Bull. Environ. Contam. Toxicol. (1995) 55:122–129

Bulletin of Environmental Contamination and Toxicology

Bioconcentration Factors (BCF) of Silver in Wild *Agaricus campestris*

J. Falandysz, D. Danisiewicz

Environmental Chemistry and Ecotoxicology Research Group, Faculty of Chemistry, University of Gdańsk, ul. J. Sobieskiego 18, PL 80-952 Gdańsk, Poland

Received: 17 June 1994/Accepted: 17 February 1995

Silver is an element naturally occurring in small concentrations in different environmental sites. However, many anthropogenic sources of silver led to contamination of this element in soil surfaces, pastures and coastal marine areas in different parts of the world (Sanders and Cibik 1988; Beresford 1992). Estimates are that 40% of the 1.15×10^4 t of silver produced annually worldwide, will escape into the environment (Bowen 1985). Due to municipal waste discharge and/or industrial effluents with high silver concentrations, 100 x above the background level have been reported in invertebrate species from polluted marine areas (Bryan *et al.* 1983; Presley *et al.* 1990). The *meta*-stabile radioisotope, ^{110m}Ag, is a main component of the liquid effluents from nuclear facilities under normal operating conditions (Martin and Thomas 1990). The presence of ^{111}Ag and ^{110m}Ag also has been widely found throughout Europe in the 1986 Chernobyl fallout (Byrne 1988; Whitehead *et al.* 1988; Beresford 1992).

Silver ions are environmentally harmful. High toxic effects have been observed at low concentrations, especially in aquatic species (USEPA 1980; Shivaraj and Patil 1988).

Under natural conditions silver is found at relatively high concentrations in tissues of squid, with highest concentrations in the hepatopancreas (Falandysz 1988, 1989, 1991). Silver has been found also in the fruiting bodies in some wild species of higher fungi (Ramage 1930; Schmitt *et al.* 1978; Jones *et al.* 1985; Byrne 1988; Falandysz *et al.* 1994a). Species of lower fungi, as well as the mushroom *Agaricus bisporus*, are known to bioacumulate high concentrations of silver when grown on an artificially enriched substrate (Byrne and Tusek-Znidaric 1990; Pighi 1989; Falandysz *et al.* 1994b).

Higher fungi are able to bioconcetrate or exclude specific metal ions. Elevated concentrations of lead, cadmium, mercury and/or copper detectable in the fruiting bodies of mushrooms could be attributed to topsoil pollution with these metals, suggesting that mushrooms are a suitable indicator of heavy metal pollution of terrestrial sites (Kalač *et al.* 1991; Falandysz *et al.* 1993).

Correspondence to: J. Falandysz

Also, wild mushrooms growing in silver-contaminated soil (5.0 μg Ag/g) contained elevated concentrations of this element. The following BCF values for silver were observed: 24 in *Hygrocybe coccineus*, 6.0 in *Agaricus macrosporus* and 4.6 in *Gomphidius roseus* (Jones *et al.* 1985). These observations suggest the potential use of mushrooms to trace terrestrial pollution of silver. Analogously, the *meta*-stabile ^{110}Ag from the 1986 Chernobyl fallout was found at elevated concentrations in the tissues of *Agaricus campestris, Lycoperdon perlatum* and *Calvatia utriformis* (Byrne 1988).

This study was made to elucidate the relationship between the silver content of soil and biconcentration potential of wild *Agaricus campestris* from sites under different use and with different concentrations of heavy metals.

MATERIALS AND METHODS

Entire fruiting bodies of wild *Agaricus campestris* with the underlying soil were collected in September 1989 and 1992 from different sites in the northern part of Poland. The sites included pasture lands that were distant from potential pollution sources, an old hippodrome and lawns exposed to pollutants of automobile traffic for many years. The fruiting bodies were cleaned of external plant or soil material and dried at 105°C. About 100g of the top soil layer (0-10 cm) were collected from the areas surrounding the mushrooms. The soil samples were placed into polyethylene bags, and returned to the laboratory. Pieces of organic debris and stones were removed and the soil was dried at room temperature.

Silver concentrations were determined on samples consisting of a whole cap and stalk of each specimen. Each sample was weighed in a silica crucible, dried at 105°C for 24 hr, carefully ashed at 420°C and then re-ashed after addition of concentrated nitric acid ($\leq$0.2 ml). The latter step was done to whiten the ash. The resulting residue was dissolved in 6 ml of 1 mol/dm^3 nitric acid. Silver, together with cadmium and lead, were determined directly from the solution. The analysis was performed using a Thermo Jarrel Ash (video 11E) atomic absorption spectrophotometer (AAS) with an oxidizing air acetylene flame and background correction with a deuterium lamp. Verification of the dry ashing procedure was done using a silver standard added to a control mushroom (from 0.1 to 50 μg per sample). This procedure gave recoveries of 82-110%, with a coefficient of variation between 5.6 and 9.8%.

The air dried soil samples were weighed into a 400-ml beaker, mixed with 70 ml of 2 M hydrochloric acid, and boiled on a hot plate for one minute - according to the procedure given in detail by Musgrove (1987). Silver concentration was determined directly from the solution using flame AAS.

Table 1. Silver concentrations in *Agaricus campestris* and soil (mg/kg dry weight) and silver bioconcentration factors (BCF) in the fruiting bodies

Species, site, year	Part	No.	Mushrooms	No.	Soil	BCF
Agaricus campestris						
Sopot (hippodrome) 1992	Caps	15	62±28(18-100)	7	0,22±0.09 (0.14-	330±210 (100-670)
	Stalks	15	38±15(16-62)		0.38)	190±100 (61-400)
Buszkowy Dolne (pasture) 1989	Whole	4	23±17(3.4-43)	1*	0.15	150
Gdańsk;Zaspa (grass) 1989	Whole	17	16±13(1.7-53)	1*	0.10	160
Gdańsk;Av.Zwycięstwa (street lawn) 1992	Caps	11	47±28(13-110)	5	0.95±0.42 (0.35-1.4)	70±58 (10-190)
	Stalks	11	42±25(9.8-84)			60±38(7.5-110)
Gniewskie Pole n/Kwidzyn (pasture) 1992	Caps	8	13±(5.9-33)	1*	0.12	110±75(49-280)
	Stalks	8	19±6(9.4-15)			160±50(78-230)
Drzewica n/Lotyń (pasture "A") 1992	Caps	8	28±16(11-56)	1*	0.20	140±81(31-280)
	Stalks	8	37±15(20-63)			190±60(100-320)
Drzewica n/Lotyń (pasture "B") 1992	Caps	8	9.3±3.4(6.1-15)	1*	0.15	62±39(41-100)
	Stalks	8	12±10(4.9-41)			80±45(33-270)

* composite sample ~1 kg (4-10 subsamples)

RESULTS AND DISCUSSION

All the fruiting bodies of *Agaricus campestris* examined contained relatively high concentrations of silver both in caps and stalks. Values observed were between 1.7 and 110 mg/kg dry weight (Table 1).

Higher concentrations of silver were found in the caps of mushrooms collected from the hippodrome lawn in Sopot and street lawns in Gdańsk than from the grass lands or pastures elsewhere.

The total range of silver concentration of soil varied from 0.10 to 1.4 mg/kg dry weight and was higher from lawns influenced by heavy road traffic (0.95 ± 0.42 mg/kg dry weight, range from 0.35 to 1.4), while other sites examined were from 0.10 to 0.22 mg/kg (Table 1).

The concentrations of silver in caps and stalks of *Agaricus campestris* collected from the street lawn and the hippodrome were independent of the silver level in soil ($<0.1<p<0.3$) (Fig.1 and 2). A slight decreasing trend of silver content of the caps with an increase in silver soil concentration was observed from specimens collected from the lawn area (Fig.1). Both the mushrooms and the soil samples examined were characterized not only with high concentrations of silver but also with lead and cadmium (Table 2).

Table 2. Lead and cadmium concentrations in *Agaricus campestris* and soil from two areas examined (mg/kg dry weight)

Element	Caps	Stalks	Soil
Av. Zwycięstwa in Gdańsk (street lawn)			
Pb	$14 \pm 5^{(11)}$	$4.4 \pm 2.3^{(11)}$	$170 \pm 30^{(5)}$
Cd	1.4 ± 0.8	0.55 ± 0.52	0.75 ± 0.20
Hippodrome in Sopot			
Pb	$4.6 \pm 5.2^{(15)}$	$4.5 \pm 5.4^{(15)}$	$19 \pm 6^{(7)}$
Cd	0.80 ± 0.31	0.34 ± 0.29	0.13 ± 0.03

number of samples ( )

Lead and cadmium, together with mercury, nickel, arsenic and antimony, are elements considered as potential competitors of silver for -SH groups in the fruiting bodies of mushrooms (Parisin and Heede 1992). Cadmium at low concentrations is able to stimulate the mycelial growth of *Agaricus abruptibulbus*, indicating a growth effect for this species of fungi (Meisch *et al.* 1981). However, our study appears to be the first to show that *Agaricus bisporus* cultivated on a substrate selectively enriched with silver increases the concentration of this element in the caps and stalks ($p<0.01$) with an increase

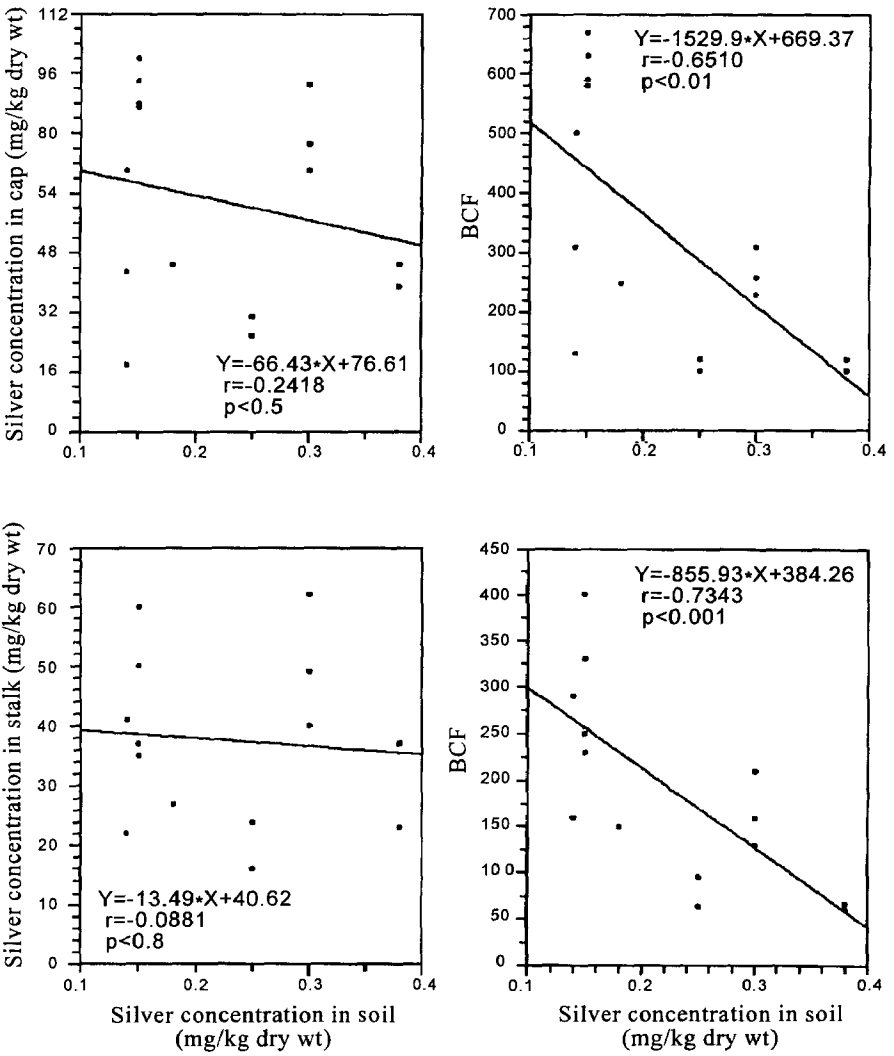

Figure 1. Correlations between concentrations of silver in caps and stalks of *Agaricus campestris* and between BCF values *versus* silver concentrations in soil from the hippodrome lawns in Sopot.

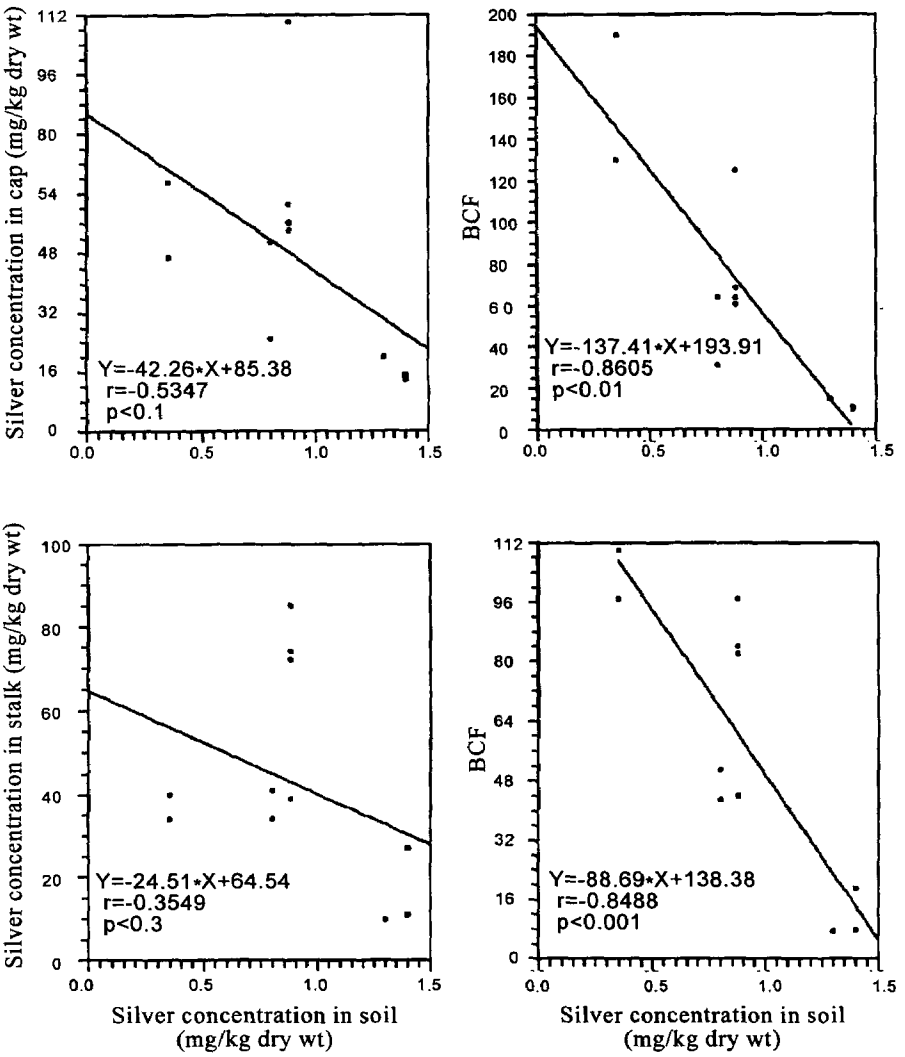

Figure 2. Correlations between concentrations of silver in caps and stalks of *Agaricus campestris* and between BCF values *versus* silver concentrations in soil from lawns in Gdańsk.

of the substrate fortification level, while the BCF values decreased (Falandysz *et al.* 1994b). It was evident from the data obtained in this study, that increased concentrations of silver in the soil, containing lead and cadmium, did not result in higher concentrations of silver in the fruiting bodies of *Agaricus campstris*. As suggested by Parisin and Heede (1992), this may imply that competition between silver and other metals binding with -SH groups has occured, since this phenomenon can influence the bioacumulation capacity of particular mushroom species for silver. Interactions of other kind also could take place.

The BCF values for silver in wild *Agaricus campestris* ranged between 70 ± 58 and 330 ± 210 (10-670) for caps and 60 ± 38 and 190 ± 60 (7.5-400) for stalks (Table 1). Specimens collected from lawns associated with heavy automobile traffic, with highest concentrations of silver in surronding soil, showed relatively low BCF values. Similar results were observed for the less polluted pasture land "B" in Drzewica (Table 1). In other studies BCF values for silver in wild mushrooms were between 100-300 for representatives of the family of *Boletaceae* (*Boletus aereus* and *Boletus edulis*) and *Lycoperdaceae* (*Bovistella radicata*) (Schmitt *et al.* 1978), between 0.06 and 3.9 for different mushrooms from Norway (Allen and Steinnes 1978) and 4.9 (range from 0.1 to 24) in specimens collected in Wales (Jones *et al.* 1985).

The BCF values for silver from the two sites studied showed a statistically significant decreasing trend with an increase in silver concentrations in the soil ($<0.001<p<0.01$) (Fig.1 and 2). The results indicate that the use of *Agaricus campestris* as a bioindicator species to trace the silver concentration is limited in soil polluted with other heavy metals. Nevertheless, the potential impact of other metals on the bioaccumulation of silver by mushrooms needs further study.

Acknowledgments. This work was supported by the Polish State Committee for Scientific Research (KBN) under Grant BW 8000-5-0219-4.

REFERENCES

Allen R O, Steinnes E (1978) Concentrations of some potentially toxic metals and other trace elements in wild mushrooms from Norway. Chemosphere 4:371-378

Beresford N A (1992) Overview of the transfer of radiosilver within the environment. Rep Inst Terrest Ecol 1990/1991. Natural Environment Research Council, England

Bowen H I M (1985) The cycles of copper, silver and gold. *In*: Hutzinger O (ed) The Handbook of Environmental Chemistry. Vol.1, Part D. The Natural Environment and the Biogeochemical Cycles: 1-27

Bryan G W, Langston W J, Hummerstone L G, Burt G R, Ho Y B (1983) An assesment of the gastropod *Littorina littorea* as an indicator of heavy-metal contamination in United Kingdom estuaries. J Mar Biol Assoc UK 63:327-345

Byrne A R (1988) Radioactivity in fungi in Slovenia, Yugoslavia, following the Chernobyl accident. J Environ Radioact 6:177-183

Byrne A R, Tusek-Znidaric M (1990) Studies on the uptake and binding of trace metals in

fungi. Part I. Accumulation and characterization of mercury and silver in the cultivated mushroom, *Agaricus bisporus*. Appl Organometall Chem 4:43-48

Falandysz J (1988) Trace metals in squid *Illex argentinus*. Z Lebensm Unters Forsch 187: 359-361

Falandysz J (1989) Trace metal levels in the raw and tinned squid *Loligo patagonica*. Food Addit Contam 6:483-488

Falandysz J (1991) Concentrations of trace metals in various tissues of the squid *Loligo opalescens* and their redistribution after canning. J Sci Food Agric 54:74-87

Falandysz J, Bona H, Danisiewicz D (1994a) Silver content of wild- grown mushrooms from the Northern Poland. Z Lebensm Unters Forsch 199:222-224

Falandysz J, Bona H, Danisiewicz D (1994b) Silver uptake by champignons *Agaricus bisporus* from artificially enriched substrate. Z Lebensm Unters Forsch 199:225-228

Falandysz J, Niestój M, Danisiewicz D, Bona H, Pempkowiak J (1993) Cadmium and lead in wild mushroom *Agaricus campestris* L. from different locations in Northern Poland (in Polish). Bromat Chem Toksykol 26:275-280

Jones K C, Peterson P J, Davies B E, Minski M J (1985) Determination of silver in plants by flameless atomic absorption spectrometry and neutron activation analysis. Intern J Environ Anal Chem 21:23-32

Kalač P, Burda J, Staškova I (1991) Concentrations of lead, cadmium, mercury and copper in mushrooms in the vicinity of a lead smelter. Sci Total Environ 105:109-119

Martin J M, Thomas A J (1990) Origins, concentrations and distribution of artificial radionuclides discharged by the Rhône River to the Mediterranean Sea. J Environ Radioact 11:105-139

Meisch H U, Scholl A R, Schmitt J A (1981) Cadmium -ein Wchsumfactor für den Schiefknolligen Anischampignon *Agaricus abriptibulbus* (Peck) Kauffmann. Z Naturforsch. 36c:765-771

Musgrove S D (1987) The distribution of heavy metals in soil and metal uptake into vegetation, at Beaumont Leys Sewage Farm, Leicester. J Assoc Publ Analysts 25:113-128

Parisin N E, Van den Heede M A (1992) Antimony uptake and correlation with other metals in mushroom species. Toxicol Environ Chem 36:205-216

Pighi L (1989) Selective accumulation of silver by fungi. Biotechnol Lett 11:275-280

Presley B J, Taylor R J, Boothe P N (1990) Trace metals in Gulf of Mexico oysters. Sci Total Environ 97/98:551-593

Ramage H (1930) Mushroom - mineral content. Nature 126:274

Sanders J G, Cibik S J (1988) Response of Chesapeake Bay phytoplankton communities to low levels of toxic substances. Mar Pollut Bull 19:439-444

Schmitt J A, Meisch H U, Reinle W (1978) Heavy metals in higher fungi.IV. Silver (in German). Z Naturforsch 33c:608-615

Shivaraj K M, Patil H S (1988) Toxicity of silver chloride to a fresh water fish (*Lepidocephalichthyes guntea*). Environ Ecol 6:713-716

United States Environmental Protection Agency (1980) Ambient water quality criteria for silver. EPA 440/5-80-071, Office of Water

Whitehead N E, Holm E, Ballestra S (1988) Observation of ^{111}Ag and ^{110m}Ag in the Chernobyl fallout. J Radioanal Nucl Chem Lett 128:18-194