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Occurrence of Chemical Contaminants in Egyptian Edible Mushroom

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Abstract

Mushroom is considered as healthy food, it contains high level of proteins. It can be contaminated by chemical contaminants. So, this study aimed to evaluate the presence of heavy metal and pesticide residues in *Agaricus* and *Pelurotus* sp. as Egyptian edible mushroom. Results showed that, 12 elements were detected as Al, Cd, Fe, K, Mg, Mn, Na, Ni, Se, Zn, B and Pb. The average concentrations of first ten elements in winter and spring were (21.87, 17.13), (0.089, 0.077), (25.82, 29.96), (29580.86, 26748.73), (163.89, 148.20), (5.40, 6.10), (1091.38, 1232.13), (0.927, 0.714), (11.47, 9.10) and (48.62, 68.56) mg/Kg dry weight of *Agaricus*, respectively. While B and Pb were not recorded in any of the analyzed samples. In *Pleurotus sp*., the determined concentrations of the same elements were (22.12, 38.67), (0.06, 0.088), (140.93, 125.24), (21033.15, 25147.38), (116.53, 139.33), (8.66, 6.08), (1389.32, 1075.39), (0.46, 0.43), (5.10, 6.61) and (77.34, 101.94) mg/kg dry weight, during the same two seasons, respectively. Pesticide residues were also investigated in both species of mushroom. Organophosphorus (OP) pesticide residues like phorate, diazinon, chloropyrifos-Me, pirmiphos, dorsban and profenofos were not found in any of the analyzed samples, while malathion was found with an average concentration of 0.1380 and 0.1387 µg/g dry weight in *Agaricus sp.* samples in winter and spring, respectively. While, in *Pleurotus* samples it was determined as 0.1072 and 0.944 µg/g dry weight during the same two seasons, respectively. Thiometon was found in an average concentration as 0.5579 and 0.6107 µg/g dry weight in samples of *Pleurotus* in winter and spring, respectively. Organochlorine pesticides (OC), like HCB, heptachlor, dieldrin, endrin, o,p'-DDD, p,p'-DDD, o,p'-DDT residues were not found in any of the analyzed samples, while p,p'-DDT with an average concentration of 0.0032 and 0.0043 µg/g dry weight was found in samples of *Pleurotus* in winter and spring, respectively. Lindane was detected in samples of *Agaricus sp.*, with an average concentration of 0.0093 and 0.011 µg/g dry weight, also, it was recorded in *Pleurotus sp.* with an average concentration as 0.0114 and 0.0057 µg/g dry weight in the winter and spring seasons, respectively. We conclude that, The content of chemical contaminants in Egyptian edible mushrooms studied during this work are moderate, while, the heavy metals were found in low concentrations and they are less than the international acceptable limits of codex, FAO and WHO. Moreover, the positive samples for pesticide residues were in the permissible limits. So, edible mushrooms can be used in preparing our foods to gain its benefit of high nutrition value.

Key words: Mushroom, Heavy metals, Pesticides, Organochlorines, Organophosphorous

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Introduction

The occurrence of high metals in edible plants, is of considerable importance, since they might constitute a possible toxicological hazard. Heavy metals, when concentrated in living organisms should be regarded as toxins towards mammals and particularly humans. Accumulation of specific elements results mainly from pollution, and might, in some cases, constitute useful environmental markers, (Michelot et al., 1998). Increasing industrial development and urbanization have led to continuously increasing production of toxic substances, discharged into the environment with risk for living organisms, and potentially constituting serious hazards to public health. Fungi and plants are able to accumulate significant amounts of metals from their environment (Alonso et al., 2000 ; Kalac and Svoboda, 2000 and Keskinkan et al., 2004) and the ability of fungi to act as bio-sorbents of heavy metals has been extensively evaluated (Murugesan et al., 2006). Major advantages of fungal bio-sorbent materials include their good metal uptake capacities and low anticipated price. In addition, fungal bio-sorbents can be regenerated for multiple uses. Among fungi, saprophytic mushroom have proved useful for the treatment of urban wastes and agricultural by-products. Saprophytic mushrooms are also attracting interest as potential industrial bio-sorbents. The

uptake of metals by fungal biomass appears to involve a combination of two processes: bioaccumulation (i.e. active metabolism-dependent processes, which may include both transport into the cell and partitioning into intracellular components) and bio-sorption (i.e. the binding of metals to the biomass by processes that do not require metabolic energy). Several chemical processes may be involved in bio-sorption, including adsorption, ion exchange processes and covalent binding. The polar groups of proteins, amino acids, lipids and structural polysaccharides (chitin, chitosan, glucans) may take part in bio-sorption. According to, Morley and Gadd, (1995) potassium and phosphorus supplementation is very great important for fungus growth. The uptake of metals by living cells depends on species, contact time, pH of the metal solution, culture conditions, initial metal ion concentration, and the concentration of cells in the solution.

Pesticides are widely used in agricultural and residential applications as insecticides, herbicides, fungicides and rodenticides. Organochlorine pesticides, which are persistent in the environment and cause biological damage accumulate in an organism over time, OPPs and carbamate pesticides are short-lived in the environment and fast-acting on their 'target pest'. Direct mortality of wildlife from organochlorine pesticides is uncommon, however, mortality is the primary documented effect on non-target wildlife from OP and carbamate pesticides. OP are the most likely pesticides to be involved in acute human poisonings, fungal lactase enzyme produced by *Pleurotus ostreatus* has been reported, as able to perform the oxidative degradation of OP (Jauregui et al., 2003). In this concern, Abou-Arab, (2000) evaluated three species of mushroom, *Pleurotus ostreatus, Agaricus spp.* and *Lentinus edodus* for their contents of heavy metals and pesticides and stated that the concentrations of metals varied widely among the three species. Mushroom growing on contaminated substrate by metals and pesticides were able to bio-accumulate these chemicals in their fruiting bodies. The influence of processing (canning and pickling) on metals and pesticides in cultivated mushroom was also studied. The losses of lindane and malathion by different processing methods was recorded.

The aim of this work is to concentrate light on the levels of contamination of two types of mushrooms by pesticides and heavy metals during spring and winter seasons of 2007/2008 in Egypt.

Materials and Methods

Mushroom samples

A total of 40 samples of both *Agaricus* and *Pleurotus* Egyptian edible cultivated mushroom were purchased randomly from markets of Great Cairo Governorate, during winter season of 2007 and spring season of 2008. The purchased samples were refrigerated at -4 ^{o}C until analyzed.

Determination of heavy metals

Approximately 10g of dried and homogenized mushroom was placed in a porcelain crucible and ashed in an oven (muffle furnace) at 430-450 °C for 15 – 20 hr, (kalac and svoboda, 2000). The ashed material was dissolved in 5 ml concentrated HNO_3, evaporated to dryness, heated again to 450 °C, dissolved in HNO_3 and diluted with de-ionized water to a definite volume and a final HNO_3 concentration of 1 %, the concentration of the specific metals in the previous aqueous solutions were measured by ICP-OES 2000 DV, (Optical Emission Spectrometer optima 2000 DV), which has the flow details: in the table below (data about ICP- OES 2000 DV). The apparatus set points of measuring are listed in the following Table (1).

Determination of pesticide residues

Pesticide residues were determined according to AOAC, (1995). Chromatographic analysis was performed with a Hewlett-Packard 5890 system with Ni^{63} electron capture detector (ECD), fitted with HP-1 capillary column (cross linked methyl silicon gum. 30m length x 0.25mm diameter x 0.25 µm film thickness). The oven temperature was programmed from 160°C to 220 °C with rate of 5°C/min, and continued for total of 30 min. Injection and detector temperatures were 220 and 300°C, respectively. Recoveries of pesticides by this method were determined by fortification of the samples with definite concentrations of pesticides standards, and the recoveries ranged between 90 to 94 %. The limit of detection (in µg/g) was 0.02 for DDT derivatives and 0.01 for the other pesticides under investigation.

Results and Discussion

Heavy metals analysis in mushroom

Metals (minerals) play an important role in life processes of microorganisms. Some metals, such as calcium, cobalt, chromium, copper, iron, potassium, magnesium, manganese, sodium, nickel and zinc, are essential, serve as micronutrients and are used for redox-processes; to stabilize molecules through electrostatic interactions; as components of various enzymes, and for regulation of osmotic pressure. Many other metals have no biological role (e.g. silver, aluminum, cadmium, gold, lead and mercury), and are nonessential and potentially toxic to microorganisms. Toxicity of nonessential metals occurs through the displacement of essential metals from their native binding sites or through specific interactions (Bruins et al., 2000). The results presented in Table (2) showed that, the average concentration of ten metals, Al, Cd, Fe, K, Mg, Mn,

Table 1 Instrument conditions of heavy metals determination

No.		Elements	Wavelength (nm)	Detection limit (mg/ L)	Intensity
1	Al	(Aluminum)	396.153	0.0280	2050
2	B	(Boron)	2490772	0.0057	1150
3	Cd	(Cadmium)	228.802	0.0027	1400
4	Fe	(Iron)	238.204	0.0046	3500
5	K	(Potassium)	766.490	42.857	22
6	Mg	(Magnesium)	285.213	0.0016	17500
7	Mn	(Manganese)	257.610	0.0014	18000
8	Na	(Sodium)	589.592	0.069	300
9	Ni	(Nickel)	231.604	0.015	620
10	Pb	(Lead)	220.353	0.042	150
11	Se	(Selenium)	196.026	0.0750	10.5
12	Zn	(Zinc)	213.857	0.0018	1020

Table 2 Heavy metals concentrations in *Agaricus* species (mg/kg dry weight)

No.	Metals	Winter			Spring		
		Min. Concn. (mg/kg)	Max. Concn. (mg/kg)	Mean (mg/kg)	Min. Concn. (mg/kg)	Max. Concn. (mg/kg)	Mean (mg/kg)
1	**Al**	20.062	23.682	21.872	17.083	17.187	17.135
2	**B**	ND	ND	ND	ND	ND	ND
3	**Cd**	0.062	0.116	0.089	0.069	0.085	0.077
4	**Fe**	24.286	27.364	25.825	27.017	32.916	29.966
5	**K**	26316.77	32844.96	29580.86	24073.86	29423.61	26748.73
6	**Mg**	145.807	181.977	163.89	133.38	163.02	148.20
7	**Mn**	4.720	6.085	5.402	6. 021	6.180	6.10
8	**Na**	1088.19	1094.57	1091.38	845.17	1619.09	1232.13
9	**Ni**	0.652	1.202	0.927	0.596	0.833	0.714
10	**Pb**	ND	ND	ND	ND	ND	ND
11	**Se**	8.757	14.186	11.471	8.645	9.573	9.109
12	**Zn**	38.45	58.79	48.62	65.085	72.04	68.56

ND= Not Detected

Table 3 Heavy metals concentrations in *Pleurotus* species (mg/kg dry weight)

No.	Metals	Winter			Spring		
		Min. Concn. (mg/kg)	Max. Concn. (mg/kg)	Mean (mg/kg)	Min. Concn. (mg/kg)	Max. Concn. (mg/kg)	Mean (mg/kg)
1	**Al**	20.393	23.836	22.115	22.970	54.371	38.670
2	**B**	ND	ND	ND	ND	ND	ND
3	**Cd**	0.056	0.064	0.060	0.059	0.117	0.088
4	**Fe**	111.745	170.112	140.928	113.64	136.85	125.240
5	**K**	18262.930	23803.37	21033.15	24923.52	25371.25	25147.380
6	**Mg**	101.185	131.882	116.533	138.088	140.568	139.330
7	**Mn**	6.011	11.314	8.662	5.647	6.526	6.080
8	**Na**	455.603	2323.033	1389.318	372.352	1778.44	1075.390
9	**Ni**	0.365	0.560	0.462	0.382	0.479	0.431
10	**Pb**	ND	ND	ND	ND	ND	ND
11	**Se**	5.668	5.730	5.099	6.117	7.095	6.610
12	**Zn**	60.603	94.073	77.338	82.155	121.735	101.940

ND= Not Detected

Na, Ni, Se and Zn were determined in *Agaricus* samples of winter and spring seasons are (21.87 and 17.14), (0.089 and 0.077), (25.83 and 29.97), (29580.86 and 26748.73), (163.89 and 148.20), (5.40 and 6.10), (1091.19 and 1232.13), (0.93 and 0.71), (11.47 and 9.11) and (48.62 and 68.56) (mg/Kg dry weight of *Agaricus sp.*), respectively. Boron and lead were not found in any of the analyzed samples.

Table 4 Concentrations of organophosphorus pesticides (ppm) in *Agaricus* mushroom

No.	Organophosphorus Pesticides	Winter			Spring		
		Min. (µg/g)	Max. (µg/g)	Mean (µg/g)	Min. (µg/g)	Max. (µg/g)	Mean (µg/g)
1	Phorate	0.0	0.0	N.D	0.0	0.0	N.D
2	Thiometon	0.0	0.0	N.D	0.0	0.0	N.D
3	Diazinon	0.0	0.0	N.D	0.0	0.0	N.D
4	Chloropyrifos-Me	0.0	0.0	N.D	0.0	0.0	N.D
5	Pirmiphos	0.0	0.0	N.D	0.0	0.0	N.D
6	Malathion	0.1236	0.1525	0.1380	0.1145	0.1629	0.1387
7	Dorsban	0.0	0.0	N.D	0.0	0.0	N.D
8	Profenofos	0.0	0.0	N.D	0.0	0.0	N.D

N.D = Not Detected

Table 5 Concentrations of organochlorine pesticides (ppm) in *Agaricus* mushroom

No.	Organochlorines Pesticides	Winter			Spring		
		Min. (µg/g)	Max. (µg/g)	Mean (µg/g)	Min. (µg/g)	Max. (µg/g)	Mean (µg/g)
1	HCB	0.0	0.0	N.D	0.0	0.0	N.D
2	Lindane	0.0085	0.010	0.0093	0.0098	0.0123	0.011
3	Heptachlor	0.0	0.0	N.D	0.0	0.0	N.D
4	Dieldrin	0.0	0.0	N.D	0.0	0.0	N.D
5	Endrin	0.0	0.0	N.D	0.0	0.0	N.D
6	o,p'-DDD	0.0	0.0	N.D	0.0	0.0	N.D
7	p,p'-DDD	0.0	0.0	N.D	0.0	0.0	N.D
8	o,p'-DDT	0.0	0.0	N.D	0.0	0.0	N.D
9	p,p'-DDT	0.0	0.0	N.D	0.0	0.0	N.D

N.D = Not Detected

Table 6 Concentrations of organophosphorus pesticides (ppm) in *Pleurotus* mushroom

No.	Organophosphorus Pesticides	Winter			Spring		
		Min. (µg/g)	Max. (µg/g)	Mean (µg/g)	Min. (µg/g)	Max. (µg/g)	Mean (µg/g)
1	Phorate	0.0	0.0	N.D	0.0	0.0	N.D
2	Thiometon	0.4267	0.6891	0.5579	0.5423	0.6792	0.6107
3	Diazinon	0.0	0.0	N.D	0.0	0.0	N.D
4	Chloropyrifos-Ms-	0.0	0.0	N.D	0.0	0.0	N.D
5	Pirmiphos	0.0	0.0	N.D	0.0	0.0	N.D
6	Malathion	0.0991	0.1153	0.1072	0.0874	0.1013	0.944
7	Dorsban	0.0	0.0	N.D	0.0	0.0	N.D
8	Profenofos	0.0	0.0	N.D	0.0	0.0	N.D

N.D = Not Detected

Table 7 Concentrations of organochlorine pesticides (ppm) in *Pleurotus* mushroom.

No.	Organochlorine Pesticides	Winter			Spring		
		Min. (µg/g)	Max. (µg/g)	Mean (µg/g)	Min. (µg/g)	Max. (µg/g)	Mean (µg/g)
1	HCB	0.0	0.0	N.D	0.0	0.0	N.D
2	Lindane	0.010	0.0125	0.0114	0.0046	0.0068	0.0057
3	Heptachlor	0.0	0.0	N.D	0.0	0.0	N.D
4	Dieldrin	0.0	0.0	N.D	0.0	0.0	N.D
5	Endrin	0.0	0.0	N.D	0.0	0.0	N.D
6	o,p'-DDD	0.0	0.0	N.D	0.0	0.0	N.D
7	p,p'-DDD	0.0	0.0	N.D	0.0	0.0	N.D
8	o,p'-DDT	0.0	0.0	N.D	0.0	0.0	N.D
9	p,p'-DDT	0.0023	0.0040	0.0032	0.0031	0.0054	0.0043

N.D = Not Detected

With respect to *Pleurotus sp.* mushrooms, results in Table 3 showed concentrations of the same metals determined in the same seasons. The average concentrations recorded are (22.12 and 38.67), (0.06 and 0009), (140.93 and 125.24), (21033.15 and 25147.38), (116.53 and 139.33), (8.66 and 6.08), (1389.32 and 1075.39), (0.46 and 0.43), (5.10 and 6.61) and (77.34 and 101.94) (mg/kg of dry weight of *Pleurotus* mushroom), respectively.

Toxicological and environmental studies have prompted interest in the determination of toxic elements in food. Mushrooms surely do not constitute a significant portion of the human diet, but the consumption of wild and cultivated mushrooms has become increasingly popular in recent years. Many metals are essential, e.g. Na, K, Cu, Zn, Co, Ca, Mg, Mn and Fe, but all can exert toxicity when present above certain threshold concentrations. Other metals; Cs, Al, Cd, Hg and Pb, have no known biological function but all can be accumulated by fungi (Gadd, 2006). Many results for different researchers showed that, heavy metals concentration in mushrooms was clearly high. The results are in parallel with Melgar et al., (2007), who explained the accumulation of heavy metals in fungi such as *Agaricus macrospores* and stated that, fungi shows potential for the removal of heavy metals from aqueous solutions contaminated by zinc, copper, mercury, cadmium or lead. Also, the results are in agree with Ouzouni and Riganakos, (2007), who analyzed different species of wild edible mushrooms from different regions of Greece for their metal (Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb, Cd, Al, As and Sn) content. Metals concentrations in their samples were ranged between 739-1165 µg/g dry wt.(Mg), 0.41-13 (Cr), 11.4-100 (Mn), 46.3-317 (Fe), not detected-3 (Co), 0.28-10.1 (Ni), 3.80-32.6 (Cu), 35.9-96.9 (Zn), 0.00-1.37 (Pb) and 0.08- 0.41 µg/g dry wt. for Cd. As, Sn and Al concentrations were under the detection limit of the applied method.

Determination of pesticides residues in mushroom

The extensive and massive use of pesticides in agriculture has serious impacts on the environment, compromising soil and water quality and major concern has been to protect water resources (Stegmann et al., 2001). Eight compounds of organo-phosphorus pesticides residues were analyzed as phorate, diazinon, chloropyrifos-Me, pirmiphos, dorsban, profenofos, thiometon and malathion. The results in Tables (4, 5, 6 and 7) show that, first six pesticides were not detected in any of the analyzed samples in both types of *Agaricus* or *Pleurotus* mushrooms through seasonal winter or spring 2007/ 2008, while malathion was found with an average concentration of 0.1380 and 0.1387 ppm (µg/g) in samples of *Agaricus* mushroom in winter and spring, respectively. While, in *Pleurotus* mushrooms samples, malathion concentrations were 0.1072 and 0.944 ppm (µg/g), respectively.

On the other hand, pesticide residues of thiometon was detected in an average concentration as 0.5579 and 0.6107 (µg/g) in samples of *Pleurotus* mushrooms in winter and spring, respectively.

For organo-chlorine pesticide residues, nine compounds were determined; HCB, lindane, heptachlor, dieldrin, endrin, o.p'-DDD, p,p'-DDD, o,p'-DDT and p,p'-DDT. In samples of *Pleurotus* mushrooms, p,p'-DDT residue was only found from these group with an average concentration of 0.0032 and 0.0043 ppm or (µg/g), in winter and spring, respectively. These concentration of DDT not high but it is very important, because we that is still a long time without analyzing. While lindane residues were detected an average concentration of 0.0093 and 0.011 ppm or (µg/g) in samples of *Agaricus* mushrooms in the winter and spring seasons, respectively. And also, it was detected in *Pleurotus* mushrooms with an average concentration were 0.0114 and 0.0057 (µg/g) in samples for winter and spring seasons, respectively.

From previous results in present study, it can be reported that, pesticide residues in Egyptian edible mushroom of *Agaricus* and *Pleurotus* in winter and spring 2007/2008, were not of high concentrations, but there have very important indictors about health of consumers. So, many other studies can support these results. Local and international studies like (Abou-Arab, 2000) and (Jauregui et al., 2003) can be taken in consideration.

Conclusion

The content of chemical contaminants in Egyptian edible mushrooms studied during this work are moderate, but it is very important in food quality and health of consumers, heavy metals divided in two groups, first is nutrient minerals like., K, Mg and Fe which are found in an optimum concentrations and it can be decided that, mushroom are good source of these minerals. While, the second group which is toxic or poisonous elements like Cd, Pb, As, Hg and Zn were found in low concentrations and they are less than the international acceptable limits of codex, FAO and WHO. Moreover, the majority of investigated pesticide residues of two main groups (organochlorines and organophosphorus) were not detected in this study. The determined pesticides residues of the positive samples were in the permissible limits. So, edible mushrooms can be used in preparing our foods to gain its benefit of high nutrition value.

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