Carpathian Journal of Earth and Environmental Sciences, November 2015, Vol. 10, No 4, p. 195 - 202

CHEMICAL ASSESSMENT OF SOIL QUALITY FOR ECOLOGICAL REMEDIATION STRATEGIES

Maria L. BIZO[1*], Erika A. LEVEI[2], Erika KOTHE[3], Marin ȘENILĂ[2], Cristina O. MODOI[1] & Alexandru OZUNU[1]

[1]*Babeș-Bolyai University, Faculty of Environmental Science and Engineering, Fântânele 30, 400294 Cluj-Napoca, Romania, e-mail: bizo.maria@yahoo.com*

[2]*INCDO INOE 2000, Research Institute for Analytical Instrumentation, Donath 67, 400293 Cluj-Napoca, Romania*

[3]*Friedrich Schiller University, Institute of Microbiology, Microbial Communication, Neugasse 25, 07743 Jena, Germany*

Abstract: In order to evaluate ecological remediation strategies for metal contaminated brownfields, soil characteristics and metal contents were assessed for a 12000 m^2 site impacted by non-ferrous metallurgical industry operations. Total and mobile metal concentrations, pH, total carbon and dissolved organic carbon were determined in a range at 10-30 cm and 40-60 cm depth from 16 sampling points and correlated to plant growth with respect to bioremediation using mycorrhizal trees. The results indicated a poor quality of the soil and disturbance in soil function, and revealed a high metal contamination without significant differences between distribution patterns at different depths in soil. The symbiosis allows the trees to develop an increased metal tolerance due to fungal detoxification mechanisms. The proposed land-use will allow for increased biomass of the ectomycorrhizal trees to be used as renewable energy source without harm to food chains or the environment. Our investigations thus confirm a potential ecological remediation and land-use strategy at metal contaminated agriculture/forestry sites, with the high advantage of keeping the economical implications minimal and bringing the landscape of the contaminated sites as close as possible to a natural landscape.

Keywords: soil metal contamination, bioremediation, ectomycorrhiza, renewable energy, forestry

1. INTRODUCTION

Sites contaminated with metals rise complex environmental issues and often require specific remediation strategies adapted both to the characteristics of the site and to the type and degree of pollution in order to meet specific targets for pollution control, land stabilization, and future land-use (Wong, 2003; Leyval et al., 1997). The natural recovery of contaminated sites is a function inherent to the environment, but succession requires sufficient time and thus does not represent an acceptable option for the communities living next to polluted sites. The objective of the present investigation was to determine the disturbance level of the soil quality indicators in order to develop a self-sustaining ecosystem for bioremediation of metal polluted brownfields using ectomycorrhizal (ECM) trees based on the specific characteristics of the soil in question.

The chemical assessment of the soil was conducted in a test field located in the Baia-Mare region, well known for environmental pollution due to industrial activities. The results presented in the literature (Damian et al., 2008; Damian et al., 2010; Răuță et al., 1997; Levei et al., 2009; Mihali et al., 2013) indicated that non-ferrous metallurgical industry contributed to the historical pollution of soil with heavy metals in this area, the contamination level often exceeding the thresholds set by the Romanian legislation (MO 756/1997). The pollution of the soil mainly is caused by atmospheric deposition from ore smelting and refining, as well as from other metal ore extraction and processing operations (Culicov et al., 2000).

The soil in Baia-Mare developed on volcanic bedrock consisting of andesites and on sedimentary bedrock consisting of marl, clay and/or alluvial deposits leading to predominant soil types of andosols on volcanic bedrock, regosol, eutricambosol, districambosol on sedimentary bedrock and alluvial deposits (Damian et al., 2008). Thus, geogenic backgrounds for several metals, among them Zn, Cu and As, already were high (Modoi et al., 2011; Bird et al., 2009).

Soil functions are not accessible for measurement directly, but can be assessed by measuring soil quality indicators, where the chemical indicators are related to nutrient cycling, water retention and buffering capacity (Doran & Parkin, 1996). Considering the industrial activities that existed in the region and the previous studies (Frentiu et al., 2009; Levei et al., 2009), the total contents and mobile fractions of Cu, Zn and Pb were chosen to be assessed at the selected brownfield site. Since mobile metal fractions interfere with plant physiology and development, these were specifically addressed. Carbon content as determinant for growth of fungi and plants and their mutually beneficial symbiosis was of specific interest, since mycorrhizal symbioses can influence all other soil indicators and is tied in to other soil functions (Doran & Parkin, 1996).

2. MATERIALS AND METHODS

2.1. Study area and soil sampling

For the field investigation, a 12000 m^2 study area in Ferneziu district, North-East Baia Mare, situated near a former Pb metallurgical plant was established. The plant is in a preserving stage since end of 2012. The field features a positive relief between 290 m and 340 m. 15 sampling points (S1-S15) were selected covering the area close to the smokestack presently demolished (Fig. 1).

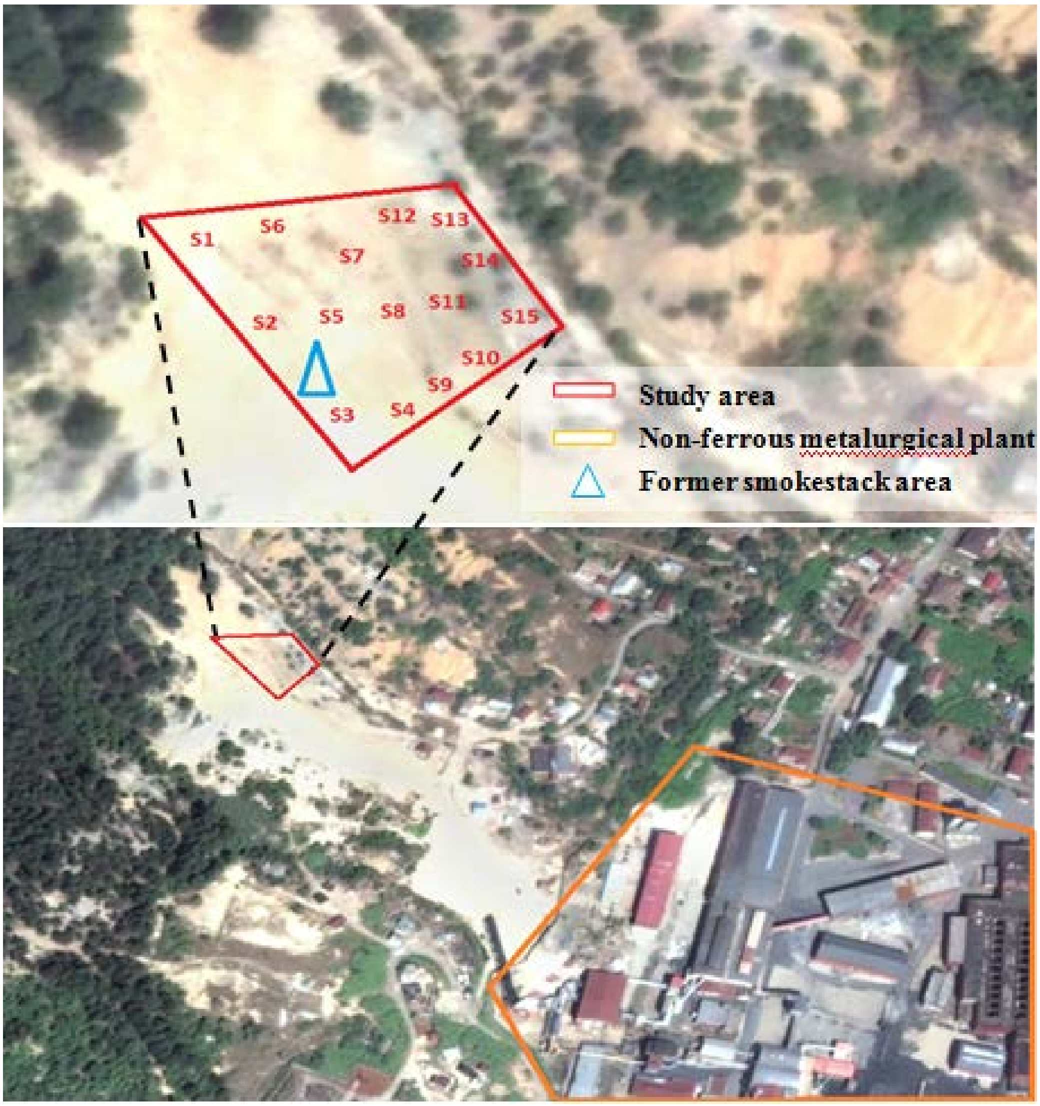

Figure 1. Study area situated in Ferneziu district, NE Baia-Mare

Soil samples were taken from a range between 10-30 cm and 40-60 cm depth at each sampling point using a hand auger sampler (at S6 and S15, only 10-30 cm were sampled as the very compact soil texture did not allow a deeper drilling). Samples S1, S2 and S3 were situated in the area where the smokestack demolition took place and have a different composition, being mixed with demolition waste consisting of small pieces of brick, ash or unidentified rocks. S1 has mainly a black color, S2 is whitish-grey and S3 is a dark grey, while the other samples are mainly brown or orange-brown. For reference, one soil sample (R) has been collected from an area considered unpolluted and located approximately 15 km away from the investigated area, at the shore of Firiza Lake, the storage reservoir used for water supply of the town Baia-Mare.

2.2. Sample preparation and analysis

The soil samples were dried at 105°C for 24 h, crushed, and sieved through a 2 mm sieve. The fraction below 2 mm was collected, homogenized and stored in polyethylene bags until analysis.

The pH of soils was measured in a suspension 1/5 (w/v) soil to water extract using a 350i multiparameter probe (WTW, Germany). The total carbon (TC) content was determined by combustion and infrared detection of the resulting CO_2 using the solids module of a Multi N/C 2100S Analyzer (Analytic Jena, Germany). The dissolved organic carbon (DOC) was determined by thermocatalytic high temperature oxidation and infrared detection of using the liquid module of a Multi N/C 2100S Analyzer (Analytic Jena, Germany) in 1/10 (w/v) soil to water extract. The extract obtained by adding 10 ml of ultrapure water to 1 g samples and shaking (7 rpm) for 24 h at 20±5°C was filtered through 0.45 µm pore size PTFE membrane filters before analysis.

The total concentration of Cu, Zn and Pb was determined by digestion of 1 g sample with 28 ml aqua regia, under reflux conditions. BCR sequential extraction (Zimmerman & Weindorf, 2010; Okoro et al., 2012; Vodyanitskii, 2006) was applied to assess the metals' mobilization in soil in different conditions. For the acid-extractable fraction (AE), 1 g sample was extracted in 40 ml of 0.11 M CH_3COOH for 16 h at 20±5°C, under continuous shaking (15 rpm). The extract was centrifuged at 4500 rpm for 10 minutes, filtered and analyzed. From the residue, the reducible fraction (RED) was determined by extraction with 40 ml of 0.1 M NH_2OH HCl (pH=2 with HNO_3) for 16 h under continuous shaking at 20±5°C. The oxidizable fraction (OX) was determined by adding 10 ml of 8.8 M H_2O_2 to the residue and by shaking for 1 h at room temperature. Then another 10 ml 8.8 M H_2O_2 (pH=2) were added and heated to 85°C in a water bath, until the sample volume was reduced to approximately 1 ml. After cooling, 50 ml of 1 M NH_4OAc (pH=2 with HNO_3) were added and the slurry was shaken for 16 h at 20±5°C. For the determination of the residual fraction (RES), 28 ml aqua regia (21 ml of 12 M HCl and 7 ml of 15.8 M HNO_3) was added to the residue and kept at room temperature for 16 h. The mixture was then heated under reflux conditions for 2 h. The solution was filtered and diluted to 50 ml with 0.5 M HNO_3.

The Cu, Zn and Pb concentration of the extracts were determined by inductively coupled plasma optical emission spectrometry using an OPTIMA 3500 DV spectrometer (Perkin Elmer, USA).

3. RESULTS AND DISSCUSIONS

The total metal contents are presented in table 1. Cu exceeded the alert threshold (250 mg/kg) for less sensitive soil use in samples S5, S13, S14 at both depths, and the intervention threshold (500 mg/kg) for less sensitive soils use in samples S1, S2, S3 both at 10-30 and 40-60 cm depth. In the case of Zn, the concentration exceeded the intervention threshold (1500 mg/kg) at the sampling points S2 and S3 at both depths. The Pb concentration exceeded the intervention threshold (1000 mg/kg) in all samples, except samples S10 and S11 at both depths. The highest metal concentrations were found in samples S1-S3. However, high Pb concentrations were also found in samples S5, S7, S13 and S14, where Cu and Zn were much lower. These sampling points are situated approximately 500 m East of the metallurgical plant. Due to the predominant W to E wind direction, Pb emission from the plant is the very likely source of pollution (Damian et al., 2010).

Generally, the metal contents were similar in both depths, indicating long term pollution. However, for S2 and S5 the Pb contents were twice higher at 10-30 cm depth than at 40-60 cm depth, indicating a more recent, additional pollution. While, as expected, Cu and Zn contents in the reference soil sample were below the alert thresholds, Pb exceeded the alert levels at both depths suggesting a higher spread of the pollution than initially considered. The soil pH (Table 1) in the investigated area was extremely to moderately acidic (3.57 -5.57), with an exception of S2, where the pH was slightly alkaline (7.90 at 10-30 cm depth, and 7.50 at 40-60 cm depth).

Table 1. Total concentrations of Cu, Zn and Pb, pH, total carbon (TC) and dissolved organic carbon (DOC) in soil samples from the study and reference areas and the corresponding legislative thresholds

	Cu (mg/kg)		**Zn** (mg/kg)		**Pb** (mg/kg)		**pH**		**TC** (mg/kg)		**DOC** (mg/kg)	
Depth (cm)	**10-30**	**40-60**	**10-30**	**40-60**	**10-30**	**40-60**	**10-30**	**40-60**	**10-30**	**40-60**	**10-30**	**40-60**
Study area												
S1	1555	1560	501	561	11003	9804	5.06	4.73	8720	4400	304	276
S2	1484	1157	5342	4931	9733	4498	7.90	7.50	13700	11400	309	290
S3	1538	1397	5626	5407	11132	11637	3.57	3.37	9360	7720	297	329
S4	31.5	36.4	235	180	1083	1295	5.16	4.95	4810	4370	394	310
S5	337	327	458	491	11131	5313	4.57	4.62	11900	7660	560	295
S6	183	-	558	-	2166	-	5.16	-	5560	-	210	-
S7	205	217	174	394	9838	10184	4.49	4.49	10800	8870	425	616
S8	60.5	161	113	468	2311	2960	4.46	4.54	11600	7740	599	397
S9	186	197	174	180	4815	3978	4.18	4.27	15400	9160	751	514
S10	29.6	29.2	211	118	137	132	5.32	5.57	5340	3240	216	127
S11	139	93.7	556	535	393	447	5.15	5.08	7600	6690	381	307
S12	226	312	231	480	5539	4703	4.52	4.48	10200	9110	769	436
S13	268	311	461	472	11337	11582	4.22	3.97	10100	12800	953	750
S14	327	317	418	467	10937	10380	4.33	4.16	11700	12800	499	554
S15	139	-	480	-	1490	-	5.50	-	13500	-	534	-
Minimum	29.6	29.2	113	118	137	132	3.57	3.37	4810	3240	210	127
Maximum	1555	1560	5626	5407	11337	11637	5.50	5.57	15400	12800	953	750
Average	447	470	1036	1130	6203	5916	4.90	4.74	10019	8151	480	400
Reference area												
	70.6	115	241	141	536	340	4.50	4.38	51900	27200	1941	1547
Legislated thresholds*												
Alert	250		700		250		-		-		-	
Intervention	500		1500		1000							

*alert/intervention threshold values for less sensitive soil use according to Order 756/1997

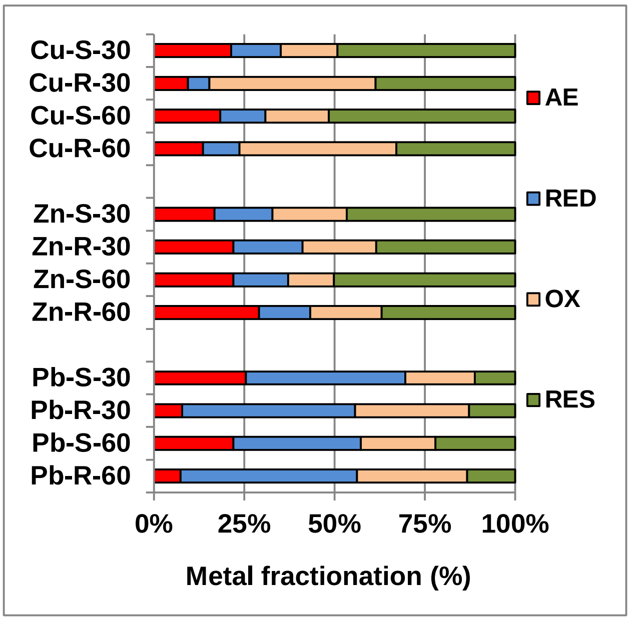

Figure 2. Cu, Zn and Pb distribution among fractions in the study (S) and reference areas (R)

These atypical pH values may result from soil amendments during demolition of the smokestack. The soil TC was significantly lower at the test site than from the reference sample, with average TC showing a non-significant trend to decreasing values with depth. Again, DOC was higher in the reference sample than the average DOC contents of soil samples of the investigated area.

The partitioning of Cu, Zn and Pb according to BCR extraction scheme is presented in table 2. The distribution pattern was similar for Cu and Zn, and different for Pb, in both depths (Fig. 2). The metal distribution pattern in the reference area was similar to that of the study area for Zn, while significant differences were found for Cu and Pb which were twice and three times higher than those from the reference area, respectively.

About 20% of the total metal content found in the acid-extractable fraction was considered mobile and thus potentially available for plant uptake (Gleyzes et al., 2002; Singh & Kalamdhad, 2013). About 15% of the total Cu and Zn and 42% of the total Pb were found in the reducible fraction, considered to be mobilizable under certain environmental conditions (Maiz et al., 2000; Frentiu et al., 2008; Singh & Kalamdhad, 2013). Despite the role of pH in determining metals mobility, soil pH alone cannot explain the high variation of the mobile and mobilizable Pb fractions. This variation could be a consequence of different Pb contamination events which is supported also by the absence of overlap between the points with the highest total Pb concentrations and those with highest mobile Pb concentrations.

The metals found in the oxidizable fraction (bound to organic matter and sulphides) are considered to be mobilizable in oxidizing conditions (Filgueiras et al., 2002). About 16 % Cu and Zn and 20% Pb were found to be bound in this fraction. Metals found in the residual fraction are considered immobile and unlikely to be released in the environment under natural conditions, thus not posing a risk for the environment (Trajkovic et al., 2014). The majority of Cu (50%) and Zn (47%) were found in residual fraction, while only about 15% of the Pb was found to be immobile.

Considering the high content of metals found in mobile and mobilizable fractions, the soil pH (with an average of 4.82) may favor their mobilization and uptake by plants, as acidic environments enhance the mobility of metals. Especially for Pb, a serious threat for the environment was found, exceeding thresholds for soil use.

Table 2. Partitioning of Cu, Zn and Pb (mg/kg) according to BCR extraction scheme (AE-acid extractable, RED-reducible, OX-oxidisable, RES-residual).

		Cu				**Zn**				**Pb**			
Metal fraction		**AE**	**RED**	**OX**	**RES**	**AE**	**RED**	**OX**	**RES**	**AE**	**RED**	**OX**	**RES**
Study area													
S1	10-30 cm	840	376	317	429	122	53.2	45.0	211	2816	3192	815	1460
	40-60 cm	532	362	520	349	238	118	107	218	1384	1788	1025	3842
S2	10-30 cm	243	304	466	647	1580	1684	1440	623	2848	3232	790	1079
	40-60 cm	118	118	282	290	1500	1472	630	496	888	1648	335	762
S3	10-30 cm	13.2	12.3	38.5	1548	110	31.7	965	4604	212	4560	2170	3915
	40-60 cm	11.0	10.1	31.4	1686	96.4	22.3	565	5412	212	4560	2015	3205
S4	10-30 cm	0.36	2.40	2.70	34.0	11.2	22.0	20.0	119	159	238	106	536
	40-60 cm	2.40	2.72	4.05	31.0	9.52	15.2	22.4	105	420	980	190	126
S5	10-30 cm	68.8	39.8	34.2	97.0	67.2	31.6	72.5	151	3308	6520	1945	291
	40-60 cm	67.6	38.2	23.1	78.0	165	109	77.0	151	1792	1956	331	88.5
S6	10-30 cm	29.9	27.8	23.4	63.0	152	215	111	243	540	952	189	97.3
	40-60 cm	-	-	-	-	-	-	-	-	-	-	-	-
S7	10-30 cm	48.4	25.5	23.0	69.0	48.0	26.0	51.5	94	3008	5440	1075	199
	40-60 cm	30.2	17.2	12.6	101	259	61.6	48.0	133	2076	1920	351	3193
S8	10-30 cm	13.1	12.0	17.4	31.0	9.60	6.80	22.7	81.8	1268	1024	403	156
	40-60 cm	35.2	19.9	14.0	46.9	237	57.6	41.6	100	1252	1204	240	76.0
S9	10-30 cm	37.0	20.1	25.5	48.9	9.84	5.72	23.3	93.6	1976	1944	493	180
	40-60 cm	54.0	30.5	17.9	35.3	110	20.0	22.0	68.1	670	680	172	1560
S10	10-30 cm	1.60	2.20	4.15	16.0	11.2	13.7	13.3	150	2.04	20.4	7.70	86.4
	40-60 cm	8.60	1.64	3.25	17.1	1.40	4.12	5.05	95.7	107	35.3	4.40	4.09
S11	10-30 cm	16.4	20.7	11.0	59.8	170	245	113	137	43.6	203	53.5	17.7
	40-60 cm	8.60	12.7	8.30	44.3	202	218	86.5	136	40.4	172	46.7	214
S12	10-30 cm	58.4	29.0	24.8	78.7	88.8	20.1	35.5	126	2152	3052	670	149
	40-60 cm	84.4	42.4	22.9	81.9	288	85.6	55.0	129	1196	1408	352	885
S13	10-30 cm	31.6	24.1	43.5	112	15.1	17.6	122	257	2544	4280	6050	1523
	40-60 cm	40.0	27.8	36.0	128	15.8	19.3	128	210	2620	3120	5950	963
S14	10-30 cm	67.2	42.0	37.8	83.3	64.0	26.2	74.0	167	2844	6080	3060	474
	40-60 cm	67.6	39.1	36.2	84.6	124	37.4	80.0	167	2736	5160	3420	539
S15	10-30 cm	7.44	12.4	13.4	87.5	118	81.2	50.5	128	102	524	146	353
	40-60 cm	-	-	-	-	-	-	-	-	-	-	-	-
Min	10-30 cm	0.36	2.20	2.70	16.0	9.60	5.72	13.3	81.8	2.04	20.4	7.70	17.7
	40-60 cm	2.40	1.64	3.25	17.1	1.40	4.12	5.05	68.1	40.4	35.3	4.40	4.09
Max	10-30 cm	840	376	466	1548	1580	1684	1440	4604	3308	6520	6050	3915
	40-60 cm	532	362	520	1686	1500	1472	630	5412	2736	5160	5950	3842
Average	10-30 cm	**98.4**	**63.4**	**72.2**	**227**	**172**	**165**	**211**	**479**	**1588**	**2751**	**1198**	**701**
	40-60 cm	**81.5**	**55.6**	**77.8**	**229**	**250**	**172**	**144**	**571**	**1184**	**1895**	**1110**	**1189**
Reference area													
10-30 cm		7.44	4.68	36.2	30.5	75.6	65.6	70.0	132	41.6	254	167	68.0
40-60 cm		5.92	4.36	18.9	14.3	72.0	35.2	48.8	91.6	26.5	175	109	47.8

Since soil pH is suitable for growth and function of fungi (able to develop between pH 2 and 7, with an optimum at pH 5; Smith & Doran, 1996), use of ectomycorrhizal fungi for reforestation is possible. Ectomycorrhizal symbiosis is known to sustain growth on brownfields contaminated with metals (Gherghel & Krause, 2012; Bizo et al., 2013). Thus, the effect of mycorrhizal fungi on plant growth should be evaluated.

The difference between the reference samples and those from the investigated field indicates a substantial problem with soil quality at this brownfield. The average carbon contents (10 g/kg TC and 480 mg/kg DOC) would allow for ectomycorrhizal trees to develop, as the symbiosis should be favored in the existing conditions. A self-sustaining ecosystem seems the optimal solution for land-use, and should be viable since ectomycorrhizal fungi use the carbon from their host plant, while the plant is supplied with nutrients and water by the fungi (Smith & Read, 2008). Benefiting also from the fungal detoxification mechanisms, the trees are protected and can tolerate increased metal concentrations (Söderström & Read, 1987). Thus, this type of self-sustaining ecosystem could develop in the present conditions, it could represent a first preliminary step in succession, and finally even develop to a complex ecological system with high biodiversity level.

ECM roots and fungi are also linked to the production of DOC (Högberg & Högberg, 2002). Our analysis indicated a large difference between the reference soil samples and the ones taken near the non-ferrous metallurgical plant. The results indicated a low activity of soil microbes, fungi and microorganisms, which is reflected in the lack of vegetation at the investigated field site. ECM fungi are known to improve soil respiration, an indicator for the soil's capacity to sustain the growth of plants (Parkin et al., 1996). A direct connection was observed between the soil respiration and the activity of ECM roots and their extramatrical mycelium (Högberg et al., 2001), where a loss of 50% soil respiration was linked to the loss of activity of ECM symbiosis.

4. CONCLUSIONS

The assessment of the study area situated in the proximity of a Pb non-ferrous metallurgical plant indicated poor soil quality and high metal concentrations exceeding alert and intervention thresholds. Both mobile and mobilizable fractions were enriched with metals. In addition, the low contents of total carbon and dissolved organic carbon indicated a disturbance in soil function. The chemical assessment identified the site as a brownfield. For bioremediation, ectomycorrhizal trees with enhanced resistance to the existing metal loads could nevertheless be a viable solution which should be further studied.

In general, the area might also benefit from technical measures of decontamination, specifically considering the area around sampling points S1, S2 and S3. Here, the highly contaminated soil should be removed and be safely deposited in an adequate industrial waste dump in order to remove the source for future pollution of deeper soil horizons.

From an ecological point of view, the metal concentrations in the mobile fraction constitute the ecotoxicological risk, because the metals from this fraction can be taken up by plants and would create a possible pathway to enter the food chain. Phytostabilization by metal tolerant plants would represent a suitable *in situ* remediation strategy that could reduce the solubility of the present contaminants by inducing changes in the chemical form of the contaminant, thus decreasing ecotoxicology.

REFERENCES

Bird, G., Macklin, M.G., Brewer, P.A., Zaharia, S., Balteanu, D., Driga, B. & Serban, M., 2009. *Heavy metals in potable groundwater of mining-affected river catchments, northwestern Romania*. Environmental Geochemistry and Health, 31,741–758.

Bizo, M., Formann, S., Krause, K., Roşu, C. & Kothe, E., 2013. *Resistance of young stresses caused by heavy metals such as Cs and Cd*. Environmental Engineering and Management Journal, 12, 2, 325-330.

Culicov, O.A., Frontasyeva, M.V., Steinnes, E., Okina, O.S., Santa, Zs., & Todoran R., 2000. *Atmospheric deposition of heavy metals around the lead and copper-zinc smelters in Baia Mare, Romania, studied by the moss biomonitoring technique, neutron activation analysis and flame atomic absorption spectrometry*. Journal of Radioanalytical and Nuclear Chemistry, 254, 1, 109-115.

Damian, F., Damian, Gh., Lăcătuşu, R., Macovei, Gh., Iepure, Gh., Năprădean, I., Chira, R., Kollar, L., Raţă, L. & Zaharia, D., C., 2008. *Soils from the Baia Mare zone and the heavy metals pollution*. Carpathian Journal of Earth and Environmental Sciences, 3, 1, 85-98.

Damian, Gh., Damian, F., Năsui, D., Pop C. & Pricop C., 2010, *The Soils Quality from The Southern – Eastern Part of Baia Mare Zone Affected by Metallurgical Industry*. Carpathian Journal of Earth and Environmental Sciences, 5, 1, 139-147.

Doran, J.W. & Parkin, T.B., 1996. *Quantitive indicators of soil quality: a minimum data set.* In: Doran, J.W., Jones, A.J. (EDS.), Methods for Assessing Soil Quality. Soil Science Society of America, Special Publication 49, Madison, WI, 25-37.

Filgueiras, A.V., Lavilla, I. & Bendicho, C., 2002. *Chemical Sequential Extraction for Metal Partitioning in Environmental Solid Samples*. Journal of Environvironmental Monitoring, 4, 823-857.

Frentiu, T., Ponta, M., Levei, E., Gheorghiu, E., Kasler, I. & Cordos E.A., 2008. *Validation of the Tessier scheme for speciation of metals in soil using the Bland and Altman test.* Chemical Papers 62, 1, 114-122.

Frentiu, T., Ponta M., Levei E. & Cordos E., 2009. *Study of partitioning and dynamics of metals in contaminated soil using modified four-step BCR sequential extraction procedure*. Chemical Papers 63, 2, 239–248.

Gherghel, F. & Krause, K., 2012. *Role of Mycorrhiza in Re-forestation at Heavy Metal-Contaminated Sites*. In: *Bio-Geo Interactions in Metal-Contaminated Soils,* Kothe E., Varma A. (Eds.), Soil Biology 31, Springer, Heidelberg, Dortrecht, London, New York, 183-199.

Gleyzes C., Tellier S.M. & Astruc M., 2002. *Fractionation Studies of Trace Elements in Contaminated Soils and Sediments: A Review of Sequential Extraction Procedure*.Trends in Analytical Chemistry, 21, 451-467.

Högberg, P., Nordgren, A., Buchmann, N., Taylor, A.F.S., Ekblad, A., Högberg, M.N., Nyberg, G., Ottosson-Löfvenius, M. & Read, D.J., 2001. *Large-scale forest girdling shows that current photosynthesis drives soil respiration*. Nature, 411, 789-792.

Högberg, M.N. & Högberg, P., 2002. *Extramatrical ectomycorrhizal mycelium contributes one-third of microbial biomass and produces, toghether with assosiated roots, half the dissolved organic carbon in a forest soil*. New Phytologist, 154, 791-795.

Levei, E., Frențiu, T., Ponta, M., Șenilă, M., Miclean, M., Roman, C. & Cordoș, E., 2009. *Characterization of soil quality and mobility of Cd, Cu, Pb and Zn in the Baia Mare area Northwest Romania following the historical pollution*. International Journal of Environmental Analytical Chemestry, 89, 8-12, 635-649.

Leyval, C., Turnau, K. & Haselwandter, K., 1997. *Effect of heavy metal pollution on mycorrhizal colonization and function: physiological, ecological and applied aspects*. Mycorrhiza, 7, 139-153.

Maiz, I., Arambarri, I., Garcia, R. & Millan, E., 2000. *Evaluation of heavy metal availability in polluted soils by two sequential extraction procedures using factor analysis.* Environmental Pollution, 110, 1, 3-9.

Mihali, C., Oprea, G., Michnea, A., Jelea, S.G., Jelea, M., Man, C., Șenilă, M. & Grigori L., 2013. *Assessment of heavy metals content and pollution level in soil and plants in Baia Mare area, NW Romania*. Carpathian Journal of Earth and Environmental Science, 8, 2, 143-152.

MO 756/1997. Ministerial Order approving the Regulation concerning the assessment of environmental pollution. Official Gazette 1997, Romania, Part I, no. 303bis/06.11.1997 [In Romanian].

Modoi, O.C., Vlad, Ş.N., Stezar, I.C., Manciula, D., Gagiu, A.C. & Mărginean S., 2011. *Integrated tailing dams management in Baia Mare area, Romania*. Environmental Engineering and Management Journal, 10, 1, 43-51.

Okoro, H.K., Fatoki, O.S., Adekola, F.A., Ximba, B.J & Snyman, R.G., 2012. *A Review of Sequential Extraction Procedures for Heavy Metals Speciation in Soil Sediments*, 1, 3, 181. doi: 10.4172/scientificreports.181.

Parkin, T.B., Doran, J.W. & Franco-Vizcaino, E., 1996. *Field and Laboratory Tests of Soil Respiration*. In: Doran J.W., A.J. Jones, editors. Methods for assessing soil quality. Madison, WI. 231-45.

Răuță, C., Ciobanu, R., Lăcătușu, R., Dumitru, M., Latiș, L., Dulvara, E., Gameț, E., Bud, V., Lungu, M., Enache, R. & Toti, M., 1997. *The state of soil pollution with heavy metals within Baia-Mare area*. Soil Science, 29B, 143-154.

Singh, J. & Kalamdhad, A.S., 2013. *Chemical speciation of heavy metals in compost and compost amended soil -a review*. International Journal of Environmental Engineering Research, 2, 2, 27-37.

Smith, S.E. & Read D.J., 2008. *Mycorrhizal Symbiosis* (3rd Ed.), Academic Press Ltd, London, UK, 295-320.

Smith, J.L. & Doran, J.W., 1996. *Measurement and use of pH and electrical conductivity for soil quality analysis*, pp. 169-185. In: Doran JW, Jones AJ, Editors, Methods for Assessing Soil Quality. Soil Science Society of America Special Publication 49, SSSA, Madison, WI.

Söderström, B. & Read, D.J., 1987. *Respiratory activity of intact and excised ectomycorrhizal mycelial systems growing in unsterilised soil*. Soil Biology and Biochemistry, 19, 231-236.

Trajkovic, I., Licina, V., Antic-Mladenovic, S. & Wenzel, W., 2014. *Hazardous elements speciation in sandy, alkaline coal mine overburden by using different sequential extraction procedures.* Chemical Speciation and Bioavailability, 26, 2, 85-91.

Vodyanitskii, Yu.N., 2006. *Methods of Sequential Extraction of Heavy Metals from Soils: New Approaches and the Mineralogical Control (A Review)*. Eurasian Soil Science, 39, 10, 1074-1083.

Wong, M.H., 2003. *Ecological restoration of mine degraded soils, with emphasis on metal contaminated soils*. Chemosphere, 50, 775-780.

Zimmerman A.J. & Weindorf D.C., 2010. *Heavy Metal and Trace Metal Analysis in Soil by Sequential Extraction: A Review of Procedures,* International Journal of Analytical Chemistry, article ID 387803, 1-7.

Received at: 17. 10. 2014
Revised at: 10. 08. 2015
Accepted for publication at: 02. 09. 2015