

**Transition Metals**  
**Cr, Co, Ni, Cu, Zn,**  
**Cd, Hg, and Pb**

**4**



Mycorrhizal fungi acquire essential macronutrients, such as phosphorus (Burgess et al. 1993), and are efficient at taking up and accumulating microelements (Smith and Read, 1997). However, this ability includes the accumulation of non-essential elements and trace metals, such as the heavy metal cadmium (Cd), which is an element of concern for food quality, essential zinc (Zn), and the trace element copper (Cu) (Falandysz et al. 2008). All Cu in the organic surface of coniferous forest soils layer may be accumulated in ectomycorrhizas (Berthelsen et al. 1995). The accumulation of these elements can have important consequences for their retention, mobility, and availability in forest ecosystems.

Most heavy metals are not chemically degraded (Kirpichtchikova et al. 2006) but they are accumulated in surface layers of soils (Basta et al. 2005). Thus, these elements tend to bioaccumulate, and sporocarps mainly of ectomycorrhizal macrofungi can contain extremely high levels of heavy metals. Cadmium is intensively accumulated by fungi (Collin-Hansen, 2002, Rudawska & Leski, 2005), and relatively high Cu and Zn concentrations (bioaccumulation values higher than 1) in certain species of wild growing fungi are reported (Blanuša et al. 2001; Elekes et al. 2010).

Soil fungi, especially fungal sporocarps, are involved in the recycling of heavy metals in forest ecosystems through bioaccumulation (Lepp et al. 1987), and fungal sporocarps have been suggested as a useful object for monitoring environmental pollution (Byrne et al. 1976). Furthermore, the capacity for retaining metal among species of fungi is wide (Pérez et al. 2007) and the capability of fungi to accumulate elements differs (Campos et al. 2009). Essential nutrients, such as cobalt (Co) and nickel (Ni), and non-essential lead (Pb) appear to be excluded from fungi, as they do not accumulate (Berthelsen et al. 1995;

Holan and Volesky, 1995). Similarly, mushroom fruit bodies do not accumulate chromium (Cr) (Berthelsen et al. 1995) or mercury (Hg) (Falandysz et al. 2012).

Although fungal sporocarps only comprise a few percentage of the total fungal biomass, i.e. biomass of mycelia in soil constitutes a major part of the total biomass of fungi (Horton and Bruns 2001), the majority of fungal biomass in soil is located in the upper soil horizons below the soil surface (Bååth, 1980). If Cd levels in sporocarps of ectomycorrhizal fungi are similar to those in soil mycelium (Berthelsen et al. 1995), a noticeable amount of soil metal located within soil fungi will be expected.

Mycelium, particularly sporocarps, accumulates Cd and fungal sporocarps may contain much higher Cd content than most plants (Byrne et al. 1976), up to ten times higher cadmium concentrations than in the soil in which they grow (Lepp et al. 1987). Consequently, the consumption of sporocarps of edible fungi with high Cd contents represents an important pathway by which Cd enters the human food system (Zurera-Cosano et al. 1988).

Thus, fungal mycelium appears important in the uptake of cadmium, copper, and zinc from soil, and their accumulation by soil fungi may be related to their ability to solubilize minerals of those metals, converting them into oxalates that are precipitated by the fungus in the local environment and in association with the mycelium (Fomina et al. 2005). When cadmium, copper, and zinc are taken up from the soil, other interactions may occur. Cadmium and zinc are in the same size and have similar chemical properties and zinc ions may act as antagonists of cadmium and copper. Even though ectomycorrhizal fungi profoundly affect forest ecosystems through mediating nutrient uptake and maintaining forest food webs, there are few studies on the ability of fungal mycelium to accumulate cadmium, copper, and zinc in mycelia (Thomet et al. 1999). The accumulation of metals in

mycorrhizal biomass in field conditions is studied to a much lesser extent and the rhizosphere appears to be important for understanding the transfer of metals from soil to fungi (Berthelsen et al. 2000). However, the fungi/soil concentration ratio for metals is not well studied under field conditions; neither is the difference between the uptake of metals from soil to fungi (mycelium/soil ratio) and transport within fungal thalli (sporocarps/mycelium ratio).

The concentration of chromium in soil-root interface fraction and fruiting bodies of fungi is 4-7 times lower than in the bulk soil (Table 4.1; Vinichuk, 2012a).

**Table 4.1** Mean concentrations of transition metals ( $\text{mg kg}^{-1}$  DW) in soil fractions and fungi, mean values  $\pm$  standard deviation<sup>1</sup>. (Vinichuk, 2012a, 2012b, 2013).

Element	Bulk soil	Rhizo sphere	Soil-root-interface	Fungal mycelium	Fruit bodies
Cr	2.79 $\pm$ 0.65 <sup>a</sup>	4.31 $\pm$ 1.4 <sup>a</sup>	1.05 $\pm$ 0.33 <sup>b</sup>	2.65 $\pm$ 0.94 <sup>a</sup>	0.19 $\pm$ 0.09
Co	0.79 $\pm$ 0.44 <sup>a</sup>	1.06 $\pm$ 0.6 <sup>a</sup>	0.59 $\pm$ 0.29 <sup>a</sup>	0.98 $\pm$ 0.65 <sup>a</sup>	0.11 $\pm$ 0.13
Ni	3.45 $\pm$ 2.1 <sup>a</sup>	4.62 $\pm$ 2.1 <sup>a</sup>	2.01 $\pm$ 1.0 <sup>a</sup>	3.13 $\pm$ 1.9 <sup>a</sup>	0.55 $\pm$ 0.34
Cu	10.4 $\pm$ 7.8 <sup>a</sup>	13.1 $\pm$ 5.5 <sup>a</sup>	11.9 $\pm$ 4.5 <sup>a</sup>	15.8 $\pm$ 5.7 <sup>a</sup>	28.8 $\pm$ 17.3
Zn	38.5 $\pm$ 24.7 <sup>a</sup>	31.9 $\pm$ 9.6 <sup>a</sup>	44.2 $\pm$ 5.4 <sup>a</sup>	69.7 $\pm$ 22.1 <sup>b</sup>	120.2 $\pm$ 5.7
Cd	0.29 $\pm$ 0.13 <sup>a</sup>	0.35 $\pm$ 0.11 <sup>a</sup>	0.81 $\pm$ 0.39 <sup>b</sup>	1.5 $\pm$ 1.6 <sup>b</sup>	3.1 $\pm$ 3.1
Hg	0.18 $\pm$ 0.1 <sup>a</sup>	0.16 $\pm$ 0.04 <sup>b</sup>	0.10 $\pm$ 0.03 <sup>b</sup>	0.24 $\pm$ 0.11 <sup>b</sup>	0.70 $\pm$ 0.96
Pb	18.4 $\pm$ 8.6 <sup>a</sup>	16.5 $\pm$ 6.2 <sup>a</sup>	7.7 $\pm$ 2.4 <sup>b</sup>	12.6 $\pm$ 4.7 <sup>a</sup>	0.25 $\pm$ 0.17

<sup>1</sup>Means within rows with different letters (a or b) are significantly different ( $p < 0.01$ ).

The concentration of Cr in fungal mycelium is not differing from the concentration in bulk soil and also Cr does not accumulate in either mycelium or in fruit bodies: bioconcentration ratios of this element do not exceed 1 (Table 4.2).

The concentration of Co and Ni in sporocarps is lower than the concentration in bulk soil and mycelium. Among other species, *Cortinarius armeniacus* and *Cortinarius* sp. have the highest content of all metals studied (Table 4.3).

Species of the genus *Cortinarius* absorb Cr more intensely (two orders of magnitude) than other studied species (Vinichuk, 2012a).

**Table 4.2** Element bioconcentration ratios (BCR:  $\text{mg kg}^{-1}$  DW in specific fraction) / ( $\text{mg kg}^{-1}$  DW in bulk soil), mean values  $\pm$  standard deviation).  
Adapted from Vinichuk, 2012a, 2012b, 2013).

Element	Rhizo-sphere	Soil-root-interface	Fungal mycelium	Fruit bodies
Cr	1.09 $\pm$ 0.22	0.27 $\pm$ 0.24	0.78 $\pm$ 0.12	0.13 $\pm$ 0.09
Co	1.07 $\pm$ 0.45	0.62 $\pm$ 0.29	1.34 $\pm$ 0.76	0.22 $\pm$ 0.34
Ni	1.18 $\pm$ 0.40	0.49 $\pm$ 0.14	0.98 $\pm$ 0.38	0.21 $\pm$ 0.14
Cu	1.3 $\pm$ 0.5	1.2 $\pm$ 0.6	1.9 $\pm$ 0.8	3.4 $\pm$ 2.2
Zn	1.5 $\pm$ 0.6	2.2 $\pm$ 0.9	2.4 $\pm$ 1.4	3.3 $\pm$ 2.1
Cd	1.6 $\pm$ 0.7	4.0 $\pm$ 2.8	5.7 $\pm$ 4.6	8.8 $\pm$ 9.2
Hg	1.4 $\pm$ 0.7	0.87 $\pm$ 0.46	1.74 $\pm$ 1.0	2.7 $\pm$ 1.1
Pb	1.18 $\pm$ 0.50	0.56 $\pm$ 0.26	0.87 $\pm$ 0.60	0.013 $\pm$ 0.008

**Table 4.3** Element bioconcentration ratios (BCR:  $\text{mg kg}^{-1}$  DW in fungi) / ( $\text{mg kg}^{-1}$  DW in bulk soil) for fungal sporocarps.

Sampling plots according to Vinichuk et al. (2010b)	Species	Cr	Co	Ni	Cu	Zn	Cd	Hg	Pb
4	<i>Boletus edulis</i>	0.01	0.013	0.28	1.22	1.55	3.37	1.93	0.004
6	<i>Cantharellus tubaeformis</i>	0.04	0.048	0.12	4.39	2.23	1.09	0.89	0.011
10	<i>Collybia peronata</i> <sup>a</sup>	0.13	0.316	0.22	7.24	0.46	18.78	11.69	0.015
7	<i>Cortinarius armeniacus</i>	0.03	0.795	0.48	3.98	3.60	33.23	5.89	0.013
5	<i>C. odorifer</i>	0.02	0.034	0.05	0.42	3.85	7.19	0.97	0.016
8	<i>C. spp.</i>	0.99	1.084	0.45	6.74	5.14	17.23	2.34	0.030
8-10	<i>Hypholoma capnoides</i> <sup>a</sup>	0.50	0.045	0.18	3.02	0.52	2.27	1.09	0.005
1	<i>Lactarius deterrimus</i>	0.01	0.004	0.07	0.65	3.60	3.89	1.42	0.009
3	<i>L. scrobiculatus</i>	0.01	0.198	0.16	3.28	2.48	6.92	1.05	0.016
6	<i>L. trivialis</i>	0.02	0.113	0.31	3.33	2.93	4.41	1.23	0.024
5-7	<i>Sarcodon imbricatus</i>	0.02	0.237	0.21	2.09	8.37	9.87	9.17	0.019
2	<i>Suillus granulatus</i>	0.01	0.005	0.01	1.93	2.82	0.91	0.84	0.008
8-10	<i>Tricholoma equestre</i>	0.25	0.024	0.22	5.54	5.06	5.80	0.38	0.004

<sup>a</sup>Saprophyte.

Fungi vary in their ability to take up chromium: particularly high concentrations of this element are found in fungal species with wood as a substrate, such as *Rhizina undulata* Fr. (Jonnalagadd et al. 2006). In addition, hexavalent chromium, Cr (VI) is taken up by fungi in quantities that are one order of magnitude higher than the total uptake of chromium (Figueiredo et al. 2007).

Metabolic processes in fungi occur most intensively in their fruiting bodies, but data indicate concentrations of both nickel and chromium in mycelium of fungi is 6-14 times higher than the concentration in fruit bodies (Vinichuk, 2012a). Differences between the concentrations of elements in the fruit bodies and mycelium of fungi suggest both elements are absorbed by the fungal mycelium, whereas, only a small part is transferred to fruiting bodies.

The concentration of Cr in fruiting bodies of fungi does not depend on metal content in the soil. According to bioconcentration ratios, values of chromium and nickel in species of fungi and forest soil fractions can be placed in the decreasing order: rhizosphere>bulk soil > mycelia> soil-root interface > fruiting bodies (Vinichuk, 2012a).

In bulk soil, the concentrations of Cu and Cd are not different from the concentrations in the rhizosphere, although the values for both elements are slightly higher in the rhizosphere fraction (Table 4.1). In the rhizosphere fraction, Zn and Pb concentrations are lower than in bulk soil. The soil-root interface fraction has a higher Cd concentration than bulk soil, but the concentrations of Cu and Zn in the soil-root interface fraction are similar to the concentrations in the bulk soil and rhizosphere fractions. Zinc and cadmium concentrations are higher in fungal mycelium fractions than in the bulk soil and rhizosphere fractions.

Although, the fungal mycelium fraction is more concentrated with Cu, this is not statistically significant. In the soil-root interface fraction, the increase in Cd was 4 times larger than in bulk soil, and in mycelium, the increase in Cd was 5.7 times larger than in bulk soil. Zinc concentration increased by a factor of 2.2 in the soil-root interface fraction and 2.4 in mycelium, compared with bulk soil. Copper concentrations vary widely among analyzed fractions. However, no significant difference in Cu concentrations among different soil fractions is found (Table 4.1).

BCR defined as the concentration of the element ( $\text{mg kg}^{-1}$  DW) in the specific fraction divided by the concentration of the element ( $\text{mg kg}^{-1}$  DW) in bulk soil for the 0-10 cm soil layer had a similar pattern, but the enrichment of Cu, Zn, and Cd in fungal material was more evident, particularly in the sporocarps (Table 4.2). The bioconcentration ratios for mentioned elements vary among the species: the sporocarp: bulk soil bioconcentration ratios are presented in Table 4.3. Most species of fungi, except *Lactarius deterrimus* and *Cortinarius odorifer*, accumulate Cu, and most fungal species, except saprotrophic fungi *Hypholoma capnoides* and *Collybia peronata*, accumulate Zn. All fungal sporocarps, except *Suillus granulatus*, accumulate Cd. The bioconcentration ratio values for Cd are high, for example, the BCR for *Cortinarius armeniacus* is above 30. Alonso et al. (2003) also find differences in the concentrations of metals (Cd, Cu, and Zn) and their bioconcentration potential.

Fungal sporocarps accumulate larger amounts of Cu, Zn, and Cd than mycelium. For example, in fungal sporocarps collected from the same plots where soil samples and mycelium are extracted, Cu concentrations are about 1.8 times higher than Cu concentrations in mycelium. The concentration of Zn in fungal sporocarps is about 1.4-fold higher than in the corresponding fungal mycelium, and the concentration of Cd is about 1.5-fold higher (Tables 4.2 and 4.3).



For most living cells, Cu is both an essential micronutrient and a toxic heavy metal. Mycorrhizal fungi extensively accumulate copper (Blanuša et al. 2002; Falandysz et al. 2011). Results obtained from the top layers of coniferous forest soils in central Sweden (Vinichuk, 2012b) indicate that copper concentration increases in the order: bulk soil < soil-root interface < rhizosphere < fungal mycelium < fungal sporocarps. However, the statistically higher concentration of copper, compared to that in bulk soil, is only found in fungal sporocarps (Vinichuk, 2012b), as is reported in other studies (Collin-Hansen et al. 2002; Elekes et al. 2010), where the concentration of Cu is higher in fungal sporocarps than in topsoil. Copper accumulation ( $\text{BCR} > 1$ ) is found in the majority of fungal sporocarps species analyzed, and both Blanuša et al. (2002) and Elekes et al. (2010) report copper accumulation in all sporocarps, irrespective of species. Although copper concentration in mycelium is about 1.5-2-fold higher than in soil, this does not differ significantly from bulk soil.

Although mycorrhizal fungi sporocarps are more capable of accumulating copper than mycelium, the data for Cu accumulation by mycelium *in situ* are limited (Brzostowski et al. 2011). The values for mean Cu concentration in mycelium are lower than reported values for ectomycorrhiza ( $337 \pm 140 \mu\text{g g}^{-1}$  mycorrhiza) from the top organic layer of Norwegian coniferous forest soils contaminated with Cu (Berthelsen et al. 1995).

Zinc concentrates in mushroom thalli and increases in the order: bulk soil < soil-root interface < fungal mycelium < fungal sporocarps. The concentration of Zn in rhizosphere appears lower than in bulk soil, when the concentration of Zn is slightly (not significantly) higher in the soil-root interface fraction than in bulk soil. The concentration of zinc is about 2-fold higher in fungal mycelium and about 3-fold higher in sporocarps than in bulk soil (Vinichuk, 2012b). Alonso et al. (2003) and Elekes et al. (2010) also find a similar concentration of

Zn in fungal sporocarps. Data on zinc concentration in mycelium extracted from the soil in which sporocarps grow are limited. However, Berthelsen et al. (1995) report mean Zn concentrations of  $456 \pm 201 \mu\text{g g}^{-1}$  in mycorrhiza, which is higher than the values obtained by Vinichuk (2012b, 2013). The difference may be due to the area studied, as the study by Berthelsen et al. (1995) was located in a part of Norway exposed to considerable amounts of airborne deposition of heavy metals, such as Cd and Zn and concentrations of naturally occurring Zn in the biota and/or litter in the area studied by Vinichuk (2012b, 2013) are in a range of  $50\text{--}200 \text{ mg kg}^{-1} \text{ DW}$  (Brun et al. 2010).

Cadmium concentrations increase in the order: bulk soil < rhizosphere < soil-root interface < fungal mycelium < fungal sporocarps. Fungi appeared to have high preference for cadmium, as the accumulation of Cd by fungi, both mycelium and especially fungal sporocarps, is pronounced. Cadmium concentration in mycelium is about 5 times higher than in bulk soil, and cadmium concentration in sporocarps is about 2 times higher than in mycelium extracted from soil of the same plots where fungal sporocarps are sampled.

The accumulation of cadmium by fungal sporocarps appears species-dependent. Fungi have a tendency to accumulate Cd: the mean BCR is about 6:1 for mycelium and 9:1 for sporocarps (Vinichuk, 2012b, 2013). The ability of fungi to accumulate Cd is documented, and extremely high levels of cadmium in fruiting bodies of some fungi, especially the toxic *Amanita* sp., are reported by Kalač et al. (1991) and Rudawska & Leski (2005). This might explain the species-wide variation in both mycelium and sporocarps, as the standard deviation values for cadmium are as high as the mean values. However, not only fungal thallus is enriched with Cd, as the rhizosphere and soil-root interface fractions are noticeably enriched with Cd, although this is only significantly different for the soil-root interface fraction.

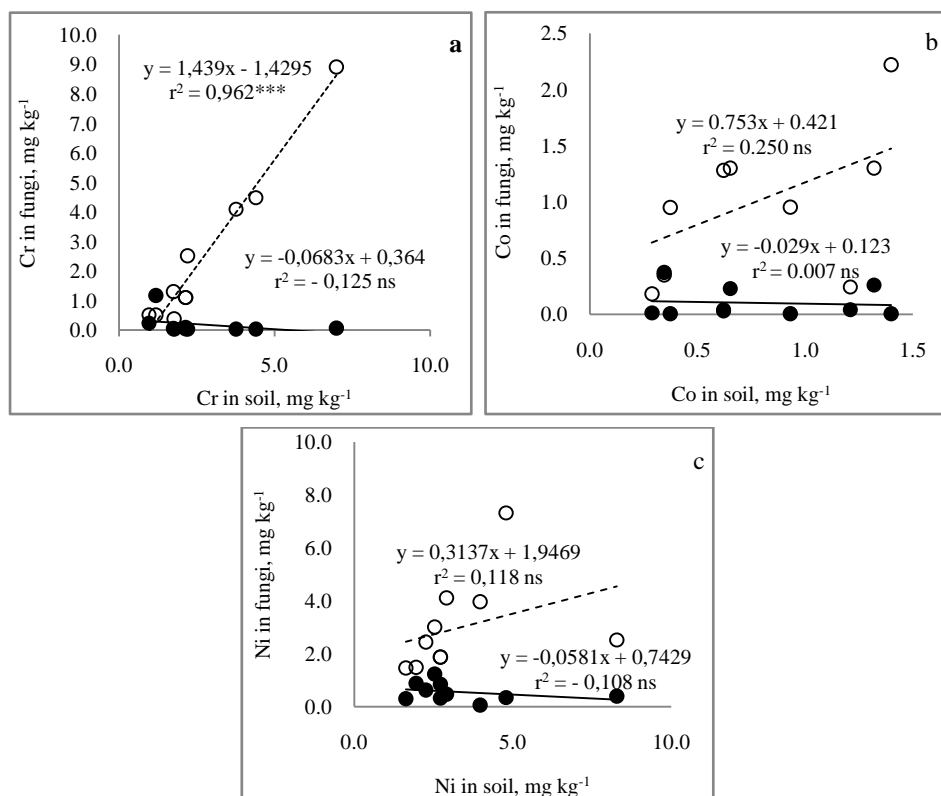
The concentrations of all three metals (Cu, Zn, and Cd) in sporocarps are about two times higher than in fungal mycelium; although Thomet et al. (1999) report similar concentrations of Cd and Zn in isolated mycelia and stems of corresponding fruiting bodies.

Fungi (mycelium and sporocarps) preferentially accumulate Cd over Zn and Cu. Thus, based on the BCR values obtained for fungal sporocarps and mycelium, (Table 4.2), the bioaccumulation of the metals can be ranked in the order:  $\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$ , with a relative ratio of 100:41:38. In terms of the amounts of metals accumulated by mycelium and sporocarps per mass unit, the metals can be ranked in the order  $\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$ , with a relative ratio of 41:13:1.

Fungi tend to accumulate mercury: the Hg content is slightly higher in rhizosphere and lower in soil-root-interface fraction than in soil, and Hg concentration is about 1.5-2.0 times higher in fungal mycelium and about 2.5-3.0 times higher in fruit bodies than in bulk soil (Tables 4.1; 4.2; and, 4.3).

## **Relationships between Transition Metals Cr, Co, Ni, Cu, Zn, Cd, Hg, and Pb in Soil and Fungi**

The total element content in the soil or soil biota provides little insight in elucidating into element availability and uptake mechanism. As the interactions between plants, nutrients (metals), and fungi are complex, the relationships between Cr, Co, Ni, Cu, Zn, Cd, Hg, and Pb concentrations in fungi (both fungal fruit bodies and mycelium) and soil can be useful. The concentrations of some metals found in fungi are related to its concentration in soil when uptake of other metals in fungi is independent on soil concentration.

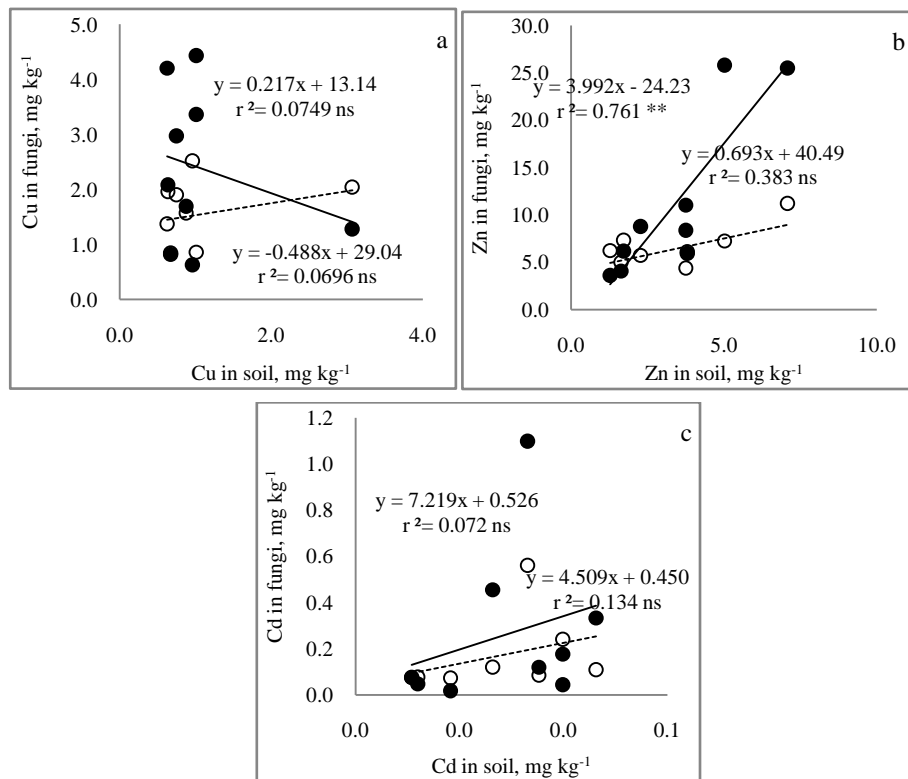


**Figure 4.1** Relationships between concentration of Cr (a), Co (b) and Ni (c) in fungal sporocarps (filled circle, solid line) and soil mycelium (empty circle, dotted line) in relation to the soil in which they are growing. \*\*\*  $p < 0.001$ . Adapted from Vinichuk, (2012a, 2012b).

Thus, the concentration of Cr and Ni in fruit bodies of fungi appear independent of the concentration of the elements in the soil (Figure 4.1). There is a close relation ( $r^2 = 0.962$ ) between the concentration of Cr in fungal mycelium and the concentration in soil, but Co and Ni concentration in the fungal mycelium only weakly relate to its soil concentration. A lack of relationship between Cr content in mushrooms (fruiting bodies) and the content in soil (total and mobile forms) is reported by Sybyrkyna (2012). There are no significant correlations

between the concentrations of Cr, Co and Ni in fungi and soil pH or between the concentrations and soil organic matter content (data are not presented).

The relationships between the concentration of Cu, Zn, and Cd in fungal sporocarps and soil mycelium in relation to the concentration in the soil they were growing are displayed in Figure 4.2.

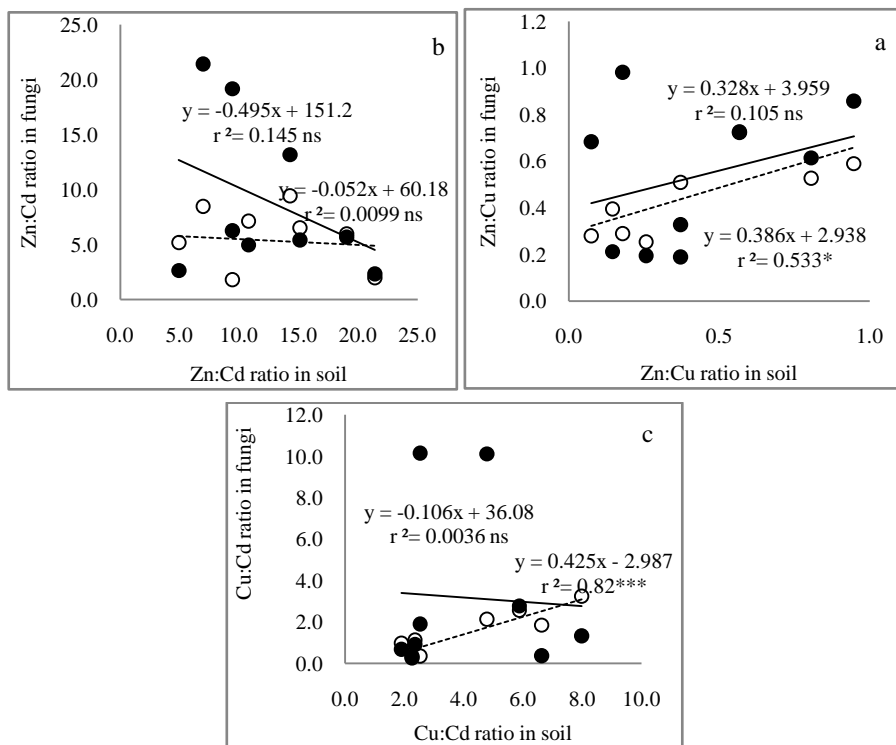


**Figure 4.2** Relationships between the concentration of Cu (a), Zn (b) and Cd (c) in fungal sporocarps (filled circle, solid line) and soil mycelium (empty circle, dotted line) in relation to the concentration in the soil they were growing. \*\*  $p < 0.01$ .

Adapted from Vinichuk, (2012a, 2012b, 2013).

Sporocarps and mycelium Cu concentrations do not depend on soil concentrations; however, Zn concentrations in soil correlate to Zn concentrations

in both sporocarps and mycelium. There were no significant correlations between Cd in soil and in either mycelium or in sporocarps (Vinichuk, 2013).



**Figure 4.3** Ratios of Zn:Cu (a), Zn:Cd (b), and Cu:Cd (c) in fungal sporocarps (filled circle, solid line) and soil mycelium (empty circle, dotted line) in relation to the ratios in the soil they were growing. \*  $p < 0.05$ ; \*\*\*  $p < 0.001$ , (Vinichuk, 2013).

Thus, the only metal concentration in soil that correlates with the concentration in sporocarps, and to a certain extent in mycelium, is essential Zn. There are no correlations between Cu in soil and in mycelium or sporocarps, or between Cd in soil and in mycelium or sporocarps. The concentrations of Cd and chemically related Zn strongly correlate in both mycelium and sporocarps (data not presented), whereas, Cu only poorly correlates with Cd in sporocarps and not correlate in mycelium (Vinichuk, 2013). Schmitt & Meisch (1985) and

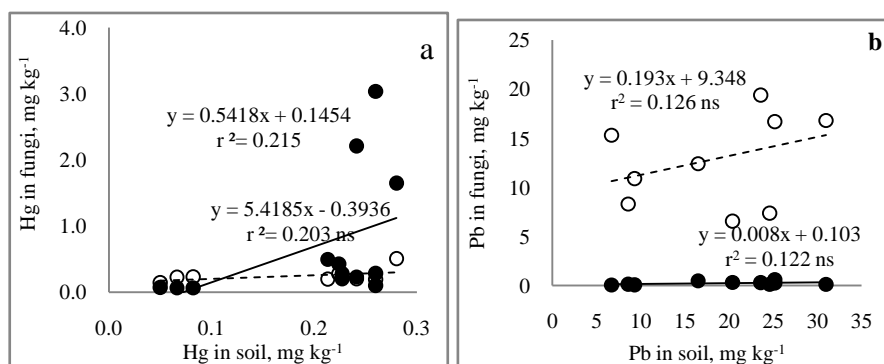
Thomet et al. (1999) also find cadmium uptake by fungi does not correlate with the uptake of zinc and copper.

The possible competition between Cu, Zn, and Cd in various transfer steps and the relationships between the concentrations of these three metals in soil, mycelia, and fungal sporocarps are estimated (Vinichuk, 2013). When comparing ratios between Cu, Zn, and Cd in soil and fungi (Figure 4.3), there is a moderate and strong positive correlation between the Zn:Cu and Cu:Cd ratios in soil and fungal mycelium (Figure 4.3a, b, c).

The relationships between Zn:Cu, Zn:Cd, and Cu:Cd ratios in fungal sporocarps and soil mycelia, with respect to the soil in which they were growing (Figure 4.3), indicate differences in the uptake of these metals by fungi. The close positive correlations between Zn:Cu ratios in fungal mycelium and in soil suggest the uptake of both metals by fungi is balanced and there are similarities in the uptake mechanism. However, metal accumulation capability of fungi is species specific and mainly depends on its accumulation mechanism (Demirbaş 2002). The opposite phenomenon is observed for Zn:Cd ratios in soil and fungi: the relationships between Zn:Cd ratios in soil mycelium, sporocarps and in soil are absent or even negative. The relationships between Cu:Cd in soil and fungi are unclear: there is a high positive correlation for mycelium, but no correlation for sporocarps. The lack of correlation in the Zn:Cd and Cu:Cd ratios in sporocarps is probably due to the variable concentration of Cd in sporocarps, indicating species dependent competition between Cu or Zn and Cd. The extent of Cd and Zn transfer from soil to mushrooms is species-specific and influenced by the availability of the two heavy metals and the age of the mushroom (Thomet et al. 1999). The variation in heavy metal content among edible mushrooms species also depends on the ability of the species to extract elements from the substrate (Radulescu et al. 2011), and there are significant

linear correlations between lead and cadmium concentrations in certain species i.e. *Boletus edulis* and *Paxillus involutus* (Kalač et al. 1991). In addition, there is a competitive interaction between Cd and Zn in the growth of fungi and on the nutrient uptake capacity of root systems (Krznaric et al. 2008).

There is a very weak correlation in Pb concentration in both sporocarps and mycelium whereas mercury content in soil appears to be correlated with the concentration of Hg in mycelium and in fruit bodies of fungi (Figure 4.4.a).



**Figure 4.4** Relationships between concentration of Hg (a) and Pb (b) in fungal sporocarps (filled circle, solid line) and soil mycelium (empty circle, dotted line) in relation to the concentration in the soil in which they were growing.

The mercury content in fungal sporocarps varies, whereas, the opposite is observed for mycelium (Vinichuk, 2013).

Correlation coefficients among the concentration of transitions metals in fruit bodies of fungi are presented in Table 4.4. Uptake of Cd and Cu by fungi correlates well with Hg and uptake of Ni is related to concentration of Co, Cd, and Pb.



**Table 4.4** Correlation coefficients among the concentration of elements in fruitbodies of fungi (Vinichuk, 2013).

	Cr	Co	Ni	Cu	Zn	Cd	Hg
Co	0.51*						
Ni	0.14	0.64*					
Cu	0.21	0.40	0.37				
Zn	0.35	0.33	0.41	0.42			
Cd	0.09	0.51*	0.66*	0.41	0.41		
Hg	-0.11	0.31	0.43	0.67*	0.10	0.75**	
Pb	0.26	0.46	0.62*	0.58*	0.22	0.44	0.39

\*  $P < 0.05$ , \*\*  $P < 0.01$

The capability of fungal species to accumulate essential (Co, Ni) and non-essential (Pb) metals differs (Pérez et al. 2007; Campos et al. 2009; Vetter, 2005). The concentrations of Co, Ni, and Pb are generally evenly distributed between soil fractions and mycelium, whereas, the concentration of these metals in sporocarps is lower. Thus, elimination of the metals from sporocarps appears effective. Lead elimination from the sporocarps is more pronounced, as the concentration in sporocarps is about 70 times lower than in bulk soil and about 50 times lower than in mycelium. Similarly, Campos et al. (2009) observe only absorption of Pb, but not accumulation, in the ectomycorrhizal fungus *Cantharellus cibarius*. The differences in metal concentrations between the mycelium and the sporocarps (assuming they belong to the same species) indicate there is no further transport of Co, Ni, and Pb within sporocarps after being taken up by mycelium from soil, i.e. these metals are not actively transported from mycelium to sporocarps. In organic soils, Pb is more strongly bound to soil, whereas, e.g. Cd is only weakly bound (Villaverde et al. 2009).

The estimated values for soil mycelium biomass range from 30 to 60 mg DW of mycelium per one gram DW of soil (0-5 cm layer). Assuming the dry bulk density in the upper layers of the soil in the Forsmark area (Forsmark lies in

east-central Sweden, N 60°22'; E 18°13') is  $0.4 \text{ g cm}^{-3}$  (Lundin et al. 2004), fungal mycelium is an important constituent of the organic surface soil, comprising between 3 and 6% by volume in the upper 5-cm of the forest soil. Based on the metal concentrations in bulk soil, rhizosphere, soil-root interface fractions, and mycelium extracted from the same soil, fungal mycelium appear to accumulate relatively small fractions of soil metals. Assuming the concentration of chromium ( $2.65 \text{ mg kg}^{-1}$  dry weight) and nickel ( $3.13 \text{ mg kg}^{-1}$  dry weight) in the mycelium, mycelium of upper forest soil layer may comprise 2.9-5.8% of chromium and 2.7-5.4% of nickel from their total content in soil. Fungal mycelium can also comprise between 4.6-9.1% of the total Cu in soil, 5.4-10.9% of the total Zn in the soil, and 15.5-31.7% of the total Cd in the soil. In fungal mycelium, the accumulation is estimated to be 3.5-6.9% for cobalt, 2.0-3.9% for Pb and 4.0-8.0% for Hg. Estimates of fungal biomass in soil may be relevant: Berthelsen et al. (1995) report similar data for fungal biomass in forest soil from Norway. Although the fungal content of Cu, Zn, and Cd was higher in Norwegian forest soil, possibly due to the difference in concentration level of metals in soil, as the study area in Norway had been exposed to airborne deposition of heavy metals, thus, explaining the higher accumulation by mycelium of fungi. The fungal content of Pb (2-4%) was similar to the < 3% reported by Berthelsen et al. (1995). In the mycelium of fungi in the upper (0-5 cm) layer of forest soil can be allocated 2.9-5.8% of the total amount of chromium in soil.