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The contribution of glomalin-related soil protein to Pb and Zn sequestration in polluted soil

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ABSTRACT

The distribution of lead and zinc in glomalin-related soil protein (GRSP), a widespread glycoprotein presumably produced by arbuscular mycorrhizal fungi (AMF) in soil, and in some other soil fractions (soil organic matter — [SOM], carbonates, phosphates, etc.) was studied in soils from an area near a lead smelter that differed in SOM, carbonates and heavy metal (HM) content. Total GRSP represented 5.4–21.2% of the SOM and was positively correlated with the soil Pb and Zn concentrations ($r=0.57$ and 0.66, $p=0.007$ and $p=0.001$ for Pb and Zn, respectively). Pb and Zn were predominantly bound to carbonates and organic matter. The amount of lead bound to GRSP varied between 0.69 and 23.4 mg g^{-1} DW GRSP which is 0.8–15.5% of the total soil Pb. The amount of GRSP-bound metal was positively correlated with the total concentration in the case of Pb ($r=0.90$, $p=0.000$) but the opposite was found for Zn ($r=-0.41$, $p=0.048$), indicating that GRSP predominantly binds Pb. The percentages of HM-GRSP in HM-SOM were variable and were not correlated with SOM content.

1. Introduction

Heavy metals (HMs) are associated with a number of soil components, which determine their behavior in the soil and influence their bioavailability. Depending on the soil properties driving speciation, heavy metals can be retained in different soil phase fractions such as exchangeable on clay minerals, bound to iron and manganese oxides, bound by carbonates and absorbed by soil organic matter (SOM). The latter can be, together with soil pH, regarded as the most important parameter controlling heavy metal behavior in soils (Leštan and Grčman, 2001; Boruvka and Drabek, 2004). The organic fraction of the soil is very complex; however, most commonly accepted chemical procedures for heavy metal speciation treat it as one moiety. Extraction of this moiety in one single extraction step neglects a detailed distribution of metals among individual organic fractions (Tessier et al., 1979; Ure et al., 1993). Few studies dealing with this problem suggest that metals predominantly bind to fulvic acids proportional to the level of pollution. In contrast, binding is less pronounced on humic acids, for which a limited amount of sorption sites for the metals is assumed (Boruvka and Drabek, 2004). Humic substances, however, are not the only fraction of the organic matter with HM binding capacity. In the mixture of organic material insoluble in aqueous systems, humin, there are several compounds that may significantly contribute to the metal binding phenomenon (Hayes and Clapp, 2001).

It was suggested that one of these compounds is glomalin, a glycoprotein presumably produced by arbuscular mycorrhizal fungi (AMF) (Wright and Upadhyaya, 1996; Nichols,

Abbreviations: GRSP, glomalin-related soil protein; EEG, easily extractable fraction of GRSP; TG, total GRSP; SOM, soil organic matter; HM, heavy metals; AM, arbuscular mycorrhiza; AMF, arbuscular mycorrhizal fungi.

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2003). This compound has been detected in large amounts in numerous soils (Nichols, 2003; Wright and Upadhyaya, 1998), which has been attributed to the fact that AMF colonize 80% of vascular plant species (Trappe, 1987) and have a global distribution. Large glomalin pools could also result from its high persistence in the soil (Rillig et al., 2001).

Currently, glomalin in soils is quantified as glomalin-related soil protein (GRSP), an alkaline-soluble protein material linked to AMF, defined by the extraction conditions (Rillig, 2004; Nichols and Wright, 2006), whose biochemical nature is still to be revealed. GRSP, transferred to soil via release from hyphae (Driver et al., 2005), appears to be a complex of repeated monomeric structures bound together by hydrophobic interactions (Nichols, 2003). It attaches to soil and helps to stabilize aggregates (Rillig and Mummey, 2006). It contains tightly bound iron (0.04–8.8%) (Nichols, 2003; Wright and Upadhyaya, 1998; Rillig et al., 2001), but does not contain phenolic compounds such as tannins (Rillig et al., 2001). Cations are bound to GRSP in amounts that vary for different soils (Nichols, 2003; Wright and Upadhyaya, 1998; Chern et al., 2007) and recently González-Chávez et al. (2004) clearly showed a high binding capacity of GRSP for some heavy metals (Cu, Cd and Pb). On the basis of their research it has been suggested that this sequestration could be important for heavy metal biostabilization in polluted soil. This presumption has, however, not been reviewed by further studies that would specifically use polluted soils that differ in the content of particular heavy metals and, in general, those soil characteristics that influence HM mobility. Therefore it was decided to examine the role of GRSP for binding of two heavy metals, Pb and Zn, in polluted soil originating from the area of the lead smelter. In this particular soil organic matter content and the content of carbonates are the most important determinants of metal availability (Leštan and Grčman, 2001). In our study the objectives were i) to assess the presence of GRSP in soils constituting different SOM and HM concentrations and ii) to compare the rate of HM sequestration by GRSP and by SOM.

2. Material and methods

2.1. *Sampling*

The soil was sampled in June, 2004, in the vicinity of Žerjav lead smelter (in the valley of the Meža River, northern Slovenia). At this site, very high concentrations of lead, zinc and also cadmium can be found in the soil as a result of long-lasting lead ore smelting activities (Souvent, 1992). Concentrations as high as 5900 mg kg^{-1} and 1300 mg kg^{-1} are reported for Pb and Zn, respectively (Kugonič et al., 1999). In the close vicinity of the smelter, especially in the so-called Dead Valley area (a small side valley on the right bank of the Meža River), HM and SO_2 emissions from the smelter have caused a serious degradation of the environment (deforestation, soil contamination and erosion). There is a clear correlation between distance from the source of pollution and vegetation diversity and growth, with pollution effects best visible in the direct vicinity of the smelter.

Samples (0–10 cm depth) were taken from 21 locations that followed a transect along the ridge above the Dead Valley. At

Table 1 – Properties of the topsoil from 21 locations in Žerjav (N Slovenia) used for sequential extraction and GRSP analyses

Location	pH	Organic matter [mg g^{-1}]	C/N	Gravel [% w/w]	Carbonates [%]	Pb [mg kg^{-1}]	Zn [mg kg^{-1}]	GRSP	
								EEG* [mg g^{-1}]	TG** [mg g^{-1}]
1	7.1	260	13.7	6.4	47.2	2860	480	3.20	30.51
2	7.1	322	16.9	3.2	33.4	5490	940	1.99	41.12
3	7.1	202	13.8	2.1	53.0	5490	1150	4.62	21.53
4	7.0	216	13.0	4.2	56.5	6510	840	2.64	29.92
5	7.1	150	13.2	10.6	16.4	2510	880	3.74	28.02
6	6.4	476	15.3	1.0	6.8	18400	1240	1.97	67.14
7	7.3	164	13.6	9.3	64.6	4740	500	3.37	34.69
8	7.1	183	15.1	7.7	59.3	2820	320	2.39	32.84
9	7.3	142.5	15.6	4.4	62.5	3770	400	3.29	19.51
10	7	187	15.2	13.1	63.9	7330	740	2.56	24.15
11	7.1	164	17.6	6.2	73.4	3540	590	2.95	23.43
12	7.1	288	14.6	3.3	39.5	5180	690	1.18	43.64
13	6.8	47	20.9	21.3	88.8	4250	460	2.28	6.51
14	6.6	103	17.0	18.6	83.7	15,820	800	4.55	8.78
15	6.4	165	18.0	14.3	65.2	9870	600	3.39	20.92
16	5.7	297.5	14.7	3.3	43.9	16,720	1450	3.22	38.31
17	7	43	17.8	49.2	94.8	2260	240	3.53	5.98
18	6.9	61	19.0	33.0	86.4	2240	340	4.72	3.32
19	7.4	54.5	13.1	26.7	33.7	270	62	2.52	4.08
20	7.3	143	15.0	8.8	35.6	4480	650	4.30	11.24
21	7.5	40.5	13.8	33.3	40.3	340	67	2.23	7.74
max	7.5	476	20.9	49.2	94.8	18,400	1450	4.72	67.14
min	5.7	40.5	13.0	1.0	6.8	270	62	1.18	3.32
median	7.1	164	15.1	8.8	56.5	4480	600	3.20	23.43

*Easily extractable Bradford-reactive soil protein.
**Bradford-reactive soil protein after extensive extraction.