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Minerals and Toxic Elements in Wild Mushrooms Species from Regions of Hidalgo State in Mexico

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The macroelements and trace elements contents of six edible, two non-edible and one medicinal mushrooms and soils collected from different regions of Hidalgo State of Mexico were analyzed. Metals occurred in mushrooms follow the trends: K >> Al > Mg > Fe > Cu > Mn > Cr > Pb > Cd meanwhile the tendency of metals present in soils was Al > Fe > K > Mg > Mn = Cu > Cr; Pb and Cd. With the calculation of the bioconcentration factor it could be separated mushrooms in hyper accumulators (BCF > 1) and hypo accumulators (BCF < 1). Hyper accumulators mushrooms were for Cu > K > Mn > Mg, while for hypo accumulators the tendency for the metals was Cr > Al > Fe. Consumption of edible mushrooms do not represent a risk for the health and they are excellent source of minerals.

Keywords: Mushroom, Essential elements, Deleterious metal, Bioaccumulation.

INTRODUCTION

The diversity of mushrooms and their attractive colours, textures and flavours have made them a well accepted food in human diet. In some countries as in China they are highly consumed having a rate of mushroom consumption between 20-24 kg per capita annually [1] and in Mexico mushrooms are consumed for tradition by people that buy them in local markets of Tlaxcala, Puebla, Hidalgo and other states [2]. Mushrooms have also been largely known because of their valuable benefits for human heatlh including antioxidant, antiviral, anticarcinogenic, anticoagulant, cardiovascular problems and reducing blood cholesterol [3-6].

Mushrooms are organisms capable of bioaccumulating significant amounts of different elements including toxic species such as cadmium [7], gold [8], lead [9], mercury [10], silver [11] and radionuclides [12]. Several concentrations of these and other elements are found in mushrooms fruiting bodies according to their geographic location and environmental conditions where they grow such as weather, organic matter, pH of soils, genotype and pollution.

The study of metals in mushrooms is a field widely explored, there have appeared hundreds of reports since the decade of 1970 describing macro and microelements contents in macrofungi [13], the possibility of use of mushroom for environmental monitoring [14], radiactive contamination before and after the Chernobyl accident [15], the influence of environmental pollution on metallic elements accumulation [16-18] chemotaxonomical and mycological systematics significance of trace element accumulation [19] and mushroom cultivation on artificially metallic element-enriched substrates and media. Even though mushrooms are potent bioaccumulators of metals, some reports consider them as effective and reliable bioindicators [13], however other authors don't consider them as effective bioindicators [20].

The ability displayed by mushrooms to accumulate an element from a substrate is expressed by the bio concentration factor (BCF) that involves the ratio of the element content in the fruiting body to the content in substrate. The BCF may be used to define a mushrooms as hyper or hypo-bioaccumulator if this BCF is above or under the unit, respectively [13].

Mexico posses a very rich fungal biodiversity, due its favourable environmental conditions, but as far as we know there is not enough information about the mineral composition of essential and deleterious minerals in wild edible, medicinal and non-edible mushroom species from Mexico. The aim of this study is determine contents of toxic (Cd, Cr and Pb) and other elements (Al, Cu, Fe, K, Mg and Mn) in fruiting bodies (cap and pileusof nine species of some regions of Hidalgo and the soil where they were collected and compare them with the BCF in order to gain more information about the studied species.

EXPERIMENTAL

Wild edible (E), non-edible (NE) and medicinal (M) mushrooms were collected in different regions of Hidalgo state in Mexico. Those regions were Los Reyes (Acaxochitlán), La Desviación, Paxtepec (Santiago) and El Susto (Tulancingo) in Hidalgo State, Mexico (Fig. 1). The sampling was done during the rainy season (August-October) of 2014. The samples were analyzed and identified by comparison with mycology keys [21,22]. The habitat and localities of wild edible, non-edible and medicinal macrofungi are described in Table-1.

All samples were dried until constant weight at 60 °C in a drying oven. Then the dried samples were reduced to a fine powder (20 mesh) using an electric mill (IKA basic). Applying the method of the USEPA [23] the samples were digested in an acid solution of HNO_3 in a microwave oven Mars X-5 (1200 W) with a maximum temperature of 170 °C, then passed through the AAS system (Agilent atomic absorption spectrophotometer model 2200) using different lamps adjusted to several wavelengths 236.7 (Al), 228.8 (Cd), 357.9 (Cr), 324.7 (Cu), 372 (Fe), 404.4 (K), 202.6 (Mg), 279.5 (Mn) and 217 nm(Pb). The determination for the metallic elements was obtained as mg/kg of dry weight [24]. For the mushrooms species and soils, determinations were carried out by triplicate.

TABLE-1
LOCALITIES OF WILD MACROFUNGI COLLECTED IN SOME REGIONS OF HIDALGO STATE

No.	Class, family and taxa of macrofungi	Locality and habitat
1	*Amanita caesarea* (Scoop. Fr) Pers. :Schwein (E)	La Desviación 20.00874°N, -98.156775 O
2	*Amanita muscaria* (L. :Fr) Pers (NE)	El Susto 20.07383°N -98.508621 O
3	*Amanita pantherina*(DC. ; Fr) (NE)	El Susto 20.07383°N -98.508621 O
4	*Boletusedulis*(Bull. :Fr) (E)	El Susto 20.07383°N -98.508621 O
5	*Cantharelluscibarius*(Fr.) (E)	El Susto 20.07383°N -98.508621 O
6	*Ganodermalucidum*(Leyss) P. Karst (M)	Los Reyes 20.15208°N -98.1846966 O
7	*Lactariusindigo*(Schwein. Fr) (E)	Paxtepec 20.03371°N -98.425871 O
8	*Ramaria flava* (Schaeff.) Quél (E)	Los Reyes 20.15208°N -98.1846966 O
9	*Sarcodoncalvatus* (E)	Los Reyes 20.15208°N -98.1846966 O

(E) = Edible mushroom; (NE) = Non-edible mushroom; (M) = Medicinal mushroom

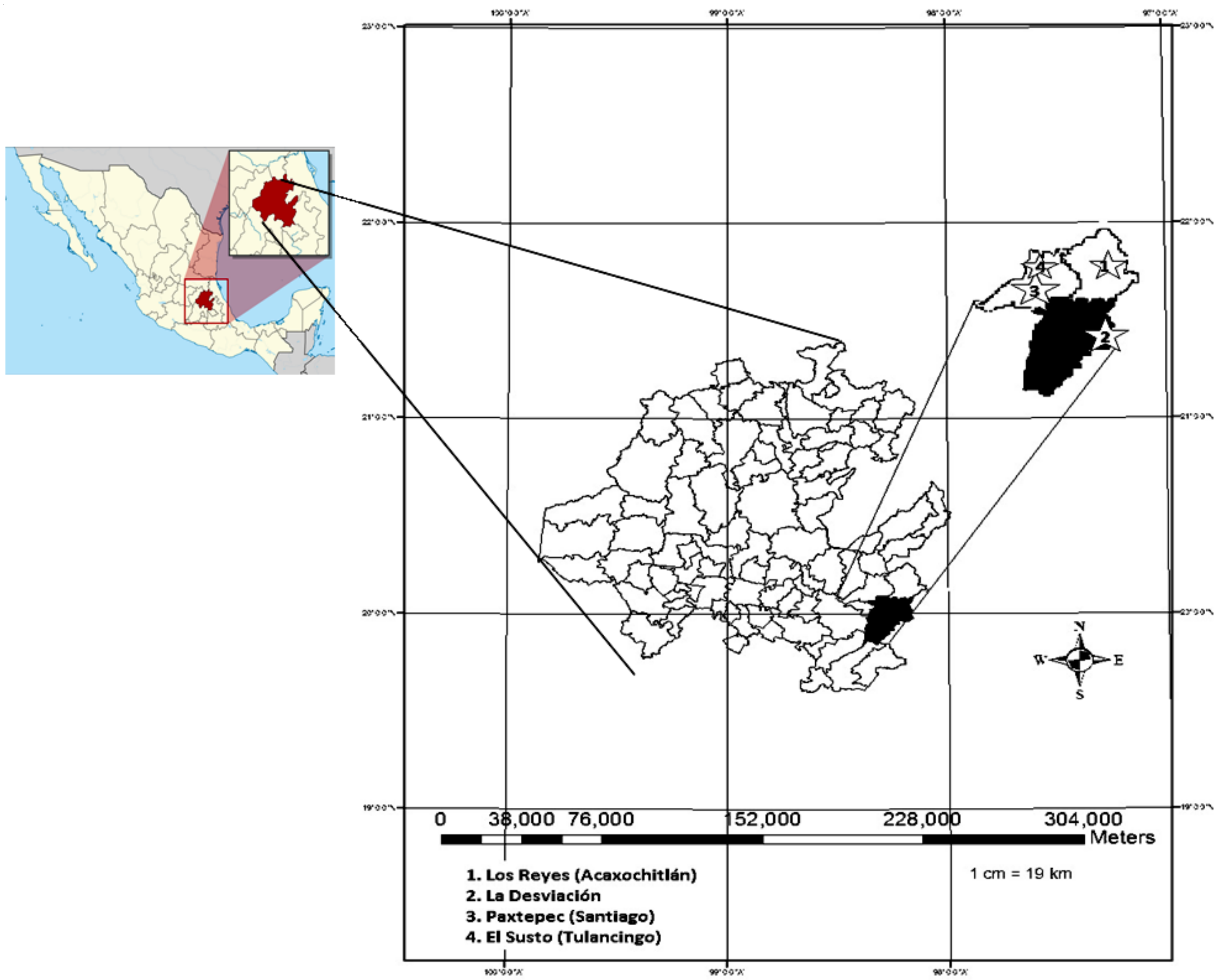

Fig. 1. Macrofungi collection area

RESULTS AND DISCUSSION

The concentrations of elements present in wild edible, non-edible and medicinal mushrooms and their soils were they were collected are presented in Tables 2 and 3. According to the results, the predomining element in mushrooms was K with a range between 2,187.32 and 34,926.32 mg/kg dw for *G. lucidum* and *A. pantherina*, respectively. In second place of abundance among the nine species studied it was Al with a range of concentrations between 500 and 4,218.18 mg/kg dw for *G. lucidum* and *A. caesarea*, respectively. Magnesium was the third element present in the mushrooms samples, it content was in an interval between 576.93 and 1119.32 mg/kg dw for *R. flava* and *A. pantherina*. The other elements such as Fe, Cu, Mn, Cr were in minor content values in a range from 443.36 to 4.33 mg/kg dw. Finally Pb and Cd were not detectable at detection limit values in mg/L in AAS of 0.0006 and 0.0003 for lead and cadmium, respectively (Table-2).

The contents of metals present in soils, the highest values were obtained for Al and Fe with 57,690.70 and 39,852.75 mg/kg dw, respectively. The minimum detected contents were for Cr with 5.33 mg/kg dw while for Pb and Cd there were no detected any content. From the regions studied, "La Desviación" presented the highest values in Fe, while the region of "El Susto" presented the highest values of Cr. The region of "Los Reyes" was the richest in elements such as Mn, Cu, Al, K and Mg (Table-3).

The BCF is an useful parameter to know the capability of the mushrooms to bioaccumulate metals. Table-4 listed the BCF for seven of the nine species analyzed. Due for Pb and Cd there were not any content detected neither in mushrooms samples nor in soils. For the specie *A. muscaria* the BCF could not been determined because the mushroom was grown over dead leaves.

Potassium is present in a high amount in mushroom ashes. The maximum value detected for this element was for *A. pantherina* with 34,936.32 mg/kg dw. For *B. edulis* it has been reported a content between 21,800 and 29,000 by Ayaz *et al.* [25] and Falandysz and Borovièka [13]. In present study, the content of K was lower. This difference may be due the maturation stage of carpophores and local conditions where it was grown. *C. cibarius* displayed a content similar as reported by Chen *et al*. [26] with 28,900 mg/kg dw. In general all the mushrooms studied displayed high values of potassium, specially the edible species (*A. caesarea*, *B. edulis*, *C. cibarius*, *L. indigo*, *R. flava* and *S. calvatus*). For *R. flava* it was determinated a greater content compared with 22710 mg/kg dw reported by Kaya *et al*. [27]. It has been reported that potassium levels are between 20-40 fold higher in fruiting bodies than in underlying substrates, the mean content of potassium in all

TABLE-2
CONTENTS OF ELEMENTS OF WILD EDIBLE MUSHROOMS

No.	Amount of elements (mg/kg dryweight)								
	K	Mg	Al	Cu	Mn	Pb	Cd	Cr	Fe
1	29,384.21	878.07	4,214.18	456.44	64.41	0.03	nd	6.33	1,971.68
2	16,219.30	959.19	733.33	146.82	14.09	3.81	0.12	4.91	305.62
3	34,926.32	1,119.32	923.33	285.63	40.92	4.01	nd	5.08	336.15
4	18,880.70	877.31	541.67	299.06	10.42	3.09	nd	4.91	215.73
5	29,342.11	979.06	566.67	169.09	16.68	3.29	nd	4.50	127.34
6	2,187.72	663.24	500.00	137.96	76.36	nd	nd	4.16	29.21
7	15,445.61	886.57	1,195.59	108.25	12.28	nd	nd	2.74	286.52
8	6,352.63	576.93	1,762.89	951.16	nd	nd	nd	4.41	471.54
9	26,868.42	748.89	750.00	576.12	8.64	nd	nd	4.16	246.44
Mean	19,956.34	854.29	1,243.07	347.84	30.48	2.84	0.12	4.58	443.36
Minimum	2,187.72	576.93	500.00	108.25	8.64	0.03	0.12	2.74	29.21
Maximum	34,926.32	1,119.32	4,214.18	951.16	76.36	4.01	0.12	6.33	1,971.68

nd: Not detected

TABLE-3
CONTENTS OF ELEMENTS OF SOILS COLLECTED FOR DIFFERENT MUSHROOMS

No.	Amount of elements (mg/kg dryweight)								
	K	Mg	Al	Cu	Mn	Pb	Cd	Cr	Fe
1	566.67	453.99	61837.36	93.12	1.32	nd	nd	4.50	110866.27
2	ns	ns	ns	ns	ns	ns	ns	ns	ns
3	610.53	280.23	49545.46	27.14	108.31	nd	nd	5.83	21248.54
4	592.98	191.38	92109.86	19.71	30.27	nd	nd	4.91	36569.15
5	589.47	293.66	31399.31	28.85	97.31	nd	nd	5.66	8962.82
6	422.81	185.30	113805.24	215.08	124.39	nd	nd	5.41	31183.54
7	622.81	529.78	49161.13	95.69	120.07	nd	nd	5.08	40742.82
8	877.19	543.09	36476.17	0.96	1.61	nd	nd	5.66	53000.08
9	531.58	708.75	27191.11	123.11	116.00	nd	nd	5.58	16248.77
Mean	601.76	398.27	57690.70	75.46	74.91	nd	nd	5.33	39852.75
Minimum	422.81	185.30	27191.11	0.96	1.32	nd	nd	4.50	8962.82
Maximum	877.19	708.75	113805.24	215.08	124.39	nd	nd	5.83	110866.27

nd: Not detected; ns. No simple available

TABLE-4
BIOACCUMULATION FACTOR (BCF)

No.	Amount of elements (mg/kg dryweight)								
	K	Mg	Al	Cu	Mn	Pb	Cd	Cr	Fe
1	51.85	1.93	0.07	4.90	48.80	–	–	1.41	0.02
2	–	–	–	–	–	–	–	–	–
3	57.21	3.99	0.02	10.52	0.38	–	–	0.87	0.02
4	31.84	4.58	0.01	15.17	0.34	–	–	1.00	0.01
5	49.78	3.33	0.02	5.86	0.17	–	–	0.79	0.01
6	5.17	3.58	0.00	0.64	0.61	–	–	0.77	0.00
7	24.80	1.67	0.02	1.13	0.10	–	–	0.54	0.01
8	7.24	1.06	0.05	990.79	nd	–	–	0.78	0.01
9	50.54	1.06	0.03	4.68	0.07	–	–	0.75	0.02
Mean	34.80	2.65	0.03	129.21	7.21	–	–	0.86	0.01
Minimum	5.17	1.06	0.00	0.64	0.07	–	–	0.54	0.00
Maximum	57.21	4.58	0.07	990.79	48.80	–	–	1.41	0.02

nd: Not detected

the samples analyzed was in agreement with this range [20]. Since potassium is an essential nutrient required for maintenance of total body fluid volume, acid and electrolyte balance, its deficience has been associated with hypertension and cardiovascular diseases. The WHO recommends for an adult a daily intake of K of 3150 mg the consumption of edible species may contribute to this daily ingest recommended [28]. All the mushrooms studied showed are hyper accumulators of K. This element must achieve essential functions for fungal growth and metabolism and can be excellent sources of this mineral [29].

Magnesium(II) has been reported in a range between 330 to 1,200 mg/kg dw for *B. edulis* [13]. In present work, the content of Mg agreed with this interval. However for the other edible species the content of this element obtained was 576.93 mg/kg dwfor *R. flava* and 979.06 mg/kg dw for *C. cibarius*. In the literature there is reported a higher content of Mg: 1170 mg/kg dw for *R. flava* [27] and 1280 mg/kg dw for and *C. cibarius* [26]. Those differences may correspond to differences between the geographic location of analyzed mushrooms, different maturation stages of the carpophores and environmental conditions of growth.

Magnesium(II) occurs in soils at the chemical form of calcium magnesium carbonate [$CaMg(CO_3)_2$)] and it exists extensively on the earth's surface as limestone and dolomite. Dolomites react with oxalic acid produced by some fungi, the magnesium oxalates produced increase the bioavalaibility of this element to the mushrooms [29,30]. The mushrooms analyzed were hyper accumulators of magnesium in spite of presenting the lower BCF values considered for hyper accumulators organisms. Magnesium is the fourth most abundant cation in the body and the second most abundant cation in intracellular fluid, it serves as cofactor of about 350 cellular enzymes and also its involvement in protein and nucleic acid synthesis. Low levels are associated with endothelial dysfunction, increased vascular reactions, hypertension and coronary heart diseases [31]. It has been recommended for American women 300 to 354 mg/day and for American men 420-483 mg/day of Mg [32].

Aluminium(III) has been reported in mushrooms in varied ranges from 8.5 to 365 mg/kg dw [20] and others from 50 to 1500 mg/kg dw [33]. The analyzed samples presented values higher than the reported ranges and were from 500 to 4214.18 mg/kg. This can be due to the richness of aluminium found in soils. Those concentrations in analyzed soils specialy from the regions of Los Reyes and El Susto were the highest ones for all the metals studied and that could be attributed to anthropogenic activities that includes compounds that contain aluminium used for different purposes, such as in water treatment, paper making, contaminants in fertilizers, alloys with other metals and municipal solid wastes. Also aluminium is present in rocks and soils as aluminium oxide combined with silicium dioxide and magnesium oxide forming silicates, they are the largest class of minerals comprising 30 % of all minerals and making up 90 % of the earth's crust [29]. It is known that mushrooms are capable of bioaccumulate this metalloid, however the mean value of BCF obtained was 0.03, this is reasonable due the extremely high content of this element in soils in a range between 27,191.11 and 113,805.24 mg/kg dw. The joint FAO/WHO Expert Committee on Food Aditives recommends a provisional tolerable weekly intake value for aluminium as 1 mg/kg body weight/week [33], consumption of edible mushrooms, specialy *A. caesarea* constitutes a great source of Al.

Copper(II) has been reported in fruiting bodies of mushrooms from unpolluted areas in a range between 20 to 100 mg/kg dw and for polluted areas up to 427 mg/kg dw [20]. The copper(II) contents analyzed were above these ranges, the lower content corresponds to *L. indigo* with 108.25 mg/kg dw and the highest was for *R. flava* with 951.16 mg/kg dw, Kaya *et al*. [27] reported Cu(II) content of 10.58 mg/kg for this mushroom.The high values obtained suggest a possible contamination of soils in the studied areas.In the studied soils Cu(II) was present in a range between 0.96 to 215.08 mg/kg dw with a mean value of 75.46 mg/kg dw. Since Cu(II) is necessary for the activation of lignocellulosic laccases in saphrofitic mushrooms [34] they absorb Cu(II) from soils through the segregation of oxalic acid to solve Cu(II) from minerals [31]. All the mushooms except *G. lucidum* can be consideratd as hyper accumulators of Cu(II), specialy *R. flava* with a BCF of 990.79. According to the variations in the BCF it seems that genotype of the species seems to be predominant to explain the bioaccumulation effect of Cu(II) in the studied mushrooms.

Manganese(II) is an important metal for mushrooms necessary for the activation of the enzyme manganese-peroxidase implicated in degradation of lignin [35]. From the analyzed mushrooms Mn(II) was present in concentrations between 8.64 and 76.36 mg/kg dw and it was specialy present in *G. lucidum*, this high content is reasonable due *G. lucidum* posses manganese peroxidase enzymes and requires Mn(II) for their activation [36]. It has been reported that Mn(II) occurs in mushrooms in a range between 10 and 60 mg/kg [20]. The values obtained for the samples were according the reported range except for *G. lucidum* and *A. caesarea*. Particulary for *B. edulis* and *C. cibarius* the contents of Mn(II) were close with the reported values of 14.10 mg/kg dw and 25.2 mg/kg dw, respectively [25]. In the same way as Cu(II), Mn(II) is absorbed by oxalic acid released by mushrooms and the correspond oxalate is accumulated in the mycelia [30]. In high amounts Mn(II) is toxic for plants, ecto-mycorrhizal mushrooms avoid plants uptaking this element.

Manganese(II) occurs in rocks and soils, for the samples analyzed it was present between 1.32 and 124.39 mg/kg dw, the highest contents obtained were for the regions of "El Susto" and "Los Reyes" with contents above 100 mg/kg dw. *A. caesarea* showed to be an excellent hyper accumulator of Mn(II) with a BCF of 48.80, while all the other mushrooms were hypo accumulators. This is important due in excesive concentrations Mn(II) is toxic to fish and humans above 0.05 mg/L, according to the WHO [37].

Lead(II) is an element that occurs in mushrooms according to Kalac [20], in a range between 1.0 and 10.0 mg/kg dw. It was only detectable in *A. caesarea*, *A. muscaria*, *A. pantherina*, *B. edulis* and *C. cibarius* in a range between 0.03 and 4.01 mg/kg dw matching with the reported range. In soils there was no of Pb(II) detected and therefore BCF couldn't be calculated. The edible samples analyzed don't represent a risk at human consumption due Pb(II) because the FAO/WHO set a provisional tolerable weekly intake of Pb(II) of 25 g per kg of bodyweight, resulting into 1.50 mg Pb/week for a person with a bodyweight of 60 kg [38]. Mushrooms are efficient Pb(II) bioaccumulators and several reports show their accumulative capability in polluted areas and also their role as bioindicators of pollution [39,40].

Cadmium(II) is a highly toxic element, its absorption and bioaccumulation in the tissues increases with age and may cause renal damage due its high affinity for sulphur of thiolate [41]. For the samples analyzed there were any detectable content of Cd, except for the non-edible mushrooms *A. muscaria* with 0.12 mg/kg dw. Consumption of edible species don't represent a risk for human health due Cd(II) presence.

Chromium occurs in mushrooms in a range between 0.5 and 5 mg/kg dw and less frequently between 5 and 10 mg/kg dw [20]. The samples containing Cr were analyzed in the range between 2.74 and 6.33 mg/kg dw, with the highest value for *A. caesarea* and the minimum for *L. indigo*. Chromium is considered essential to humans because of its stability to increase glucose tolerance in type-2 diabetes mellitus in patients and due the recommended dietary intake for chromium is 0.035 mg/day for male and 0.025 mg/day for the female [27]. Edible mushroom species are a valuable source for this mineral. The analyzed soils presented Cr in a range between 4.50 and 5.83 mg/kg dw, all mushrooms except *A. caesarea* and *A. pantherina* are hypo accumulators of Cr.

Iron contents of the mushroom samples ranged from 29.21 to 1971.68 mg/kg dw. Iron contents of mushrooms samples in the literature have been reported in the range of 498.5-6967 mg/kg dw [42], 0.2-155 mg/kg [41], 65.56-7156 mg/kg [27]. Present iron values are in agreement with literature values. Mushrooms are a rich source of Fe. All known organisms requires Fe as an essential element, however ingestion of large amounts can lead to excessive levels of iron in the blood that could damage cells in the heart and liver causing even death [41]. According to FAO/WHO, it is recommended an intake of Fe for growing for an female and male above 18 years old an amount of 1.46 and 1.05 mg/day/75 kg of body weight, respectively [43]. By consumption of portions of 50 g of fresh mushroom (90 % of moisture) the intake of Fe is in a range between 0.64 and 9.86 mg of Fe for the edible species here analyzed.

Iron contents in analyzed soils was in a range between 8962.82 and 110866.27 mg/kg dw, this high content in soils is expected due the great presence of aluminium and iron oxides as reported by Acevedo *et al*. [44]. In spite of having large amounts of Fe, mushrooms were hypo accumulators of this element with a BCF mean value of 0.001, however they can be considered excellent sources of Fe for the daily intake.

Conclusion

Mushroom plays an important role as bioaccumulator of metals. They are excellent source of K > Al > Mg > Fe > Cu > Mn > Pb and Cd. From the edible mushrooms studied all of them are good source of minerals, specially *A. caesarea*, which presented the highest contents of Al, Cr, Fe and Mn, while for *R. flava* it presented the highest content of Cu. Fortunately the presence of toxic elements such as Pb or Cd does not represent a risk for the human health. It seems that the genotype of the mushroom is involved in the bioaccumulation of metals as it occurs in the genus *Amanita*where the highest BCF were for *A. caesarea* and *A. pantherina* for K > Mn > Cr > Al > Fe. Neither consumption of neither edible nor medicinal mushrooms species represents a risk for human health, also it is suggested to include edible mushrooms in human diet.

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