Zeitschrift: Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und

Hygiene = Travaux de chimie alimentaire et d'hygiène

Herausgeber: Bundesamt für Gesundheit

Band: 65 (1974)

Heft: 2

Artikel: Mercury and methyl mercury content of different species of fungi

Autor: Stijve, T. / Roschnik, R.

DOI: https://doi.org/10.5169/seals-983687

Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Siehe Rechtliche Hinweise.

Conditions d'utilisation

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. <u>Voir Informations légales.</u>

Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. See Legal notice.

Download PDF: 02.04.2025

ETH-Bibliothek Zürich, E-Periodica, https://www.e-periodica.ch

Mercury and Methyl Mercury Content of Different Species of Fungi

T. Stijve and R. Roschnik

Control Laboratory of Nestlé Products Technical Assistance Co. Ltd., La Tour-de-Peilz

Introduction

Recent recognition of the widespread occurrence of mercury and methyl mercury in fish and other aquatic organisms is a cause of much environmental concern. Numerous papers on this subject have been published during the last five years, but knowledge of the mercury content in other organisms, especially in land plants, is still rather limited.

From the studies of *Nobbs* (1) and *Saha* (2) it would appear that the natural mercury content of plants is approximately 0,04 ppm. *Lee* et al (3) determined mercury levels in vegetables and cereals from various origins. The results ranged from 0,001—0,01 ppm. *Schelenz* and *Diehl* (4) analysed foodstuffs from the German market for mercury and found that cereals, fruits and vegetables mostly contained less than 0,01 ppm. These studies did not include any edible mushrooms.

Mushrooms and other fungi are widespread plant forms. They play an important role in the decomposition of organic matter in soils and some species are well-known for their ability to accumulate specific metals. Armillaria mellea for example, is very rich in copper. Truffles contain much aluminium and the fly agaric, Amanita muscaria, accumulates vanadium to a concentration of more than 100 ppm in the dry matter of its tissues (5). Considering these facts, it is surprising that no reports on the mercury content in fungi have been published, apart from a recent paper of Stegnar et al (6), who studied the differences in mercury uptake among plants, including fungi, growing around a mercury mine and processing plant in Yugoslavia. This study included 10 species of fungi, half of them clearly defined by their botanical names, and of which 8 were found to contain high levels of mercury, i. e. more than the soil in which they had grown. One species, the common puff ball, Lycoperdon gemmatum, was found to have definite accumulating ability: in some cases the mercury concentration of its spores was over 10 times higher than that of the adjacent soil. Moreover, the authors found that this metal was partly present as methyl mercury, a compound not previously reported to occur in plants.

These interesting findings prompted us to investigate the mercury content of different species of fungi growing in areas having no record of mercury

pollution. Our aim was to find mercury accumulating species and if possible, to establish differences between accumulating abilities of various genera of fungi. Because of its high toxicity we also payed special attention to the possible presence of methyl mercury.

Sampling and analysis

As suitable places for gathering fungi we chose areas near the town of Vevey on the Lake of Geneva in Switzerland. One area was the lawn near the apartment of one of the authors. The others were mountain forests ranging from 800—1400 m in altitude. These areas had no record of mercury pollution or even of agricultural working, as was confirmed by the analyses of their soils. Some species which we wished to study do not grow or were not found in Switzerland. These particular fungi were gathered from a dike in Holland together with a representative soil sample.

Samples of each species, nearly always consisting of several fruit bodies, were cut in slices and dried in an oven at 80 °C. The dehydrated material was ground to a fine powder which was used for the analysis of total mercury and methyl mercury. In the preparation of the samples as well as during analysis, we took all normal precautions against contamination as is customary in trace analysis.

Determination of total mercury content by atomic absorption

0,5 g dry material were mineralised with 3 ml concentrated nitric acid in a teflon and stainless steel decomposition vessel (7) at a temperature of 100 ° C for 15—20 minutes. After cooling, the resulting liquid was transferred to a 30 ml test tube with a ground glass neck and diluted to 15 ml.

In the case of analysing a mushroom with a high mercury content an additional dilution step was performed after the mineralisation and an aliquot chosen such that the final 15 ml contained 100—250 ng mercury. Nitric acid was added where required to maintain a final acid concentration of 3 N.

1 ml hydroxylammonium chloride solution (20 % w/v) was added and the tube well agitated to expel nitrogen oxides.

Mercury was determined by cold vapour atomic absorption spectrophotometry using the test tube as a reduction tube by adding 20 percent stannous chloride solution in 4 N sulphuric acid according to a procedure similar to that of *Lindstedt* (8).

Operating conditions were as follows:

Perkin Elmer 303 atomic absorption spectrophotometer with a Hitachi recorder and a mercury hollow cathode lamp, wave-length 253,7 nm; the absorption cell, 220 mm long and 20 mm in diameter, had demountable quartz end-windows to permit cleaning of the inside surfaces; air flow 300 ml/minute.

The sensitivity obtained was 1—2 ng/1 % absorption, the detection limit was 1—2 ng mercury. Calibration was linear up to at least 400 ng as measured by peak heights. It was normally performed by the method of standard additions.

Confirmation of total mercury content

The validity of atomic absorption for mercury determinations has been demonstrated in numerous comparative studies. Erroneous results caused by incompletely digested samples have, however, been reported in the literature (2). Furthermore, the chemistry of fungi is relatively unknown and the possibility of interferences that could simulate a high mercury content could not altogether be excluded.

For this reason we subjected 0,5 g of finely powdered samples to the wet ashing procedure described by Woidich and Pfannhauser (9). Mercury was extracted from the digested sample solution at pH 2,5 with the classic dithizone reagent in chloroform. After suitable concentration the dithizone solution was chromatographed on thin-layers of silicagel using xylol-chloroform 2+1 v/v as a mobile phase.

Orange coloured spots of mercury dithizonate were clearly visible at Rf 0,60 and could be semi-quantitatively evaluated by comparing them to those given by

co-chromatographed aliquots of freshly prepared standard solutions.

The limit of detection was approximately 0,05 microgram, which was sensitive enough for confirming the high levels encountered in most fungi which were analysed.

Determination of methyl mercury compounds

The methyl mercury in the powdered fungi was determined by the method of $West\ddot{o}\ddot{o}$ (10, 11, 12). As we analysed dehydrated material, the sample was first soaked overnight in the prescribed mixture of water and hydrochloric acid in a closed vessel. Sample size rarely exceeded 5 g of the dry material. As extracting solvent we used toluene instead of the much more toxic benzene. The final purified extract was analysed by gas chromatography on a 5 ft x^1/s inch glass column packed with 5 percent of Carbowax 20 M coated on Chromosorb W, 100—120 mesh, HMDS treated.

This 5 percent coating of the stationary phase gave us much better results than the higher loading reported in the literature (10, 11, 12, 13). Gas chromatographic conditions were: Column temperature 140 °C. Injection temperature 200 °C. An electron capture detector with a ⁶³ Ni ion source was operated at 250 °C.

Gas flow 40 ml of nitrogen/minute.

Under these conditions the retention time of methyl mercury chloride was approximately 3 minutes.

It was found necessary to prime the freshly prepared column by repeated injections of large amounts of methyl mercury.

Best results were obtained by injecting massive doses of toluene solutions of methyl mercury iodide, about 250 ng of CH₃HgI in each injection.

We achieved a sensitivity such that 0,1 nanogram of methyl mercury chloride gave approximately a 50 percent of full scale deflection.

If the injected sample aliquot contained so much methyl mercury that the linear range of response was exceeded, the sample extract was suitably diluted

and injected again.

Very low levels of methyl mercury were determined after repeating the cysteine partitioning step: 8 ml final extract is obtained by the Westöö procedure. This extract could not be concentrated by evaporation without losing virtually all the methyl mercury chloride. For this reason, the 8 ml toluene were re-extracted with 0,8 ml aqueous cysteine solution. The aqueous phase was acidified with 0,3 ml 6 N hydrochloric acid and shaken with 1 ml of toluene. In this way an eight fold concentration was achieved, which enabled us to determine ppb levels, or to restrict sample size if the material to be analysed was scarce.

Confirmation of identity of methyl mercury chloride

Gas chromatographic evidence of the presence of methyl mercury analysed according to the Westöö procedure is normally considered adequate for routine work, because the partition step with cysteine solution has much discriminatory power. Furthermore, the peak shape of the compound observed during gas chromatography is also characteristic because, showing slight tailing, it ist more or less of the Langmuir type.

However, we performed confirmatory analysis by thin-layer chromatogra-

phy wherever possible.

For that purpose, we prepared concentrated extracts by the double partition method as described above. Suitable aliquots were spotted on silica gel thin-layer plates and the chromatograms were developed in light petroleumethyl ether 7:3 v/v, as a mobile phase. As a chromogenic reagent we used 4,4 bis (dimethylamino) thio benzophenon (10). The limit of detection was approximately 0,02 microgram.

Results and discussion

The levels of total mercury and of methyl mercury in different species of fungi are listed in the tables 1, 2, 3 and 4. High concentrations of mercury were found in the majority of fungi. We also encountered relatively small, but significant amounts of methyl mercury in most species. It would seem that most of the methyl derivative is present in the spore bearing part of the fungus: thus analysis of a single fruitbody of Agaricus arvensis gave 0,19 ppm for the stalk and

0,52 ppm for the cap, both values expressed on dry matter basis.

Of particular interest are the results for the members of the genus Agaricus as reported in table 1. All five members were found to contain mercury levels which were about 20—50 times higher than those of the soils on which they had grown. Agaricus arvensis and, to a lesser extent, Agaricus campestris are fungi which could be used as indicator organisms in the study of mercury pollution, because these species preferentially grow in areas influenced by human activities (along roads, in gardens, parks and meadows), and because they can usually be found from May till November.

Table 1
Total and Methyl Mercury Content of Fungi (ppm/dry weight)
Agaricus and Amanita species

Species	Total mercury	$\mathrm{CH_3Hg} +$	$^{0}/_{0}~\mathrm{H}_{2}\mathrm{O}$	Total Hg in Soil (dry matter)	Concentration factor
Agaricus arvensis Schff ex Fr.	7,8	0,12 (1,40/0)	87	0,38	20
ditto	8,1	$0,44 (5,1^{0}/_{0})$	92	0,38	21
ditto	6,5	$0,42 (6^{0}/_{0})$	90	0,38	17
Agaricus benesii Pilàt	6,7	0,04 (0,60/0)	87	0,12	56
Agaricus silvaticus Schff ex Secr.	5,8	0,04 (0,60/0)	70	0,12	48
Agaricus campestris Agaricus vaporarius	14,2	0,43 (2,9%)	90	0,75	19
(Pers. ex Vitt.) Moser	16,9	$0,47 (2,4^{0}/_{0})$	85	0,75	22
Amanita pantherina DC ex Fr.	0,76	0,02 (2,80/0)	89	0,14	5
Amanita vaginata Bull ex Fr.	0,05	<0,01	88	0,14	<u> </u>

Figures in brackets represent the percentage of mercury that is present as the methyl derivative.

Concentration factor = ppm of total mercury in dehydrated fungus ppm of total mercury in dried soil

Table 2
Total and Methyl Mercury Content of Fungi (ppm/dry weight). Gasteromycetes

Species	Total mercury	$ m CH_3Hg+$	$_{0}^{0}/_{0}~\mathrm{H}_{2}\mathrm{O}$	Total Hg in Soil (dry matter)	Concentration factor	
Lycoperdon gemmatum Batsch	1,1	$0,24 (20,5^{0}/_{0})$	90	0,14	8	
ditto	5,0	$0,80 (14,9^{0}/_{0})$	60	0,12	42	
ditto	7,0	$0,29 (3,9^{0}/_{0})$	60	0,12	58	
Lycoperdon umbrinum	4,3	$0,12 (2,6^{0}/_{0})$	67	0,12	36	
Lycoperdon pyriforme Schaef.						
ex Pers **	1,1	$0,06 (5,1^{0}/_{0})$	70	- 11 x 10 1 2 x 2 1 2 x 4		
Calvatia gigantea (Pers.) Lloyd	19,7	$3,5 (16,6^{0}/_{0})$	50	0,75	26	
Geaster fimbriatum Fr.	2,2	$0,07 (3,6^{0}/_{0})$	60	0,14	16	
Phallus impudicus Pers.	0,75	< 0,02	90	0,75	_	

^{**} growing on moss covered totally decayed wood.

It cannot be concluded from the results available so far that all Agaricus species accumulate mercury, but the hypothesis seems at least highly probable, because our investigation included common and fairly rare members of this genus, gathered at entirely different sites. For example, Agaricus benesii was found at 1400 m altitude near Vevey (Switzerland), whereas a bundle of Agaricus vaporarius was gathered on a dike in a Dutch polder.

Table 3

Total and Methyl Mercury Content of Fungi (ppm/dry weight)

Various species of agaricaceae

Species	Total mercury	$\mathrm{CH_3Hg}+ egin{array}{c} 0/0 \ \mathrm{H_2O} \end{array}$		Total Hg in Soil (dry matter)	Concen- tration factor
Marasmius oreades Bolt ex Fr.	4,9	$0,24 (4,5^{0}/_{0})$	93	25 <u>5-27</u>	
Russula palludosa	0,09	$0,03 (26^{0}/_{0})$	87	0,14	
Russula atropurpurea	0,09	<0,01	90	0,12	_
Lactarius deliciosus Lin. ex Fr.	0,70	<0,005	90	0,12	6
Lactarius piperatus Scop. ex Fr.	7,2	0,02 (0,30/0)	83	0,12	60
ditto Hypholoma fasciculare	5,1	<0,01	82	0,14	36
(Huds. ex Fr.) Quélet. Coprinus Comatus	1,7	<0,02	90	0,12	14
(Müller ex Fr.) Gray	2,8	0,16 (5,40/0)	92	0,38	7

Table 4

Total and Methyl Mercury Content of Fungi (ppm/dry weight)

Various species, other than agaricaceae

Species	Total mercury	$\mathrm{CH_3Hg}+ egin{array}{c} 0/0 \ \mathrm{H_2O} \end{array}$		Total Hg in Soil (dry matter)	Concen- tration factor
Inonotus hispidus**					
(Bull ex Fr.) Pat.	0,01	<0,01	83	_	
Trametes gibbosa**				1	
(Pers. ex Fr.) Fr.	0,09	<0,02	47	2012/11/2012 - GE	17 13 (Q. 14) (A
Auricularia auricula-judae.				7	
Lin. ex Fr.**	0,02	<0,01	90		-
Boletus edulis Schaef. ex Fr.	3,2	$0,04 \ (0,8^{0}/_{0})$	90	0,12	32
Boletus (Xerocomus)					
chrysenteron Bull. ex Fr.	1,3	$0,01 \ (0,8^{0}/_{0})$	90	0,12	11
Boletus (Ixocomus)		and the second			
grevillei Schum. ex Fr.	1,5	$0,10 (6,6^{0}/_{0})$	92	0,12	11
Boletus (Ixocomus)	The second				
granulatus Lin. ex. Fr.	0,90	$0,20 (21,1^{0}/_{0})$	92	0,38	2,4
Helvella lacunosa	0,18	<0,005	90	0,12	1,5
Hydnellum aurantiacum	0,54	n. d.	80	0,12	4,5
Craterellus cornucopioides	MINE OF THE	Decision agreements	BASTIST STATE	120h /842 3/8/8	District Conf.
Lin. ex Fr.	0,04	<0,005	80	0,12	
Clavaria pistillaris Lin. ex Fr.	1,7	$0,05 (3^{0}/_{0})$	84	0,12	14
Clavaria aurea Schaef. ex Fr.	0,15	$0,03 (17^{0}/_{0})$	90	0,12	1,3

^{**} growing on wood.

In this case, the use of Agaricus fungi as indicators for mercury pollution would not require distinguishing of the various species and varieties, notoriously difficult even for experienced taxonomists.

On the other hand, the genus Agaricus is fortunately easily characterised and recognisable in the field as well as in the laboratory (14). The dark purple-brown or sepia colour of the spores and of the mature lamellae, the fact that the latter are free from the stalk, the presence of a ring around the upper part of the stalk, together with a characteristic habit and colour range, make it possible to recognise the genus without using a microscope. This recognition should be possible not only for the specialist, but also for the lay-man, for example, a chemist interested in environmental problems associated with mercury.

sted in environmental problems associated with mercury.

A second genus in which mercury accumulation was found to be very marked is Lycoperdon (Table 2). The observations of *Stegnar* et al (6) on the mercury uptake and the relatively high methyl mercury content of Lycoperdon gemmatum were amply confirmed, but we determined much higher concentration factors. However, these might vary with the state of development of the individual fungus. For example, the Lycoperdon species for which we found the lowest mercury content consisted of fruit bodies which had just emerged from the soil and whose interior was still white. The samples with 5—7 times more mercury were mature yellowish-brown puff-balls close to the spore disseminating stage. Interestingly, other Lycoperdon species and even the distantly related earth star (Geaster fimbriatum) also accumulate high amounts of mercury.

Considering that the lifespan of all these fungi rarely exceeds a few days, we decided to analyse the giant puff-ball (Calvatia gigantea) which is potentially the largest of all fungi, often taking more than a month for its full development (13). We presumed that it would have time to accumulate far more mercury than its shortlived relatives, but the result of our analyses did not confirm this. Although the sample of Calvatia examined by us certainly contained far more total mercury and methyl mercury than those of Lycoperdon gemmatum and umbrinum, its accumulation as indicated by the concentration factor, was lower (Table 2).

At the time of our investigation, samples of Lycoperdon were plentiful, but the giant Calvatia could not be found in the region around Vevey. For this reason we obtained a sample of the latter species from a dike near Utrecht in Holland, where it is quite abundant.

Analysis of a soil sample from this dike indicated an unusually hig mercury content, in fact about 6 times higher than that measured in the Swiss regions of interest. Differences in the structure and the acidity of the soils, as well as other factors, would influence mercury uptake in fungi.

It is, therefore, possible that analyses of Calvatia gigantea and Lycoperdon gemmatum species grown in the same soil would have yielded different concentration factors.

Our investigations with regard to other fungi indicated notable differences in mercury uptake between members of the same genus. Lactarius deliciosus was found to contain about 10 times less mercury than its relative Lactarius pipera-

tus (Table 3). Both species were found growing close together on the same soil and they were gathered at the same time. A similar phenomenon was observed in two Clavaria's as shown in table 4.

Lesser, but still notable differences were also found between various Boletus species. Among the fungi analysed, Ixocomus seems more able to convert mercury to its methyl derivative than «true» Boletus.

Fungi growing on wood only contain very low levels of mercury, due to the extremely low mercury content of their substrate. The highest content (0,09 ppm) was determined for a Trametes gibbosa specimen which grew on the wood of a farmhouse, whereas the two other wood inhabiting species were found on live trees.

Mercury levels in commercially available edible fungi

The findings for wild species of fungi, reported in tables 1—4, raised the question of whether similar concentrations of mercury could also be found in cultivated and other commercially available mushrooms.

To provide at least a provisional answer to that question, we analysed 12 samples of edible fungi found on the Swiss market. The results of these analyses are listed in table 5.

Table 5

Total and Methyl Mercury Content of Commercially Available Fungi
(ppm/dry weight)

Commercial name	Species	Total mercury	CH ₃ Hg+	Remarks
Dried boletus	Boletus edulis	eselle ev.		grant palo regaritas Lar Sanar as an Assa
A CONTRACTOR OF THE	Schaef. ex Fr.	4,0	$0,02 (0,4^{0}/_{0})$	
ditto	ditto	3,2	$0,02 (0,5^{0}/_{0})$	
ditto	ditto	3,1	$0.03 (0.8^{\circ}/_{\circ})$	
Dried champignons Champignons	Agaricus bisporus	1,9	$0,19 (9,5^{0}/_{0})$	
de Paris Champignons de	ditto	0,17	0,005 (2,4%)	Water content 80%/0
Paris lyophilized	ditto	0,72	0,06 (7,4%/0)	
Dried Shiitake	Lentinus edolus	0,05	<0,01	A Salaran
ditto Black fungus	ditto Auricularia	0,10	<0,005	cultivated (on wood
Muh-êrh, dried	polytricha	0,03	<0,005	on wood
Dried Gyromitres	Gyromitra esculenta Pers. ex. Fr.	0,02	<0,005	
Dried Morels	Morchella conica Pers ex. Fr.	0,07	<0,02	
Chanterelle mush-	Cantharellus		Emme the	
rooms canned	cibarius	0,03	<0,01	

The levels of mercury and methyl mercury found in dried Boletus edulis are in excellent agreement with those found by Stegnar et al (6) and with our own value reported in table 4 for the same species gathered in the Swiss mountains. The mercury values determined in three samples of Agaricus bisporus, the cultivated white mushroom, varied considerably, i. e. from 0,17 ppm to 1,9 ppm, calculated on the dry matter. There is a little doubt that Agaricus bisporus is able to accumulate mercury, as indicated by our study on its wildlife relatives, but its mercury uptake is, among other factors, limited by the mercury content of the substrate on which it is cultivated. It should be possible to verify this experimentally.

Mushrooms which are cultivated on wood as is the case with Shiitake and Muh-êrh in East Asia, have only a low mercury content. In fact, the level found in Muh-êrh is not different from that encountered in its European relative, Auri-

cularia auricula-judae (Table 4).

Cantharellus cibarius, a most popular edible fungus, was found to contain very little mercury. This low accumulating ability is apparently shared by the related species, Craterellus conucopioides in which we found only 0,04 ppm. Mercury levels of the same order of magnitude were also found in Morels and Gyromitres.

Conclusions

The high mercury content of several species of fungi is due to their tremendous accumulating ability and cannot generally be related to mercury pollution.

It is, of course, to be expected that certain fungi in an area of aerial mercury pollution, for example, in the vicinity of a chlor-alkali plant, may take up mercury to give concentrations far higher than those reported in this paper. This would make them suitable as indicator organisms.

Some fungi have probably always contained appreciable levels of mercury. This should be verified by the analysis of herbarium species gathered before the industrial use of mercury and its compounds became widespread, i. e. roughly before the Second World War.

Such herbarium material is available in many museums and botanical laboratories.

It is unlikely that the consumption of edible mushrooms contributes much to the mercury intake of the average person. Although prolonged daily consumption of Calvatia gigantea would undoubtedly lead to mercury poisoning, this is impossible in practice, since this fungus is far from common and only eaten by a few mycophagists at certain times of the year (15).

In most European countries and in the USA the average consumer is somewhat reluctant to accept wild mushrooms as food, although Boletus edulis has nearly everywhere high appeal. Popularity of mushrooms fluctuates with the state of the food supply in a country. During the war years and for some time afterwards mushrooms were much sought after in countries of Central Europe. When the food supply became normal again, the interest in edible fungi descreased rapidly.

The most popular mushroom in Europa and in the USA is the cultivated Agaricus bisporus. Improvements in the cultivation of this species which occurred in the early fifties brought it within reach of every consumer, but it is doubtful whether the consumption per inhabitant in Europe exceeds 500 grams a year.

Even if this mushroom contained as much mercury as its wildlife relatives (which is unlikely), the following calculation shows that it would contribute very little to the total mercury intake:

Mercury content 7 ppm on dry matter

This corresponds to 0,7 ppm in the fresh mushrooms.

 $500 \times 0.7 = 350$ micrograms of mercury per year.

Weekly intake =
$$\frac{350}{52}$$
 = about 7 micrograms.

The acceptable weekly intake as proposed by the World Health Organisation and the Food and Agriculture Organisation is 300 micrograms of mercury.

Still, a case exists for establishing a special tolerance for mercury in cultivated mushrooms and in other fungi which are brought on the market.

Several countries have a general tolerance of 0.05 ppm of mercury in food, except for fish, in which higher levels are permitted.

Enforcement of this limit would lead to needless banning of wholesome edible fungi and would jeopardize the mushroom industry.

Acknowledgement: We thank Mr. E. Brand for supplying some interesting species of fungi.

Summary

The total mercury and methyl mercury contents of 32 wildlife species of fungi were determined. High concentrations of mercury were measured in the majority of fungi and a relatively small, but significant part of this metal was present as methyl mercury in most species (from less than 1—26 percent of total mercury).

Two genera in which mercury accumulation was very marked are Agaricus and Lycoperdon. Agaricus species contained 6,5—16,9 ppm and Lycoperdon (including a related Calvatia species) 1,1—19,7 ppm of total mercury, calculated on dry matter basis. These high levels could not be related to mercury pollution. Analysis of samples of soil on which the fungi had grown, gave generally low values and indicated concentration factors ranging from 17—56 for Agaricus and 8—58 for Lycoderdon.

High mercury accumulating abilities are thus demonstrated for these fungi. It is suggested that members of the genus Agaricus could be used as indicator organisms in the study of mercury pollution.

A small survey carried out on 12 samples of cultivated and other commercially available mushrooms revealed that dried Boletus edulis is most rich in mercury (3—4 ppm). In the cultivated white mushroom Agaricus bisporus the mercury level fluctuated from 0,17—1,9 ppm, calculated on dry matter. Fungi cultivated on wood as Muh-êrh and Shiitake only contain very low levels, i. e. 0,1 ppm and less. In spite of high mercury concentrations in edible mushrooms, their consumption contributes very little

to the mercury intake of the average person, because of their relative unimportance in the human diet.

However, a case exists for establishing a special tolerance for mercury in cultivated mushrooms and other edible fungi.

Résumé

Les teneurs en mercure et méthylmercure ont été déterminées dans 32 espèces de champignons naturels. Dans la majorité de ceux-ci, des teneurs élevées en mercure ont été mesurées. Dans la plupart de ces espèces une faible, mais significative, partie de ce métal se trouvait sous forme de méthylmercure (de moins de 1 et jusqu'à 26 % du mercure total).

Les deux genres où l'accumulation en mercure est la plus marquée, sont l'Agaricus et le Lycoperdon. Les espèces Agaricus contenaient 6,5 à 16,9 ppm de mercure total calculé sur la matière sèche, tandis que les espèces Lycoperdon (y compris les espèces Calvatia apparentées) en avaient de 1,1 à 19,7 ppm. Ces teneurs élevées ne sont pas attribuables à une pollution par le mercure. En effet, les analyses des sols sur lesquels croissaient les champignons, ont donnée en général des chiffres faibles, indicant de ce fait des facteurs de concentration de 17 à 56 pour le genre Agaricus et de 8 à 58 pour le genre Lycoperdon. Ces résultats prouvent que ces champignons sont hautement capables d'accumuler le mercure. On suggère d'utiliser les membres du genre Agaricus comme indicateurs lors d'étude sur la pollution par le mercure.

Un examen limité à 12 échantillons de champignons du commerce et de champignons cultivés a montré que parmi eux le Boletus edulis est le plus riche en mercure (3 à 4 ppm). Dans le champignon blanc cultivé, Agaricus bisporus, la teneur en mercure (toujours sur matière sèche) a varié de 0,17 à 1,9 ppm. Les champignons cultivés sur du bois, comme le Muh-êrh et le Shiitake, ne contiennent que des teneurs très faibles, de l'ordre de 0,1 ppm et même moins.

Bien que les campignons comestibles aient des teneurs élevées en mercure, leur consommation ne contribue que très peu à l'apport en mercure de l'adulte moyen, en raison de leur relative insignifiance dans le régime alimentaire humain.

Cette étude pose toutefois le problème de la fixation d'une tolérance spéciale pour le mercure dans les champignons cultivés et les autres champignons commestibles.

Zusammenfassung

Gesamtquecksilber und Methylquecksilber wurden in 32 wildwachsenden Pilzarten bestimmt. In den meisten Pilzen wurden sehr hohe Quecksilbergehalte gefunden: größtenteils lag ein kleiner aber signifikanter Anteil dieses Metalles als Methylquecksilber vor (von weniger als 1 % bis 26 % des gesamten Quecksilbers).

Zwei Gattungen, an denen Quecksilberspeicherung sehr ausgeprägt war, sind Agaricus und Lycoperdon. Agaricus-Arten enthielten 6,5—16,9 ppm Quecksilber und Lycoperdon-Arten 1,1—19,7 ppm, an der Trockensubstanz ausgedrückt. Diese hohen Werte konnten nicht mit einer Quecksilberverschmutzung in Zusammenhang gebracht werden. Quecksilberbestimmungen in den Böden, auf denen die Pilze gewachsen sind, lieferten im allgemeinen niedrige Werte und wiesen auf Anreicherungsfaktoren hin, die für Agaricus zwischen 17 und 56, für Lycoperdon zwischen 8 und 58 lagen.

Hohe Quecksilberspeicherungsvermögen sind also für diese Pilze nachgewiesen. Es wird vorgeschlagen, daß Mitglieder der Gattung Agaricus als Indikatoren für Quecksilberumweltverschmutzungsstudien dienen könnten.

Eine beschränkte Untersuchung 12 Proben kultivierter und im Handel erhältlicher Pilze zeigte, daß getrockneter Boletus edulis am reichsten an Quecksilber ist (3—4 ppm). Im kultivierten weißen Champignon Agaricus bisporus schwankte der Quecksilbergehalt zwischen 0,17 und 1,9 ppm (an der Trockensubstanz ausgedrückt). Auf Holz gezüchtete Pilze, z. B. Muh-êrh und Shiitake, enthalten nur wenig Quecksilber, 0,1 ppm und weniger. Trotz der hohen Quecksilbergehalte genießbarer Pilze, trägt ihre Verzehrung nur wenig an die Quecksilberaufnahme eines Durchschnittsmenschen bei, da sie einen relativ niedrigen Anteil der menschlichen Kost ausmachen.

Der Standpunkt ist durchaus vertretbar, eine spezielle Quecksilbertoleranz für kultivierte und andere genießbare Pilze festzulegen.

Literature

- 1. Nobbs, Ch. L.: Mercury use and social choice, OECD, Paris 1-39 (1972).
- 2. Saha, J. G.: Significance of mercury in the environment. Residue Reviews 42, 103 (1972).
- 3. Lee, D. F. et al: Pesticide Science 3, 13 (1972).
- 4. Schelenz, R. and Diehl, J. F.: Z. Lebensm. Unters.-Forsch. 151, 369 (1973).
- 5. Goudot, A. and Bertrand, D.: Les oligoéléments, Collection «Que sais-je?» No 1010, Presses Universitaires de France, 1962.
- 6. Stegnar, P., Kosta, L., Byrne, A. R. and Ravnik, V.: Chemosphere 2, 57 (1973).
- 7. Bernas, B.: Anal. Chem. 40, 1682 (1968).
- 8. Lindstedt, G.: Analyst 95, 264 (1970).
- 9. Woidich, H. und Pfannhauser, W.: Z. Lebensm. Unters.-Forsch. 149, 1 (1972).
- 10. Westöö, G.: Acta chem. Scand. 20, 2131 (1966).
- 11. Westöö, G.: Acta chem. Scand. 21, 1780 (1967).
- 12. Westöö, G.: Acta chem. Scand. 22, 2277 (1968).
- 13. Kamps, L. R. and MacMahon, B.: J. Assoc. Offic. Analyt. Chemists 55, 3, 590 (1972).
- 14. Singer, R.: Mushrooms and truffles. World Crop Books Interscience Publishers, Inc., New York (1961).
- 15. Stijve, T.: Unpublished mycological observations (1959).
- 16. Van der Aa, H. A.: Coolia 16, 17 (1973).

T. Stijve Dr. R. Roschnik Control Laboratory of Nestlé Products Technical Assistance Co. Ltd. Case postale 88

CH-1814 La Tour-de-Peilz