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BIOCONCENTRATION OF MANGANESE AND IRON IN PANAEOLOIDEAE SING.

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According to literature, the manganese content of most basidiomycetes fluctuates between 10 and 60 mg/kg, whereas the iron levels range from 100–500 mg/kg (both expressed on dry weight). The present authors report that bioconcentration of manganese is a distinguishing feature of the Panaeoloideae, as demonstrated by the analysis of 44 collections representing 15 taxons. Carpophores generally contain between 250 and 2500 mg/kg on dry weight, and, with the notable exception of *Panaeolus semiovatus, P. antillarum* and *P. phalaenarum*, their iron content is 2 to 3 times lower. This phenomenon was not observed in members of related genera such as *Psathyrella* and *Coprinus*.

Manganese is an essential element for both plants and animals. It is a component of important cellular enzymes such as decarboxylase, arginase and possibly others involved in nucleic acid metabolism (Reilly, 1991).

Generally, higher fungi do not seem to have a requirement for manganese that would necessitate the uptake of high levels. Indeed, the manganese content of most basidiomycetes fluctuates between 10 and 60 mg/kg on dry weight, whereas iron concentrations range from 100–500 mg/kg (Schmitt et al., 1977). These levels are well below the average concentrations measured in soils which are 1000 mg/kg for manganese, and even 15000 mg/kg for iron (Reilly, 1991).

Schmitt et al. (1977) analysed 262 samples of higher fungi for both metals, and observed higher than average contents in Tremellales and Auriculariales, although iron always predominated. Among the gasteromycetes the same authors reported unusually high manganese levels in a number of Phallaceae. In some of these fungi the proportion Fe : Mn was well below 1.

Tyler (1980) subjected 130 species of basidiomycetes to analysis for several elements, and found a median value of 19 mg/kg for manganese. However, he observed bioconcentration in two unrelated species, namely *Panaeolus campanulatus* (1140 mg/kg) and *Polyporus hirsutus* (735 mg/kg). Vetter (1989) analysed 80 species and reported mean values of 28 mg/kg for manganese and 305 mg/kg for iron.

So far, *Panaeolus campanulatus* is the only gilled fungus reported to have an unusually high manganese content, but this seems to be an isolated observation pertaining to only one collection (Tyler, 1980). Since *Panaeolus* species have already been analysed for various metabolites in this laboratory (Stijve et al., 1984; Stijve, 1985, 1987), it was decided to use the remaining collections for an investigation of their manganese and iron content.

For a better appreciation of the findings the investigation was extended to other dark brown and black spored Agarics, such as Strophariaceae, Coprinaceae, Agaricaceae and Bolbitiaceae. The results of the analyses are reported and discussed in this paper.

METHODS

Most species analysed were collected in Switzerland during 1983–1990. Some *Panaeolus* were obtained from Germany, the Netherlands, France, Hawaii, Brazil and Australia. The collections were either freezedried or dehydrated at 55°C in an airstream. Subsequently, the material was ground to fine powder and stored in glass jars at 10°C until analysed.

Samples were hydrolysed for 30 minutes with hot 6N hydrochloric acid (Simpson & Blay, 1966). After filtration of the extracts, manganese and iron were determined with an ARL model 3410 sequential inductively coupled plasma atomic emission spectrometer, using respectively 257.61 nm and 259.94 nm as emission lines (Gouvielos, 1989).

RESULTS AND DISCUSSION

The manganese and iron contents measured in 15 Panaeoloideae (44 collections) are listed in Table I. In most collections manganese uptake is very marked, and most often the ratio Fe : Mn is well below 1, which has not yet been observed in gilled fungi from other genera.

Uptake of both metals can even be so tremendously high that it interferes with the normal physiology of the carpophores: at one time, we collected a number of *Panaeolus sphinctrinus* growing beneath freshly planted shrubs that had received an ample supply of fertiliser supplemented with trace elements. The carpophores had an unusually light brown colour, and their gills were remarkably clear, indicating absence of spores. These sterile fruit-bodies loaded with 0.55 percent manganese and 0.2 percent iron did not contain any urea, a metabolite associated with sporulation, but had a remarkably high serotonin content (Stijve, 1987). Both urea and serotonin can be considered final metabolites in biochemical detoxification processes used to neutralise ammonia from the substrates (Iwanoff, 1924; Grosse, 1982).

The enzymes involved in the conversion of ammonia to urea apparently do not need much manganese for their activation, but it is not unthinkable that those governing the biosynthesis of serotonin need the metal. It is interesting to note that representatives of the related genera *Coprinus* and *Psathyrella* contain neither serotonin (Stijve, 1987), nor high levels of manganese (Table II).

As a matter of fact, in all dark spored agarics analysed, the iron content predominated well over that of manganese. Indeed, these more or less distantly related fungi had concentrations of both metals comparable to those reported for other Agaricales (Schmitt et al., 1977; Vetter, 1989).

Among the Panaeoloideae analysed so far, *P. semiovatus, P. antillarum* and *P. phalaenarum* – which are considered as a separate tribe called *Anellaria* by some authors (Karsten, 1879; Hora, 1957) – have manganese contents well below those of iron. This can probably be explained by the low levels of manganese in horse dung, their particular substrate. Horse dung contains about 10 times less of both manganese and iron than the average soil. The ratio Fe : Mn fluctuates between 12 and 25. Hence it is not impossible that the low amounts in the three *Anellaria* species still represent a bioconcentration phenomenon.

Large fluctuations in the concentrations of both metals were observed in *P. cyanescens* and *P. subbalteatus*. Sometimes high manganese uptake was noted, whereas in other col-

Table I. Manganese and iron levels in Panaeoloideae Sing.

Species	N	Manganese	Iron	Ratio Fe : Mn (mean)
Panaeolina foenisecii (Pers.: Fr.) Maire	6	239–471 (388)	93–374 (235)	0.60
Panaeolopsis nirimbii Watling & Young	1	560	265	0.47
Panaeolus bernicii Young, sp. nov.	1	992	102	0.10
P. fimicola (Pers.: Fr.) Quél.	1	800	464	0.58
P. clelandii Gerhardt	1	75	152	2.03
P. ater (J. Lange) Kühn. & Romagn.	1	637	187	0.29
P. olivaceus Moell.	2	587–1290	176–198	0.20
P. acuminatus (Schaeff.: ex Secr.) Quél. s. str.	2	2071–2125	651–671	0.32
P. subbalteatus (Berk. & Br. Sacc.)	6	130–557 (273)	318–956 (595)	2.18
P. campanulatus (Bull.: Fr.) Quél.	3	867–1076 (950)	208–392 (296)	0.31
P. sphinctrinus (Fr.) Quél.	4	545–912 (747)	140–379 (229)	0.31
P. sphinctrinus, sterile carpophores	1	5500!	1970!	0.36
P. semiovatus (Sow.: Fr.) Pears & Dennis	6	30–59 (38)	109–287 (214)	5.6
P. phalaenarum (Bull.: Fr.) Mos.	2	24–41	104–229	5.1
P. antillarum (Fr.) Dennis	3	15–69 (35)	102–159 (132)	3.8
P. (Copelandia) cyanescens (Berk. & Br.) Sacc.	4	126–2320 (779)	271–883 (644)	0.83

All concentrations in mg/kg on dry matter. Mean values in brackets.

lections iron clearly predominated. Here again, the explanation can be sought in the different substrates: *P. cyanescens* mostly grows on cow dung, but its mycelium probably extends to the underlying manganese-rich soil. The *P. subbalteatus* material analysed represented collections from manured lawns, horse dung, rotten straw and a mixture of these substrates. Apparently, manganese was readily available to the single collection of lignicolous *P. bernicii*. According to Young (1989) this taxon is found on nearly decomposed wood.

The new, yet unpublished taxon *P. clelandii* (Gerhardt, pers. comm.) was formerly considered an Australian variety of *P. fimicola*, but there are microscopic differences (Gerhardt, 1991). Moreover, the manganese and iron levels for single collections are totally different, and *P. clelandii* was found to contain psilocybin, baeocystin and tryptamine, which were not detected in European collections of *P. fimicola* (Stijve, 1991).

Table II. Manganese and iron levels in some dark brown and black spored agarics (other than *Panaeolus*).

Genus	Number of species	Manganese (in mg/kg dry weight)	Iron (in mg/kg dry weight)	Ratio Fe : Mn (mean)
Agrocybe	4	27–45 (35)	349–430 (387)	11.1
Coprinus	5	6–37 (19)	92–310 (209)	11.0
Psathyrella	6	6–53 (28)	64–566 (221)	7.9
Psilocybe	6	28–74 (42)	280–680 (420)	10
Agaricus	10	20–46 (30)	120–338 (168)	5.6

Average values in brackets.

CONCLUSION

A better insight in the uptake of both manganese and iron can undoubtedly be obtained by pure culture studies. Meanwhile, the results reported in this paper strongly suggest that manganese uptake is a distinguishing feature of the Panaeoloideae, just as is their ability to biosynthesize serotonin (Stijve, 1987).

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