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Bioaccumulation Potential of Heavy Metals in Edible Fungal Sporocarps from the Niger Delta Region of Nigeria

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Abstract: Contents of Ni, Cu, Pb, Mn, Cd and Zn in edible fungal sporocarps and soil from the Niger delta wetlands were determined. Results revealed a species-dependent bioaccumulating potential. *Armillariella mellea* had the highest content of Zn and Pb, while *Pleurotus sapidus* had the lowest bioaccumulating potential for Ni, Pb and Cu. Generally, the heavy metal accumulating potential decreased in the trend:Zn>Mn.Cu>Ni>Pb>Cd and were inferior to the FAO/WHO (1976) dietary standards. There was significant correlation ($p<0.05$) between soil Cd/Cd content in *Agaricus biosporus* and soil Zn/Pb content in *Agaricus biosporus*. However, the presence of detectable amounts of Pb and Cd may be a pointer to health risk associated with excessive consumption, particularly during harvest periods, and should be avoided.

Key words: Heavy metals, bioaccumulating potential, Niger Delta, fungal sporocarps

Introduction

The Niger Delta wetlands, with its creeks and tributaries harbours a rich collection of biotopes dominated by vast areas of mangrove swamp forest. However, this region, with its complex ecological form is being subjected to considerable anthropogenic perturbations, arising from oil exploration and production activities. This has resulted in the release of pollutants capable of contaminating soil and ground water. These include hydrocarbons (Odu, 1981; Ewa-Oboho, 1994) and the associated heavy metals such as Cd, Pb, Zn, Cu, Ni (Ijah and Okang, 1993). These metals are known to exert negative effect on biological processes in general (Udosen *et al*., 2001) and may influence the nutritional and biological status of mushrooms.

Edible mushrooms are consumed by wetland dwellers of the Niger Delta, because of their delicacy, abundance and also as a substitute for the more expensive seafoods. However, certain mushrooms are known to accumulate heavy metals. The accumulating potentials is affected by the species, substrate composition, age of mycelium and intervals between fruitifications (Kalac and Svoboda, 2000). Studies on metals in mushrooms have shown a correlation between fungal metal concentration and point sources of metal pollution, such as smelters and roadsides (Isildak *et al*., 2004; Bargagli and Baldi, 1984). But literature on the heavy metal levels in mushrooms from the Niger Delta wetlands is scanty. In an earlier study, we reported on the heavy metal content of edible and non-edible mushrooms within Stubbs creek, a forest reserve area in the Niger Delta region. Results indicated noticeable concentrations of Pb and Cd which are of toxicological importance. However, the heavy metal content was found to be of the trend Fe>Zn>Cu>Mn>Pb>Cd (Ita *et al*., 2006). In this study, contents of Ni, Zn, Cu, Pb, Cd and Mn in fruiting bodies of some edible mushrooms and soil sample from Ukpenekeng within the Niger Delta wetlands were determined, using atomic absorption spectrometry and correlated with the content in soil.

Materials and Methods

The sporocarps of six edible mushroom species including *Polyporus frondosis; Armillariella mellea; Pleurotus sapidus*; *Agaricus biosporus*; *Pleurotus ostreatus*; *Polyporus sulphureus*; were harvested during the rainy season month of July 2006, from Ukpenekang, an oil producing community within the Niger Delta wetlands. The harvested samples were thoroughly cleaned, dried on blotting paper, cut into pieces and dried at 105°C for 24 hrs. Dried samples were homogenized using a blender into fine powder and stored in pre-cleaned polyethylene bottles, prior to analyses. Ten soil samples from the upper soil horizon (0-10cm, after removing the surface layer of organic detritus) were also collected within the study area. The samples were sun-dried, homogenized and stored at room temperature in polythene bags until analysis. All reagents were of analytical grade, unless otherwise stated. Double deionized water was used for all dilutions. 1 g of dried and homogenized soil was weighed into a beaker (100 mL) and 10 mL of nitric acid was added. This was then heated until dryness. Thereafter, 10 mL HNO_3 (BDH) and 3 mL $HClO_4$ (BDH) were added and the solution was heated until fuming. The sample solution was obtained by processing the residue with hot 6 mol/l HCL (4 mL) and then filtered and diluted with water to 50 mL. This solution was used for AAS determination. Also, 1 g of each mushroom sample was placed in a porcelain crucible and ashed at 480°C

Table 1: Class, habitat and family of mushrooms under study

S/N	Mushroom species	Sub-class	Family	Habitat
1	*Agaricus biosporus*	Homobasidiomycetidae	Agariaceae	Tree trunks and logs
2	*Polyporus frondosis*	Homobasidiomycetidae	Agariaceae	Tree trunks and logs
3	*Armillariella mellea*	Homobasidiomycetidae	Agariaceae	Tree trunks and logs
4	*Pleurotus sapidus*	Homobasidiomycetidae	Agariaceae	Tree trunks and logs
5	*Polyporus sulphureus*	Homobasidiomycetidae	Polyporaceae	Tree stumps, trunks and logs
6	*Pleurotus ostreatus*	Homobasidiomycetidae	Polyporaceae	Logs and tree stumps

Table 2: Mean heavy metal concentrations in soil/fruiting bodies of mushrooms. (µg/gDM)* (n-10)

S/N	Sample	Ni	Cu	Pb	Mn	Cd	Zn
1	Soil	11.29±2.06	49.93±9.46	20.45±4.22	65.52±13.94	6.18±1.48	151.84±13.94
		(8.17-14.31)	(39.21-66.57)	(14.31-26.55)	(36.12-82.31)	(3.57-8.34)	(103.21-213.53)
2	*Agaricus biosporus*	1.94±0.46	18.13±2.90	1.06±0.23	30.63±3.77	0.62±0.14	43.21- 5.91
		(1.31-2.87)	(14.44-23.18)	(0.76-1.33)	(27.23-40.01)	(0.44-0.83)	(35.28-50.22)
3	*Polyporus frondosis*	0.66±0.20	19.45±3.40	0.95±0.25	18.04±1.56	0.47±0.09	38.05±3.29
		(0.34-0.98)	(14.00-22.56)	(0.67-1.42)	(16.79-20.54)	(0.35-0.61)	(31.87-42.34)
4	*Armillariella mellea*	0.51±0.06	24.68±3.65	1.21±0.22	37.88±2.27	0.37±0.06	74.92±5.06
		(0.42-0.64)	(19.08-30.18)	(0.87-1.42)	(33.45-41.11)	(0.33-0.49)	(69.21-82.47
5	*Pleurotus sapidus*	0.42±0.06	21.67±2.38	0.31±0.08	19.02±1.63	0.29±0.06	53.60±4.38
		(0.35-0.52)	(18.31-24.66)	(0.31-0.55)	(17.34-22.56)	(0.21-0.41)	(47.66-60.45)
6	*Polyporus sulphureus*	1.39±0.23	43.04±2.37	0.77±0.09	30.41±2.56	0.38±0.07	31.08±3.67
		(1.02-1.78)	(39.62-46.77)	(0.65-0.91)	(26.99-34.88)	(0.29-0.52)	(26.01-38.12)
7	*Pleurotus ostreatus*	0.87±0.09	52.57±2.95	0.59±0.10	38.53±5.08	0.34±0.09	42.73±4.62
		(0.75-1.03)	(47.78-57.45)	(0.48-0.78)	(31.23-45.98)	(0.24-0.54)	(38.56-52.23)

*mean of triplicate determinations±S.D; values in parenthesis represent minimum-maximum

for 18-24h; then the ash was dissolved in 2 mL concentrated HNO_3 (BDH), heated again at 480°C for 4h and dissolved in 1 mL concentrated H_2SO_4 (BDH), 1 mL HNO_3 and 1 mL H_2O_2 (BDH) and then diluted with double deionized water up to a volume of 25 mL. A blank digest was carried out in the same way.

For elemental analysis, an atomic absorption spectrometer (Pye Unicam, Model 919) was used. Pb and Cd levels in the samples were determined using HGA graphite furnace, using argon as inert gas. Other measurements were carried out in an air/acetylene flame.

All the experimental values are reported in µg/g of dry matter. Results are expressed as mean±S.D of triplicate analysis. Data were evaluated using two way analysis of variance (ANOVA).

Results and Discussion

Mushrooms are regarded as healthy foods with higher content of protein and carbohydrate than vegetables. They are also rich in minerals, dietary fibre and vitamins. Mushrooms have desirable taste and aroma and also give a good feeling of satiation. In addition, mushrooms also have medicinal properties and have been useful as antibacterial, antitumour, anticholesterol and antiviral agents (Nylen, 1985; Mattila *et al.*, 2000; Cochran, 1978; Chovot *et al.*, 1997). The are widely consumed by the rural dwellers in the Niger Delta region of Nigeria.

The habitat, sub-class and family of the mushroom species under study are given in Table 1, while the heavy metal content of the soil/mushrooms are presented in Table 2.

Amongst the tested mushroom species, zinc was most accumulated by *Armillariella mellea* (74.92±5.06 µg/g) (Fig. 1) and least accumulated by *Polyporus sulphureus* (31.08±3.67 µg/g). Zinc is widely spread amongst living organism due to its biological significance. Leski and Rudawska (2005) reported a zinc range of 28.6 to 179mg/kg for the fruiting bodies of wild mushrooms from the Notecka forest in West-Central Poland. Reported zinc levels in the mushrooms are in agreement with literature (Anderson *et al.*, 1982; Kalac and Svoboda, 2000; Turkekul *et al.*, 2004).

Very low concentrations of Mn were obtained in *Polyporus frondosis* (18.04-1.56 µg/g) and *Pleurotus sapidus* (19.02±1.63 µg/g) (Fig. 2). *Agaricus biosporus* accumulated high content of Mn (52.7±3.1 µg/g). Manganese is an essential component of many enzymes and also activates numerous enzymes. The Mn levels reported in this study are in agreement with reports by Falandysz and Bona, (1992); Vetter (1994). There was a significant relationship ($p<0.1$) between zinc content of soil and manganese content of *Agaricus biosporus* (Table 3).

Copper ranged from 18.13±2.90 µg/g to 52.57±2.95 µg/g in the present study (Fig. 3). The lowest Cu content was found in *Agaricus biosporus* and the highest in *Pleurotus ostreatus*. These values are higher than values reported for vegetables therefore, mushrooms should be considered as a nutritional source of the element. However, for humans, bioavailability from mushrooms is reported to be low, due to limited absorption from the small intestine (Elless *et al.*, 2000). Copper contents were generally lower than values reported by Leski and

Table 3: Significant correlations between soil heavy metal content and levels in samples

	Soil heavy metal content. (µg/gDM)				
	Cd	Cu	Ni	Zn	Pb
Cd	0.69*B* 0.63*C*	*0.68*E*			*0.60*C*
Pb		*0.59*D*		0.85*B*	
Cu		*0.68*G*		0.78*E*	*0.57*B*
Ni			*0.59*F*		
Mn				*0.54*B*	

*r values at p ≤ 0.1; others-r values at p ≤ 0.05. *B-Agaricus biosporus; C-Polyporus frondosis; D-Armllariella mella; E-Pleurotus sapidus; F-Polporus sulphureus; G-Pleurotus ostreatus*

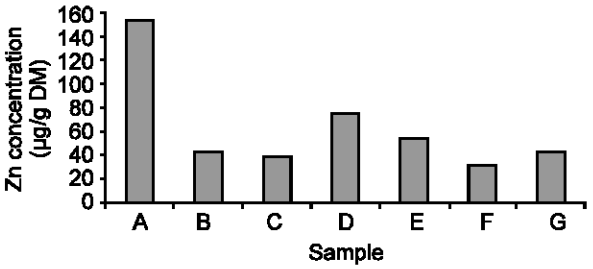

Fig. 1: Distribution of Zn in samples: A- Soil; B- Agaricus biosporus; C- Polyporus frondosis; D- Armillariella mellea; E- Pleurotus sapidus; F- Polyporus sulphureus; G- Pleurotus ostreatus

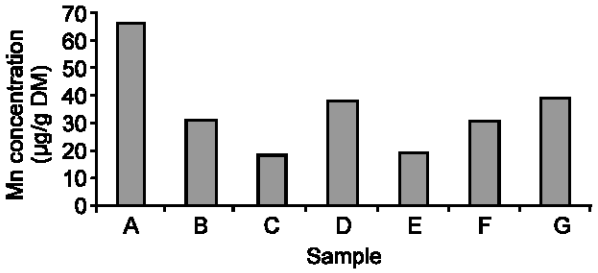

Fig 2 : Distribution of Mn in samples: A- Soil; B- Agaricus biosporus; C- Polyporus frondosis; D- Armillariella mellea; E- Pleurotus sapidus; F- Polyporus sulphureus; G- Pleurotus ostreatus

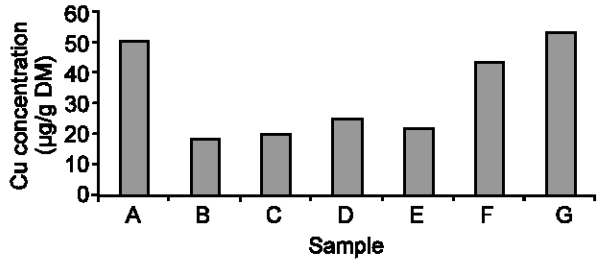

Fig 3: Distribution of Cu in samples: A- Soil; B- Agaricus biosporus; C - Polyporus frondosis; D- Armillariella mellea; E- Pleurotus sapidus; F- Polyporus sulphureus; G - Pleurotus ostreatus

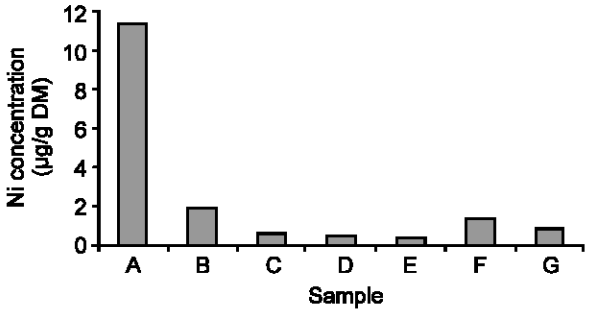

Fig. 4: Distribution of Ni in samples: A- Soil; B- Agaricus biosporus; C- Polyporus frondosis; D- Armillariella mellea; E- Pleurotus sapidus; F- Polyporus sulphureus; G- Pleurotus ostreatus

Rudawska (2005). This variation may be attributed to differences in mushroom species, uptake levels and ecosystem. On the other hand, our values are in agreement with reports by Yilmaz *et al.* (1998) and Isildak *et al.* (2004). Zinc content of soil correlated significantly with the copper content of *Pleurotus sapidus* ($p<0.05$); there was also a relationship between soil Pb and Cu in *Agaricus biosporus*; soil Cu and Cu content in *Pleurotus ostreatus* (Table 3).

The mushroom accumulating capability for Ni varied with the various species, with *Agaricus biosporus* having the highest accumulating potential (1.94-0.46 µg/g) and *Pleurotus sapidus* the least (0.42±0.06 µg/g) (Fig. 4). These values are in agreement with values in literature reported by Isildak *et al.* (2004) and Yilmaz *et al.* (1998). Nickel content in soil correlated positively with levels in *Polyporus sulphureus*.

Maximum and minimum content of Cd accumulated by the tested edible mushrooms were 0.62 and 0.29 µg/g respectively, with *Agaricus biosporus* having the highest accumulating potential and *Pleurotus sapidus*, the least (Fig. 5). The ability to accumulate cadmium is characteristic of mushrooms (Tyler, 1980; Malinowska *et al.*, 2004; Aruguette *et al.*, 1998) and is closely related with the presence of a binding compound (cadmium-mycophosphatin) which is a genetically coded feature (Schmitt and Meisch, 1985; Leski and Rudawska, 2005; Kalac and Svoboda, 2000). Cadmium is accumulated mainly in the kidneys and liver and its level in blood serum increases considerably following mushroom consumption. Observed Cd content were in agreement with reports by Turkekul *et al.* (2004) and Yilmaz *et al.* (1998). Significant relationships were observed between soil Cd and Cd content in *Agaricus biosporus* and *Polyporus frondosis* respectively (Table 3).

Lead accumulating potential of the mushrooms under study indicated that *Armillariella mellea* had the highest lead content of 1.21 µg/g, while *Pleurotus sapidus* had the least value of 0.31 µg/g (Fig. 6). Soil Zn correlated positively (p?0.05) with Pb content in Agaricus biosporus (Table 3).

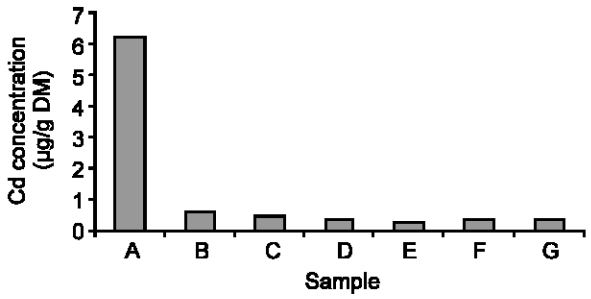

Fig. 5: Distribution of Cd in samples: A- Soil; B- Agaricus biosporus; C- Polyporus frondosis; D- Armillariella mellea; E- Pleurotus sapidus; F- Polyporus sulphureus; G- Pleurotus ostreatus

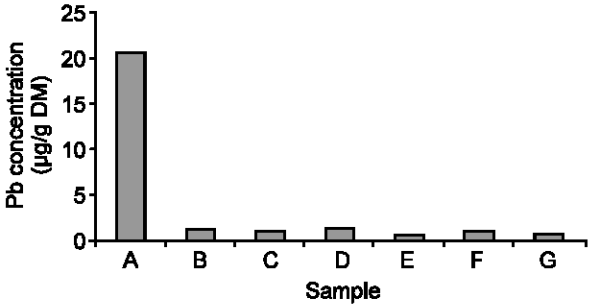

Fig. 6: Distribution of Pb in samples: A- Soil; B- Agaricus biosporus; C- Polyporus frondosis; D- Armillariella mellea; E- Pleurotus sapidus; F- Polyporus sulphureus; G- Pleurotus ostreatus

Contents of Pb and Cd are of toxicological importance. High Pb levels in food items can induce abdominal pains, vomiting, drowsiness, convulsion and malfunction of kidney/reproductive system (Goldsmith and Hildyard, 1985). Excessive exposure to Cd can result in osteomalacia, chronic renal disease resulting in hypercalciuria, proteinuria and glycosuria (Sherlock, 1986). Kalac *et al.* (1991) reported that the amount of heavy metal contents are related to mushroom species, composition of substrate, age of fruiting bodies and mycelium and distance from the source of pollution. According to Demirbas (2001), Sesli and Tuzen (1999) the variations in trace element content between species is dependent upon the ability of the species to extract elements from the substrate and on the selective uptake and deposition of elements in tissues.

The maximum level for certain contaminants in foodstuffs established by the commission of the European Committees (Commission Regulation [EC] No 466/2001) is set at 0.2 and 0.3mg/kg wet weight for Cd and Pb respectively in cultivated fungi. Assuming that the dry matter content of mushrooms is 10% (Kalac and Svoboda, 2000), these same limits for dry matter will approach 2.0 and 3.0 $mgkg^{-1}$ dry weight for Cd and Pb respectively. The Food and Agriculture Organization and the World health Organization stipulates the weekly intakes of Cd and Pb for adults at 0.42-0.49 and 1.5-1.75mg, respectively (Leski and Rudawska, 2005). For calculation, usually 300g of fresh mushrooms per meal is assumed (Kalac and Svoboda, 2000). However, during the harvest season, mushroom consumption is usually high and estimated dietary exposures to Pb and Cd may be higher than stipulated standards, hence, excessive consumption of mushrooms from this area should be avoided.

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