1. INTRODUCTION

Fungi have important biogeochemical roles in the biosphere and are intimately involved in the cycling of elements and transformations of both organic and inorganic substrates (Gadd 2007, Fig. 1). The research area of **geomycology** is focused on the interactions of fungi with geological environment.

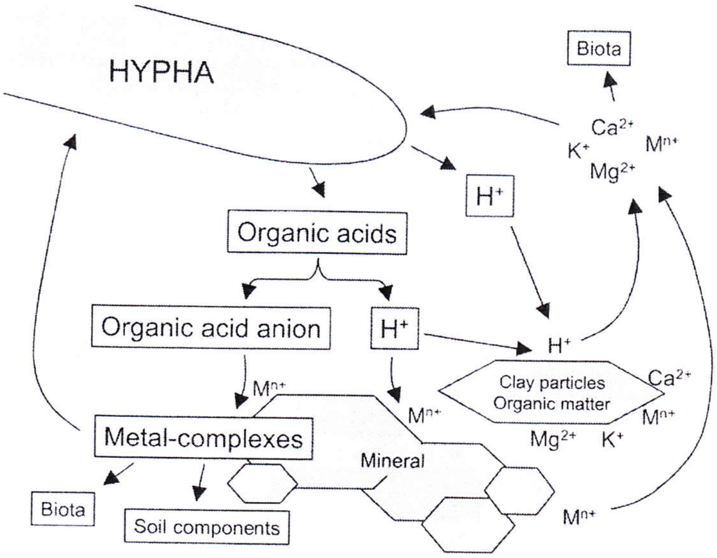

Figure 1. Proton- and organic acid ligand-mediated dissolution of metals of soils componets and minerals (Gadd 2004). Proton release results in cation exchange with sorbed metal ions on clay particles, colloids etc. and metal displacement from mineral surfaces. Released metals can interact with biomass and also be taken up by other biota, and react with other environmental components. Organic acids anions, e.g. citrate, may cause mineral dissolution or removal by complex formation. Metal complexes can interact with biota as well as environmental constituents. In some circumstances, complex formation may be followed by crystalization, e.g. metal oxalate formation.

Many macrofungal species (macromycetes, mushrooms) are capable of accumulating high concentrations of certain trace elements (including heavy metals, noble metals and metalloids) in fruit-bodies and thereby affect elemental geochemical cycling.

Many studies focused on trace elements content in macrofungal fruit-bodies have been published to date. Most of them deal with heavy metals (Hg, Pb, Cd), essential elements (Fe, Co, Se, Zn) or radionuclides (^{137}Cs) and consider environmental aspects (biomonitoring of artificial pollution) and/or health risks for mushroom consumers.

Detailed data on chemical form of arsenic (Byrne et al. 1991; Šlejkovec et al. 1996, 1997) in macrofungal fruit-bodies are available and preliminary results on some other elements have been published (e.g., Šlejkovec et al. 2000, Collin-Hansen et al. 2007).

Factors that influence the trace element content in fruit-bodies and the biological importance of the accumulation process itself are poorly known. However, many elements attain elevated concentrations in polluted areas (Svoboda et al. 2006, Komárek et al. 2007).

This study has focused on several aspects that have not been considered to date (ecological strategy of macrofungi, antimony pollution) and, moreover, some interesting results on noble metals – gold and silver – content in macrofungi are presented and discussed.

2. NOBLE METALS IN MACROFUNGI

2.1 Gold

Uptake of any element in fungal biomass is possible in soils where the element is biologically available (i.e., present in ionic form in soil solution, in colloidal form, or present in minerals that can be partially solubilized by microorganisms). In the case of gold, Reith et al. (2005) have first shown (using a sequential extraction procedure) a surprisingly high mobility of gold in Ah soil horizon in the auriferous area of the Tomakin Park Gold Mine, Australia. Its mobility may indicate that gold is easily bioavailable.

My data indicating high gold concentrations in fungal fruit-bodies from both auriferous and non-auriferous areas (Borovička et al. 2005, 2006a, in prep.) suggest that macrofungi play a significant role in gold cycling in the environment. The reported gold contents in macrofungi are the highest ever recorded among eukaryotic organisms under natural conditions. Recent studies have shown an important role of microbiota in gold mobilization in rocks and soils (for a review see Reith et al. 2007). According to Lakin et al. (1974), gold tends to be enriched in organic soil layers; gold accumulation in fungal mycelia might represent a retention factor of gold in organic soil horizons.

2.2 Hyperaccumulation of silver

The ability of macrofungi to accumulate silver has been known since the 19070's (Schmitt et al. 1978, Falandysz et al. 1994). A literature search (Borovička 2004) revealed that saprobic macrofungi usually have a higher Ag content (median 3.61 mg kg^{-1} Ag) than ectomycorrhizal fungi (median 0.65 mg kg^{-1}).

Two ectomycorrhizal macrofungal *Amanita* species of the section *Lepidella* – *Amanita strobiliformis* and *A. solitaria* were found to hyperaccumulate silver. The silver contents of both *Amanita* species that were collected in non-argentiferous areas with background silver content in soils (0.07 to 1.01 mg kg^{-1} Ag) were mostly in the range of 200-700 mg kg^{-1} with the highest content of 1253 mg kg^{-1} in one sample of *A. strobiliformis*. Silver concentrations in macrofungal fruit-bodies were commonly 800-2500 times higher than in underlying soils.

A. strobiliformis and *A. solitaria* are the first eukaryotic organisms known to hyperaccumulate silver.

3. DISTRIBUTION OF SEVERAL TRACE ELEMENTS IN ECTOMYCORRHIZAL AND SAPROBIC SPECIES FROM CLEAN AND POLLUTED AREAS

3.1 Antimony content in macrofungi from clean and polluted areas

Not a great deal is known about the biogeochemistry, environmental speciation and toxicity of antimony. Macrofungi are well-known accumulators of arsenic. In *Sarcosphaera coronaria*, hyperaccumulation of arsenic was found. However, despite the chemical similarity between arsenic and antimony, antimony contents in macrofungi are very low.

In general, antimony contents of ectomycorrhizal and saprobic macrofungi from clean areas are mostly below 100 µg kg^{-1} (Borovička et al. 2006b). No appreciable difference between saprobic and ectomycorrhizal fungi was found. Antimony contents of macrofungi from polluted areas are approx. 100x higher than those from the clean areas.

The highest ability to concentrate antimony was found in the ectomycorrhizal genera *Chalciporus* and *Suillus*. In samples from the clean areas, antimony content was in the range of 0.5-12 µg kg^{-1}. In samples from polluted areas, antimony concentrations commonly reached hundreds of mg kg^{-1}. An extremely high level was measured in a single collection of *Chalciporus piperatus* (1423 mg kg^{-1}).

3.2 Distribution of trace elements in ectomycorrhizal and saprobic macrofungi

The ecological strategy of macrofungi may also play an important role in accumulation of specific elements. Different ability of ectomycorrhizal and saprobic species to accumulate gold (Borovička et al., in prep.), selenium (Borovička et Řanda 2007) and silver (Borovička 2004) has been reported. No differences have been observed in case of antimony, cobalt, iron and zinc (Borovička et al. 2006b, Borovička et Řanda 2007). It is likely that saprobic species are releasing elements and taking them up during the decomposition of organic matter containing this element in bound or adsorbed form. In contrast, ectomycorrhizal fungi receive nutrition largely from host plants, and, therefore, their accumulation ability might be lower.

4. CONCLUSIONS

It is obvious, that macrofungi play a significant role in weathering processes and trace elements cycling in the environment. Available data indicate that macrofungi are an important factor influencing silver and gold mobilization and redistribution in topsoils; they might represent a retention factor of these elements in organic soil horizons. The differences in element uptake between ectomycorrhizal and saprobic species might result from their different ecological strategy. The ability of several macrofungal species to hyperaccumulate silver and arsenic has been clearly demonstrated, but the mechanism and biological importance of the process itself are unknown. However, some recent studies have revealed that hyperaccumulation in plants might be attributed to the „defense hypothesis“; in case of macrofungi, such importance is questionable. Investigation of the accumulation mechanisms and trace elements speciation in fruit-bodies might result in useful applications in biotechnologies (bioremediation, phytomining).