21]. All of them performed in Portugal coasts. Maximum concentration value reported by Lourenço et al. [12] for Sr was 27.7 mg/kg, this value is below the corresponding data obtained in this research: 58 mg/kg. Similar data were noted for Rb from Lourenço et al. [12] (4.29 mg/kg), and for the value obtained by this study (4.5 mg/kg). While for Pb,

Table 3. Reported regulation data for essential elements (Cu, Cr and Mn).

Element	Bourges *et al.* [52]		ASN [40]		U.S. FDA [53]	National Academies [41]		Lourenço *et al.* [12]
	RDA, µg/day	UL, mg/day	ESADDI[a]	RfD[b]	NSSP, ppm[c]	RDA/AI[d], µg/day	UL[e], µg/day	Daily Intake, mg/day
Cr	25[f]		50-200 µg/day	1 mg/kg/day	13	35		
Cu	900[g]		1.5-3.0 mg/day			900	10000	1.0-1.5
Mn		11[h]	2.0-5.0 mg/day	10 mg/day		2.3	11 mg/day	2.0-5.0

[a] ESADDI: Estimated Safe and Adequate Daily Dietary Intake for adults. [b] RfD: Reference Dose. [c] NSSP: National Shellfish Sanitation Program. Tolerances and guidance values for poisonous or deleterious substances in seafood. [d] RDA/AI: Recommended Dietary Allowances / Adequate Intakes. [e] UL: Tolerable Upper Intake Levels. [f] Suggested for adults (19-50 years old). [g] Recommended for adults. [h] For adults (≥ 19 years old).

Table 4. Range and mean values of total concentration for non-essential elements (Pb, Rb and Sr) in mantle and tentacles octopus samples from Mexico City markets. Data of Mexican regulation.

Element	Range (Mean ± SD[a]), mg/kg				Maximum concentration (maximum mean), mg/day[d]	Mexican regulation [48, 49], mg/kg
	Mantle[b]		Tentacle[c]			
	Supermarket	Local market	Supermarket	Local market		
Pb	0.1-1.1 (0.5 ± 0.3)	0.1-0.5 (0.3 ± 0.1)	0.1-1.6 (0.5 ± 0.4)	0.2-0.6 (0.4 ± 0.1)	0.16[e] (0.05)[e,f]	1.0
Rb	0.4-4.5 (1.6 ± 0.9)	0.9-3.3 (2.1 ± 0.7)	0.5-4.1 (1.3 ± 0.9)	0.6-2.6 (1.6 ± 0.7)	0.45[f] (0.21)[g]	
Sr	12-58 (20 ± 10.7)	11-30 (21 ± 5.3)	12-19 (16 ± 1.5)	11-31 (18 ± 5.1)	5.8[f] (2.1)[g]	

[a] SD: Standard deviation. [b] Number of samples (n) = 16. [c] n = 15. [d] Regarding the consumer exposure (100 g/day) for octopus edible samples, information from USDA National NDB for Standard Reference [39]. [e] Content found in octopus tentacle samples from supermarket. [f] Content found in octopus mantle samples from supermarket. [g] Content found in octopus mantle from local market.

the concentration value reported were in descending order: 4, 2.3 and 0.24 mg/kg from Seixas et al. [21], Raimundo et al. [47] and Lourenço et al. [12], respectively. There is noted that value reported by Seixas et al. [21] is appreciable higher than the maximum concentration value found by this research: 1.6 mg/kg. No appreciable differences were noted among the sampling and/or collection zones for each country (Portugal or Mexico).

In comparison with the reference values established for NOM-129-SSA1-1995 [48] and NOM-242-SSA1-2009 [49], maximum value obtained for Pb total concentration (1.6 mg/kg in octopus tentacle samples from supermarkets) exceeds the regulation value (1 mg/kg) (Table 4). No data exist for Rb and Sr. Other reported regulations data for Pb, Rb and Sr are reported on Table 5. In a similar way, previously done for essential elements, the comparison was made in mg/day. The maximum experimental values obtained for Pb and Sr exceed the value given by the ASN [40] and the regulation values (as daily intake) mentioned by Lourenço *et al.* [12].

Comparison of trace elements levels among purchase place of the octopus samples

The trace element data from mantle and tentacles of octopus samples obtained for each purchase place are presented in Figure 2. The total concentration leves of Cr are similar in both mantle and tentacle samples, and among the supermarket and local purchase market from Mexico City where they were collected. The highest values found were: 95.3 mg/kg for Cu in mantle sample from northern supermarket located in Venustiano Carranza (V.C.) delegation, 6 mg/kg for Mn in mantle sample from supermarket at northern delegation Gustavo A. Madero (G.A.M.), 1.6 mg/kg for Pb tentacle sample purchased at supermarket from western delegation Miguel Hidalgo (M.H.) delegation, 4.5 mg/kg for Rb in mantle sample from supermarket origin situated at western Delegation Alvaro Obregón (A.O.) and 58 mg/kg for Sr in mantle samples collected at supermarket located at southern Xochimilco (X.) delegation. As it was mentioned previously, the highest values were obtained for mantle samples collected at supermarkets, although it is required a larger sample size than this preliminary study to identify clearly possible "hotspot" purchase place.

The overall evaluation of the results of this work was interpreted as presence of several metal contribution sources in the organisms analyzed, with higher accumulation on octopus mantle samples from supermarket origin. By their part, Miramand and Bentley [17]; Seixas *et al.* [21]; Seixas and Pierce [20] and Villanueva and Bustamante [22], have reported that mainly the digestive gland and branchial heart appeared to play a major role in bioaccumulation process of toxic elements. These organs are located at the mantle of these marine organisms. It is worthy to mention that the several sources of metal contribution (from the sea to the distribution markets), for the analyzed samples in this survey, were not identified.

Recently, the Mexican Government has announced the creation of the Aquaculture Program, which promotes the

Table 5. Reported regulation data for non-essential elements (Pb, Rb and Sr).

Element	ASN [40]	U.S. FDA [53]	Lourenço *et al.* [12]
	Typical daily dietary intake	NSSP[a], ppm	Daily Intake, mg/day
Pb	15-100 μg/day	1.7	
Rb	1-5 mg/day		
Sr			1-5

[a] NSSP: National Shellfish Sanitation Program. Tolerances and guidance values for poisonous or deleterious substances in seafood.

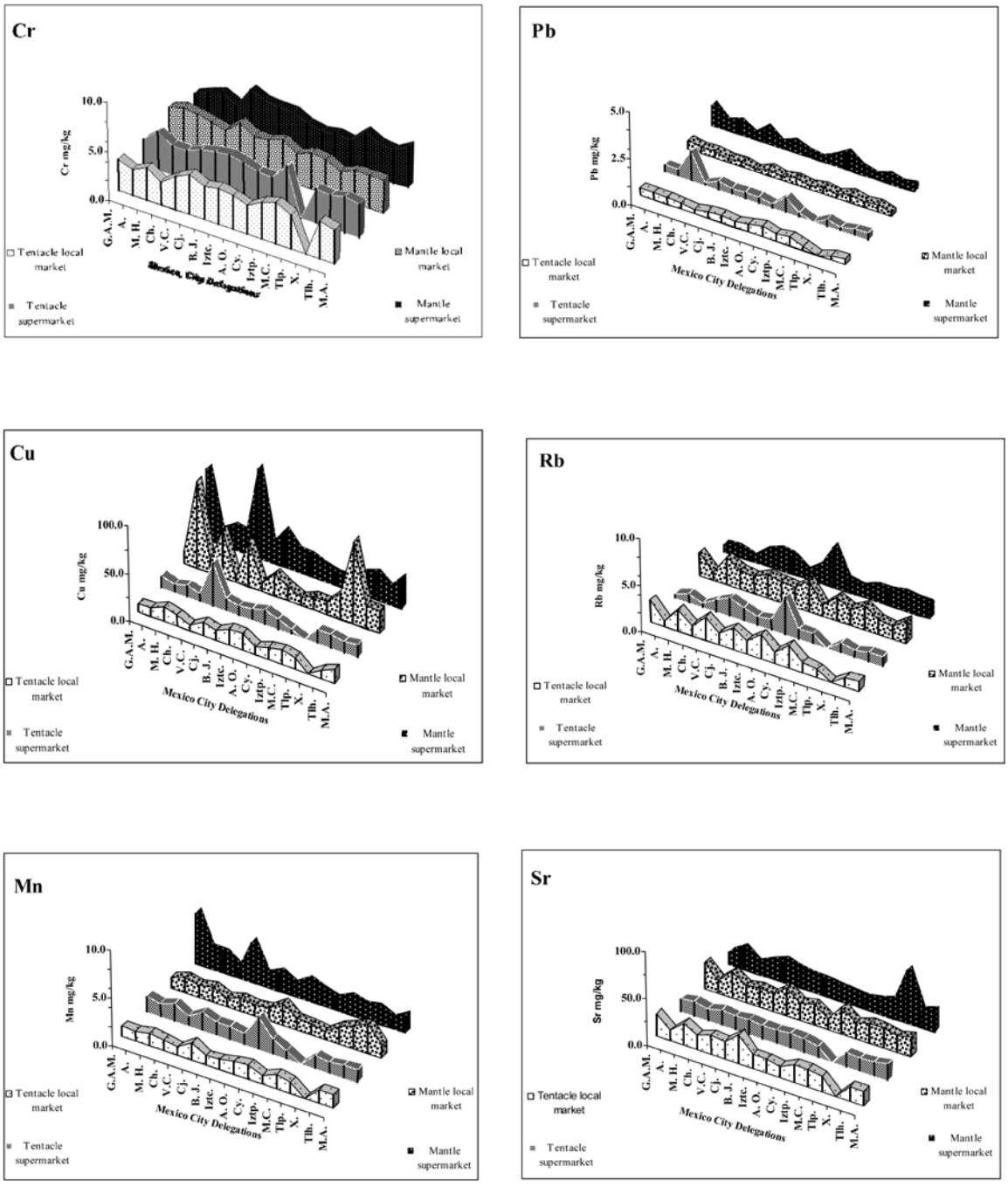

Fig. 2. Total concentration of trace elements in octopus samples collected in sixteen delegations from Mexico City, Distrito Federal. From north to south are: **G.A.M.** (Gustavo A. Madero), **A.** (Azcapotzalco), **M.H.** (Miguel Hidalgo), **Ch.** (Cuauhtémoc), **V.C.** (Venustiano Carranza), **Cj.** (Cuajimalpa de Morelos), **B.J.** (Benito Juárez), **Iztc.** (Iztacalco), **A.O.** (Alvaro Obregón), **Cy.** (Coyoacán), **Iztp.** (Iztapalapa), **M.C.** (Magdalena Contreras), **Tlp.** (Tlalpan), **X.** (Xochimilco), **Tlh.** (Tláhuac) and **M.A.** (Milpa Alta).

adequate sustainability of the fishing resources of our country and the reproduction of species with biological and economic importance in the Mexican diet [50]. This program proposed the aquaculture as a good alternative to minimize the excessive exploitation effects of fishing and to guarantee the existence of its products (fish, shrimp, oyster and octopus) in the markets, as well as a good economical employment cycle [23, 24,51]. This assay could be useful to help authorities make decisions about the regulations in metal content and distribution of octopus from the sea to the consumer table.

Conclusions

This research provides information related to the total concentration levels found for essential trace elements (Cr, Cu, Mn) and non-essential elements (Pb, Rb, Sr), in the octopus mantle and tentacles samples collected in the sixteen delegations into which Mexico City, Distrito Federal is divided. The comparison was established with the available Mexican regulation related to the content of heavy metals in food for human consumption. According to the results, it was concluded that the maximum and mean concentration values obtained for Cr (0.48 mg/day) and Cu (9.53 mg/day,), especially in mantle samples from supermarket, exceed the reference nutrition values given by NOM-051-SCFI/SSA1-2010 standard (0.022 y 0.65 mg/day for Cr and Cu, respectively). Whereas for Pb, the comparison was made regarding NOM-129-SSA1-1995 and NOM-242-SSA1-2009 standards. It was observed that the maximum concentration value obtained for this element especially for tentacle samples, from supermarkets origin (1.6 mg/kg) exceeds the Mexican regulation (1.0 mg/kg). While the maximum Pb mean concentration value (0.05 mg/day) was below the regulation (0.1 mg/day).

The above was interpreted as a bioaccumulation signal of Cr, Cu and Pb in the octopus edible parts analyzed especially from supermarket origin. These findings should constitute an effective and necessary current measure of assessing the adequacy and safety of seafoods consumed in Mexico City, and may be a basis for future monitoring studies for total elemental concentration levels and to trace or to identify contribution metal sources.

Although there is not Mexican regulation data for Mn, Rb and Sr, the results were compared with other international reference nutrition standards. The maximum total concentration value obtained for Mn in mantle samples from supermarket origin (0.6 mg/day) exceeds the values established by the USDA NDB15166 for Mn (0.025mg/day), although the value meets requirements established by ASN (2.0-5.0 mg/day) and National Academies (11 mg/day). The maximum total concentrations value obtained for Sr in mantle samples from supermarket (5.8 mg/day), exceed Daily Intake value (1-5 mg/day) reported. The highest values found in this work, particularly for Mn, Sr, Pb and Rb; correspond to supermarkets located at northern delegation Gustavo A. Madero, southern delegation Xochimilco and westerns delegations Miguel Hidalgo and Alvaro Obregón, respectively.

This work could be helpful for further research in food chemistry and regulation area to establish preventive safety and health measures, although is required a larger sample size than this preliminary study.

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