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Various content of manganese in selected forest tree species and plants in the undergrowth

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Abstract: Kula, E., Hrdlička, P., Hedbávný, J., Švec, P. 2012: Differentiated content of manganese in selected forest trees and plants in the undergrowth. – *Beskydy,* 5 (1): 19–26

The content of manganese in foliage and other parts of trees and undergrowth plants were monitored in the site with heavy level of manganese in soil. The difference between the species and also between parts of the same plant was confirmed. Manganese was accumulated from the soil environment, especially by the species *Betula pendula, Fagus sylvatica, Sorbus aucuparia, Larix decidua, Vaccinium myrtilus, Rubus ideus, Rubus fruticosus and Digitalis purpurea*, where the content of manganese in leaves exceeded 5000 mg kg^{-1}.

Keywords: manganese, *Betula, Larix, Fagus, Quercus, Acer, Digitalis, Poa, Avenella, Calamagrostis,* Ore Moutains

Introduction

Manganese is a micro-element necessary for normal growth and development of the plants. It changes its oxidation number in the range from 0 to +VII and is found in plants in the Mn^{2+}, Mn^{3+} and Mn^{4+} form. Dominant form accessible to the plants are Mn^{2+} compounds. Manganese takes part mostly in redox reactions and as an activator of enzymes (Santadrea et al. 2000). In this area, photosynthesis enzymes are very important, as well as one antioxidant enzyme, superoxide dismutase (Grønflaten et al. 2005, Marschner 2006, Racek and Holeček 1999). The size of manganese ion is between magnesium and calcium ions. Thus, manganese can substitute these ions, but on the other hand, a competition for bonding places with these elements can also occur (Marschner 2006).

The plants can suffer both the lack and the surplus of Mn. Plants growing in soils with low content of Mn in the parent rock or in soils having pH > 5.5 suffer the lack of Mn, especially if the carbonate content is higher (Marschner 2006, Mengel and Kirkby 2001). Chloroplasts are very sensitive to the lack of Mn, the biosynthesis of chlorophyll is greatly influenced. Unlike the lack of Mg, symptoms generally appear first in young leaves (Bergmann, 1988, Mengel and Kirkby 2001). The general critical value for the lack of Mn in leaves is in the range 10–20 mg kg^{-1} (Fernando et al. 2009, Marschner 2006) or 15–30 mg kg^{-1} (Bergmann 1988). The surplus of Mn is found more often than the lack. The excessive intake and thus an increased content of manganese in plants occurs in soils with pH < 5.5 (Bergmann 1988). Unlike the lack of Mn, the critical value of the surplus at which the symptoms of toxicity are manifested varies in a wide range of values. The real content of Mn depends on plant species and the conditions of growth (Marschner 2006). Toxic surplus of manganese is manifested as brown spots at fully developed leaves (in fact, these spots are MnO_2 precipitated in intercellular spaces), leaf chlorosis and necrosis in older leaves or the deformation of newly developing leaves and total growth limitation (Bergmann 1988, Horiguchi 1988, Kitao et al. 1997, Marschner 2006, Nable et al. 1988, Wissemeier and Horst 1987, Wissemeier and Horst 1992, Wu 1994). In the plants sensitive to the Mn content, the decrease of chlorophyll content up to 50 % and corresponding growth limitation (Macfie and Taylor 1992) can be observed. The toxic effect of manganese can also cause a Ca-deficiency, leading to degradation and thus the lack of auxin (Horst 1988). Manganese-induced deficiency can be found also for other elements, i.e. Ca, Mg or Fe (Kitao et al. 1997,Löhnis 1960).

The amount of manganese in soils is different according to various sources. The ranges of values 500–900 mg kg^{-1}, 50–500 mg kg^{-1} (Bergmann 1988), 300–1000 mg kg^{-1} (Marschner 2006) or 200–3000 mg kg^{-1} (Mengel and Kirkby 2001) are given in literature. According to Liu et al. (2010) it is necessary to await the increase of Mn in soils due to the anthropogenic activities. The manganese form accessible to plants is Mn^{2+} or Mn in the form of complexes. The amount of accessible Mn is influenced by redox conditions and the presence of micro-organisms in the soil. Biologic oxidation to Mn^{IV} compounds is quite common; these are insoluble in soil and unacceptable for the plants (Sigel and Sigel 1999). The amount of uptaken Mn depends on the soil conditions and on the plant species (Adriano 2001). Generally, higher content of Mn^{2+} ions can be expected in more acid soils (Mengel and Kirkby 2001), but here can occur even the intoxication, especially in the case of sensitive plants.

In soils with average content of manganese (i.e. up to 10000 mg kg^{-1}) is the amount of manganese in plant dry matter mostly in the range of 50–800 mg kg^{-1} (Fernando et al. 2009). However, values over 1000 mg kg^{-1} were also observed (Marschner 2006). Specific content depends on plant species and its organs. For example in assimilation organs of conifers the content of manganese can be up to 8000 mg kg^{-1} (Bergmann 1988). Generally the content of manganese in assimilation organs increases with the age which is in good accordance with low mobility of manganese. The sensitivity of plants to the surplus of manganese in tissues also varies (Marschner 2006). Some species are able to tolerate quite high amounts of Mn; according to the literature the limits of tolerance can be up to 12000 mg kg^{-1} (Reeves 2006). At the manganese content > 1000 mg kg^{-1} the risk of phytotoxicity cannot be excluded. Specific manifestations further depend on the pH of soil and on the sustenance with other elements. The difference within the species must be also taken in account, for example *Betula pendula* Roth contained lesser amount of manganese in leaves than *Betula pubescens* Ehrh. (Koricheva and Haukioja 1995).

In the framework of the project „Betula“ implemented in the air polluted area of east Ore Mountains and Děčín Sandstone Highlands, large amount of manganese, excessing above mentioned values, was found in birch leaves. In the soils with high Mn content (up to 3200 mg kg^{-1}) some values of Mn content reached above the level of 10000 mg kg^{-1} (Hrdlička and Kula 1998, 2004, 2007). Even at these rather high concentrations the symptoms of Mn phytotoxicity were not observed in the analysed leaves. This is in a good accordance with the observation of *Betula platyphylla* var. *japonica* (Miq.) Hara seedlings (Kitao et al. 1997).

Plants having > 1000 mg kg^{-1} of Mn in their tissues without toxicity symptoms can be called the accumulators. However, there are also plants able to accumulate even higher amounts of metals. These are called „hyperaccumulators“. Such plants can be used to remove the metal contamination, mostly from soils, by the means of phytoremediation (Liu et al. 2010, Reeves and Baker 2000). Each element has a limit of its content in the plant, marked as a hyperaccumulation. For manganese, the common limit is at least 10000 mg kg^{-1} (Baker et al. 1994, Boyd 2004, Reeves and Baker 2000, Verbruggen et al. 2009). Manganese hyperaccumulators are for example *Apocynaceae*, *Celastraceae*, *Clusiaceae*, *Myrtaceae* and *Proteacae* (Proctor et al. 1989, Reeves and Baker 2000).

The aim of this paper is to define the differences in the maximum levels of manganese in the leaves, rhytidome and other parts of the selected trees, bushes and herbs growing in the same habitat conditions characterized by increased content of manganese in the soil.

Site description

Permanent research area, used for a continuous monitoring, is situated in eastern Ore Mountains, in the area Litvínov, altitude 488 m a.s.l., southwest exposition (approximately 50°38'N; 13°37'E). Parent rock is granite (Czech and Slovak geological map, 2012). The dynamic changes assessment of the elements content in the leaves of birch *B. pendula* showed that the amount of manganese in the site is above the lower limit values of the optimal/increased content classification group. Long-term values of the manganese content were high (1995: average 8790 mg kg^{-1}, max. 9743 mg kg^{-1}; 1998: 5230/6783 mg kg^{-1}; 2001: 7723/10212 mg kg^{-1}; 2004: 5946/8544 mg kg^{-1}; 2007: 11570/15730 mg kg^{-1}) (Hrdlička and Kula 1998, 2004, 2007). The investigation proved that enhanced content of manganese in birch leaves was a reaction to higher content of Mn in the soil (3250 mg kg^{-1} – Hrdlička and Kula 2004).

The site was divided into three segments. The segments (marked Mn-1 to Mn-3) were different in kind of trees and herbaceous plants (see below). The content of manganese in the soil profile was: in fallen leaves (Mn-1/6603 mg kg^{-1}, Mn-2/4720 mg kg^{-1}, Mn-3/8597 mg kg^{-1}; highest values); the level of manganese in Ah horizon was also differentiated (Mn-1/1216 mg kg^{-1}, Mn-2/770 mg kg^{-1}, Mn-3/2854 mg kg^{-1}).

In the Mn-1 part, the forest cover contains *B. pendula* (60%), *Sorbus aucuparia* L. (20%), *Quercus robur* L. (10%) and *Fagus sylvatica* L. (10%), with disseminated *Prunus avium* (L.) L. and *Aesculus hippocastanum* L. In the undergrowth there is mostly *Digitalis purpurea* (L.) (30%), *Calamagrostis epigeios* (L.) Roth (20%), *Poa nemoralis* L. (20%) and *Avenella flexuosa* L. (10%). In the Mn-2 part, *B. pendula* has 100% representation with disseminated *Q. robur* L., *S. aucuparia*, *Acer pseudoplatanus* L. and new underplanting of *Picea abies* (L.) Karst., *Pinus sylvestris* L. and *Tilia cordata* Mill. Dominant plants in the undergrowth are *C. epigeios* (40%), *Rubus idaeus* L. (20%), *Rubus fruticosus* L. (10%), *A. flexuosa* (20%), *P. nemoralis* (10%). In the part Mn-3 the forest cover contains *B. pendula* (60%), *Larix decidua* Mill. (20%) and *S. aucuparia* (20%), in the undergrowth is *C. epigeios* (40%), *R. fruticosus* (20%) and *P. nemoralis* (20%). For the list of trees and herbaceous plants see Tab. 1.

Material and methods

Samples were collected during the whole vegetation period (May 6th – October 8th 2010). In this paper, samples gathered on September 2nd 2010 are evaluated. Samples of 9 tree species and 14 plants of a herb layer: leaves and rhytidome from trees and bushes; roots, leaves, stems and flowers from herbs were taken and put individually into paper bags. After the open air pre-drying at laboratory conditions the samples were oven-dried at the temperature 70 °C. Rhytidome was removed from the branches with a ceramic knife. Clean samples were ground in the vibration mill (both containers and balls made of tungsten carbide) to the particle size < 0.5 mm.

Sample mineralisation was performed by the means of microwave decomposition in MW ETHOS SEL (Microwave Solvent Extraction Labstation) with the mixture of HNO_3 and ultra-pure water 1:1 v/v (5 ml + 5 ml), sample weight was 0.1–0.5 g. After slow heating, mineralisation temperature was reached (210 °C) and kept for 20 min., ultra-pure water was added to the mineralised sample to total volume 25 ml. Quantitative determination of manganese was performed by the means of atomic absorption spectrometry (AAS) at the wave length 279.5 nm (Hedbávný,2010). The average values including standard deviations (for n = 3) were calculated from gathered data.

Results

Average measured values of the manganese content from September 2nd 2010 are given in the Table 1 together with max. values found during the vegetation period. Figure 1 shows average content of manganese in foliage and selected organs; values are sorted by manganese content in foliage.

Distinct differences were identified in the average manganese content among the trees before the end of the vegetation period (September 2nd 2010) in assimilation organs (1525–7852 mg kg^{-1}) (Tab. 1). Highest average amount of manganese (>7000 mg kg^{-1}) was found in leaves of *S. aucuparia* and needles of *L. decidua,* while decreased level (< 3000 mg kg^{-1}) was characteristic for assimilation organs of *P. abies* (1-year-old needles), *P. avium* and *A. hippocastanum*. Values for remaining trees important for forestry (*Q. robur, B. pendula, F. sylvatica*) oscillated around the level of 5000 mg kg^{-1} (Fig. 1). Peak values of the manganese content in trees were measured inconsistently during the vegetation period. The concentration of Mn in the larch needles was 12542 mg kg^{-1} (October 8th 2010) before needle fall, the maximum value in beech leaves was 10308 mg kg^{-1} (August 4th 2010).

Although individual species in the herb undergrowth mostly have lower concentrations of manganese in leaves in comparison with trees, higher difference was found there (446–8040 mg kg^{-1}). Assimilation organs (leaves) of *R. ideaus* and *R. fructicosus* show extreme average values over 7000 mg kg^{-1} (September 2nd 2010); maximum values for all these species reached almost 11000 mg kg^{-1} in the end of the vegetation period (Tab. 1, Fig. 1). Increased concentration of manganese was characteristic for another perennial plant, *V. myrtillus* (4922 mg kg^{-1}). On the other hand, grass species show relatively low level of manganese (1041–1250 mg kg^{-1}). Medicinal herb *D. purpurea* had increased concentration of manganese in leaves of two years old plants (2892 mg kg^{-1}) with peak value 8424 mg kg^{-1} (July 3th 2010) (Tab. 1).

Rhytidome from branches of investigated trees and bushes collected at the same time as the samples of assimilation organs (September 2nd 2010) also demonstrated different amounts of manganese (1759–4962 mg kg^{-1}). Specific position has *P. avium*, because only in this tree the concentration of manganese found in rhytidome was higher than in leaves and peak amount samples (8323 mg kg^{-1}) were collected on July 3th 2010 (Tab. 1).

Tab. 1: Mean and maximal content of manganese in organs selected plants (site Litvínov, 2010).

Plants	Organs	Mean ± stand. dev.* (mg kg^{-1})	Maximum** date	(mg kg^{-1})	Limit value# (mg kg^{-1})
Oak	leaf	5368 ± 121	3.7.	6337	60–2500 (F)
***Quercus robur* L.**	rhytidome	3785 ± 815	4.8.	5651	
Birch	leaf	5125 ± 481	8.10.	8244	30–100 (B)
***Betula pendula* Roth**	rhytidome	1759 ± 254	8.10.	2541	
Beech	leaf	5488 ± 2356	4.8.	10309	60–2500 (F)
***Fagus sylvatica* L.**	rhytidome	1931 ± 615	8.10.	2541	
Maple	leaf	3124 ± 226	8.10.	6323	30–100 (B)
***Acer pseudoplatanus* L.**	rhytidome	3952 ± 1315	8.10.	6173	
Rowan	leaf	7852 ± 265	2.9.	8183	
***Sorbus aucuparia* L.**	rhytidome	2032 ± 508	4.8.	3511	
Horse chestnut	leaf	2714 ± 279	8.10.	4314	
***Aesculus hippocastanum* L.**	rhytidome	1775 ± 634	2.6.	3774	
Cherry	leaf***	1525	8.10.	2125	30–100 (B)
***Prunus avium* (L.) L.**	rhytidome***	4962	3.7.	8323	
Larch (*Larix decidua* Mill.)	needle	7012 ± 1337	8.10.	12542	35–200 (B)
Norway spruce (*Picea abies* (L.) Karst.)	needle	2144 ± 111	8.10.	2945	20–2000 (F)
Raspberry	leaf	7165 ± 1755	8.10.	10953	30–100 (B)
***Rubus idaeus* L.**	stem	2114 ± 530	2.6.	6967	
Blackberry	leaf	8040 ± 2585	2.9.	10928	30–100 (B)
***Rubus fruticosus* L.**	stem	1987 ± 125	2.6.	4471	
Blueberry	leaf	4921 ± 1487	2.9.	7022	
***Vaccinium myrtillus* L.**	twigs	2745 ± 653	3.7.	3767	
Elderberry (*Sambucus nigra* L.)	leaf	985 ± 58	2.6.	1303	
Wavy hair-grass (*Avenella flexuosa* L.)	leaf	1041 ± 221	3.7.	1874	
Sticky groundsel (*Senecio viscosus* L.)	leaves and stem	955 ± 237	8.10.	2894	
Foxglove	leaf	2892 ± 1118	3.7.	8424	
***Digitalis purpurea* (L.)**	root	2149 ± 476	4.8.	4257	
Bluegrass	leaf	1250 ± 305	8.10.	2392	35–100 (B)
***Poa pratensis* L.**	bloom	1623 ± 55	8.10.	2576	
Sorrel	leaf	446 ± 75	4.8.	5626	
***Rumex acetosa* L.**	bloom	328 ± 65	4.8.	1007	
Wood small-reed	leaf	1093 ± 415	6.5.	1765	
***Calamagrostis epigejos* (L.)**	bloom	662 ± 56	3.7.	1226	
Nightshade	leaf	1585 ± 246	8.10.	2514	
***Atropa bella-donna* L.**	stem	664 ± 69	2.9.	764	
Male fern (*Dryopteris filix-mas* (L.) Schott	leaf	1306 ± 80	8.10.	2442	
Downy hemp-nettle (*Galeopsis speciosa* Mill.)	leaves and stem	3371 ± 988	3.7.	4715	
Hypericum (*Hypericum perforatum* L.)	leaves and stem	1273 ± 364	8.10.	2234	

References: (F) – Fürst (2005); (B) – Bergmann (1988)

* sampling on 2.9.2010

** date of sampling (2010) related to maximum

*** only one sample, others three samples

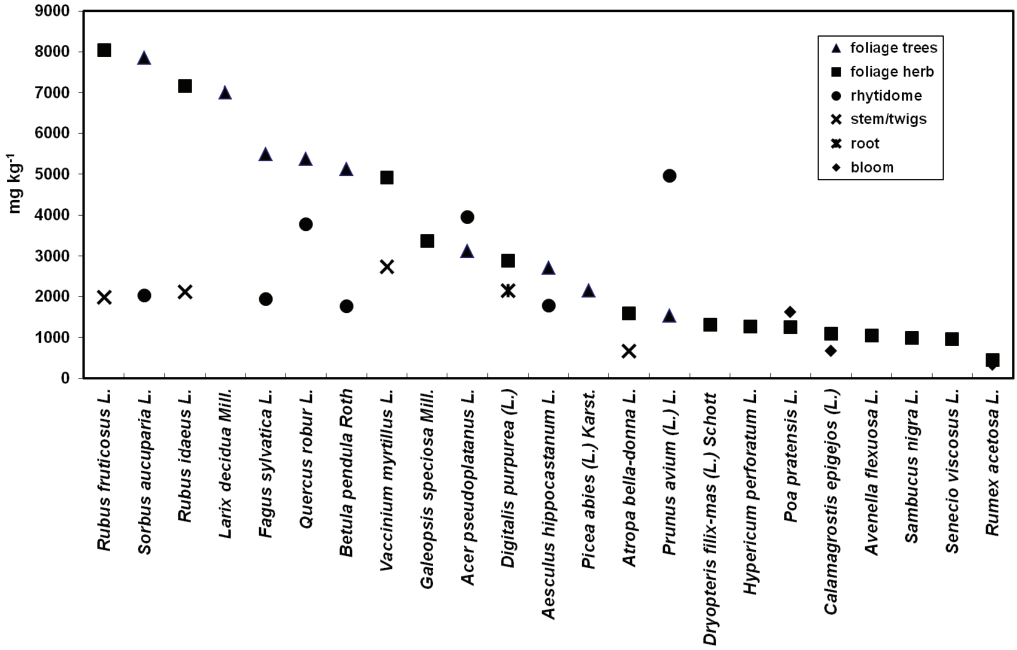

Fig. 1: Average content of manganese in foliage and organ selected plants (sorted by content of manganese in foliage).

Discussion

The content of manganese in monitored area was differentiated i) among individual parts of the same plant (leaves vs. rhytidome, leaves vs. roots etc.), ii) among the same parts of different plants. Highest inter-species differences in the manganese content described Reimann et al. (2007) between *Dryopteris filix-mas* (L.) Schott. (239 mg kg^{-1}) and birch leaves (2138 mg kg^{-1}). We can confirm (Fig. 1) this by our investigation (birch average 5125 mg kg^{-1}, max. 8243 mg kg^{-1} and *D. filix-mas* average 1306 max. 2442 mg kg^{-1}). The content of manganese increased during the vegetation period, it corresponded with generally very low mobility of manganese (Langheinrich et al. 1992, Marschner 2006). Optimal concentrations of manganese or even phytotoxicity level for some plants given in literature and in IUFRO sources (Bergmann 1988, Fürst 2005) was exceeded several times in the investigated species, while neither necrotic phenomenons nor perishing of plant was observed during the year 2010.

The sensitivity of plants to the surplus of Mn is different. As for the trees, *S. aucuparia, L. decidua, F. sylvatica, Q. robur, B. pendula* are very tolerant, as for herbaceous plants, are very tolerant *R. fruticosus, R. idaeus, V. myrtillus* (in all leaves samples content of manganese > 5000 mg kg^{-1}, Fig. 1).

Soil environment (horizon, humidity, nutrient content, etc.) is a limiting factor for the manganese content in leaves. In various trees, a difference of manganese content in leaves was found (Heilmeier et al. 2000) according to the basalt (the amount of Mn in soil 1284 mg kg^{-1}) and rhyolite bedrock (325 mg kg^{-1}), specifically for *F. sylvatica* (3600–4600/700–1000 mg kg^{-1}), *S. aucuparia* (2600–3100/2100–3200 mg kg^{-1}) and *P. abies* (2700–2900/900–2100 mg kg^{-1}). Our results indicate comparable amount of Mn in the assimilation organs of *P. abies* (2781 mg kg^{-1}), the values for *F. sylvatica* and *aucuparia* were significantly higher (Tab. 1). In the case of *L. decidua* needles the content of Mn found during our research (max. 12542 mg kg^{-1}) shows high rate of accumulation (due to the content of Mn in soil – 3250 mg kg^{-1} – Hrdlička and Kula 2004) in comparison with the values 911–1400 mg kg^{-1} for plants growing on the soil with low manganese content (Skřivan et al. 2002). Similar conclusions can be deduced for *F. sylvatica* – Litvínov max. 10309 mg kg^{-1} (Tab. 1) vs. 372–953 mg kg^{-1} (Machava and Barna 2005).

Higher amount of manganese can be found in tissues of *V. myrtillus.* In plants growing on soil substrate with manganese content 300–400 mg kg^{-1} were found values 888–1941 mg kg^{-1} in leaves (Gupton and Spiers 1992), in plants growing on soil substrate with manganese content 80 mg kg^{-1} was in leaves found 550 mg kg^{-1}, in stems was 1016 mg kg^{-1} (Grønflaten et al. 2005). In the low immision area in Poland was found 1044–2120 mg kg^{-1} of Mn in stems, 1540–3952 mg kg^{-1} in leaves (Kozanecka et al. 2002). In the catchment of Lesní Potok (Czech Republic), where the total content of manganese in the soil was < 818 mg kg^{-1}, the content of Mn in *F. sylvatica* leaves was 1206 mg kg^{-1} and in *P. abies* needles it was 715 mg kg^{-1} (Navrátil et al. 2007). Our values (see Tab. 1) were higher, which is in good accordance with the amount of Mn in the soil (see Hrdlička and Kula 2004). Most species from the *Ericaceae* family are the accumulators of manganese, without any signs of toxicity in leaves up to 15000 mg kg^{-1} (Korcak 1989). Another part of the undergrowth with high amount of manganese in leaves was *R. idaeus* (Kowalenko 2005, Sikiric et al. 2009, Wislocka et al., 2006). The content of manganese varied in the range 182–949 mg kg^{-1} (Wislocka et al. 2006), but also just in the range 280–360 mg kg^{-1} (Kowalenko 2005). Measured values of manganese content, 7165 mg kg^{-1} with maximum 10952 mg kg^{-1} without any signs of phytotoxicity, show high toleration to manganese. *R. fruticosus* comes from the same genus and also shows ability to tolerate high level of manganese (Tab. 1).

Conclusion

The difference among both various trees and undergrowth plant species and different tissues of the same plant growing in the same location conditions was verified.

According to the rate of accumulation and prevalence, *B. pendula, F. sylvatica, S. aucuparia, L. decidua, V. myrtilus, R. ideus, R. fruticosus* and *D. purpurea* can be classified as suitable plant species to use for the surface definition of the manganese contamination in the environment, with the realisation during the season with expected maximum content.

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