ANNEX B

VARIATION OF METAL UPTAKE BY *PINUS SYLVESTRIS* L.

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Abstract. The investigation focussed on uptake and distribution of heavy metals Pb, Cd, Cu, Zn and macronutrients K and Mg fluxes in *Pinus sylvestris* L. and soil under the sampled trees from heavily contaminated and control sites. The samples were analysed by flame atomic absorption spectrophotometry (FAAS) and graphite furnace (GFAAS). The element contents of pine wood and soil were compared between two sites, determining total and dissolved metal concentration in soil, soil properties, transfer factor (TF) and partitioning coefficient (log K_d). Results showed that the total concentrations of Pb, Cd, Cu and Zn in contaminated site were higher than the background values, particularly for Cu and Pb, however, limit values were not exceeded for all investigated metals. Mean concentrations of Pb, Zn and Mg in the wood of *Pinus sylvestris* L. were statistically ($p<0.05$) higher than in control site.

Keywords: Anthropogenic activities, *Pinus sylvestris* L., accumulation, heavy metals

Introduction

Large amounts of chemical substances in the environment (air, soil and water) have impact on humans and the natural systems. Heavy metals in substantial amounts are important environmental pollutants and their toxicity poses a problem of an increasing significance for ecological, evolutionary, nutritional, and environmental reasons (Benavides *et al* 2005). Heavy metals cause a serious problem because of their easy spread and accumulation in soil and plants (Pantera et al 2007; Stravinskienė 2005). The amount of heavy metal pollution in the environment is related with the degree of industrialization and the intensity of chemical usage (Akinola *et al* 2008). The contamination of forest ecosystems by heavy metals, such as lead (Pb), cadmium (Cd), cooper (Cu) and zinc (Zn) is a serious problem in industrial areas all over the world (Nuhoglu 2005).

Coniferous trees effectively filter pollutant particles from the air (Salemaa 2003). Moreover, the observed effect is a time-averaged result, which will be more reliable than direct determination of the pollutant concentrations in air, for a short period (Kord *et al* 2009).

Trees and especially coniferous species capture pollutants directly from the atmosphere, by deposition on the leaves or bark, or indirectly following deposition on the soil and subsequent root uptake (Nuhoglu 2006; Bellis 2002; Watmough 1999). Generally, conifers have much higher heavy metal content than decidous (Trüby 2005).

Pinus sylvestris L. is sensitive to environmental conditions changes and takes up large amounts of pollutants and translocates them into whole plant giving understanding about the quality of the environment (Mingorance *et al.* 2007).

Determination of plants chemical composition is one of the most frequently method used to monitoring of the environmental pollution. *Pinus sylvestris* L. meets many requirements for a good bioindicator among other tree species (Rudovica *et al* 2006). It is well known that changes of metal concentrations are related to the processes involving the uptake, transformation, storage and retranslocation of the elements. In pines, some metals are accumulated in roots (especially Pb), probably due to physiological barriers against metal transport to aerial parts, while others are easily transported in plants, for example Cd (Boruvka *et al* 1997; Kabata-Pendias and Pendias 2000). Therefore, the uptake of heavy metals by *Pinus sylvestris* L. is a complex process and its efficiency depends on the soil pH, redox potential, soil texture, soil organic matter content, soil metal content and metal availability (Baltrėnaitė and Butkus 2007; Seregin and Ivanov 2000). Depending on the element, tree species and availability of metal in the soil, the accumulation of metals varies (Trüby 2005). The main source of heavy metals entering the wood is related to the heavy metal uptake by roots from soils and to the heavy metal deposition from the atmosphere onto the needles and bark with partial translocation into the wood (Scherbenko *et al* 2005).

Data on the elemental composition of perennial plant organs, especially stem wood are scarce and they are especially rare for forests under conditions of aerial pollution (Shcherbenko *et al* 2008; Saarela *et al* 2005; Watmough and Hutchinson 1996). The knowledge of the

elemental content in a stem wood and other *Pinus sylvestris* L. related materials are of great environmental and industrial interests (Saarela et al 2005).

To evaluate tree responses to heavy metals, transfer factor (TF) to mirror metal uptake is calculated (Alloway 1995; Adriano *et al* 2001; Prasad et al 2006; Butkus and Baltrėnaite 2007). It allow to quantify the relative differences in bioavailability of metals to plants (Alloway and Ayres 1997). The transfer factor is based on root uptake, however plants can accumulate large amount of metals by absorption of atmospheric deposits on tree needles or bark (Alloway and Ayres 1997).

The partition coefficient (log K_d) is identified as critical parameter in sensitivity analyses of studies, looking at environmental impacts of contaminants (MacDonald and Hendersshot 2006). Moreover, it is extremely useful tool for metal risk assessment studies (MacDonald and Hendersshot 2006; Watmough et al 2005).

The aim of this work was to determine distribution of metals in the *Pinus sylvestris* L. stands and to evaluate whether atmospheric metal emissions from industry had mirrored metal concentrations in the wood of *Pinus sylvestris* L.

Materials and methods

Site description and sampling

Two sampling plots contaminated and control, located in Lithuania (Eastern Europe) were analysed in the study.

First sampling plot is located in the city of Panevėžys ($55^0 44´0´´N$, $24^0 21´0´´E$) near former TV manufacturing company (Fig 1). For more than 40 years, this factory had been manufacturing glass components, colour TV-tubes and electron-gun systems. It was the only manufacturer of TV tubes in the Baltic States from 1962 years (AB Ekranas Annual… 2004). Intensive heavy metal contamination was formed from the manufacturer aerosol emission significantly influencing the total soil geosanitary state. Heavy metals migrated into the deeper soil horizons. Moreover, high heavy metal and particularly lead concentrations are dominated in soil around company sanitary zone (Panevezys city…2007).

The second sampling place is located near the city of Kaunas () in the experimental forest of Dubrava Institute (Fig 1). The control plot have similar soil type and species, additionally, area is out of the influence of any nearby pollution source.

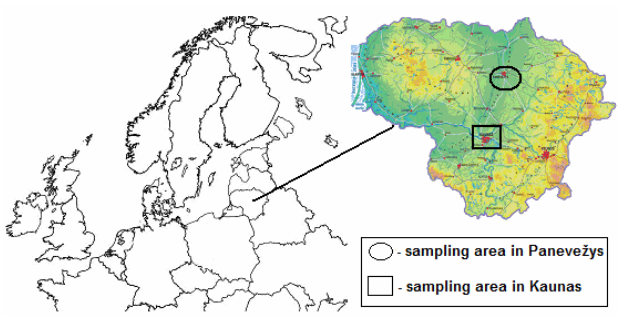

Figure 1. Location of the sampling sites in Lithuania

Figure 2. Location of the contaminated study site. The sampling plot is situated near the main stack.

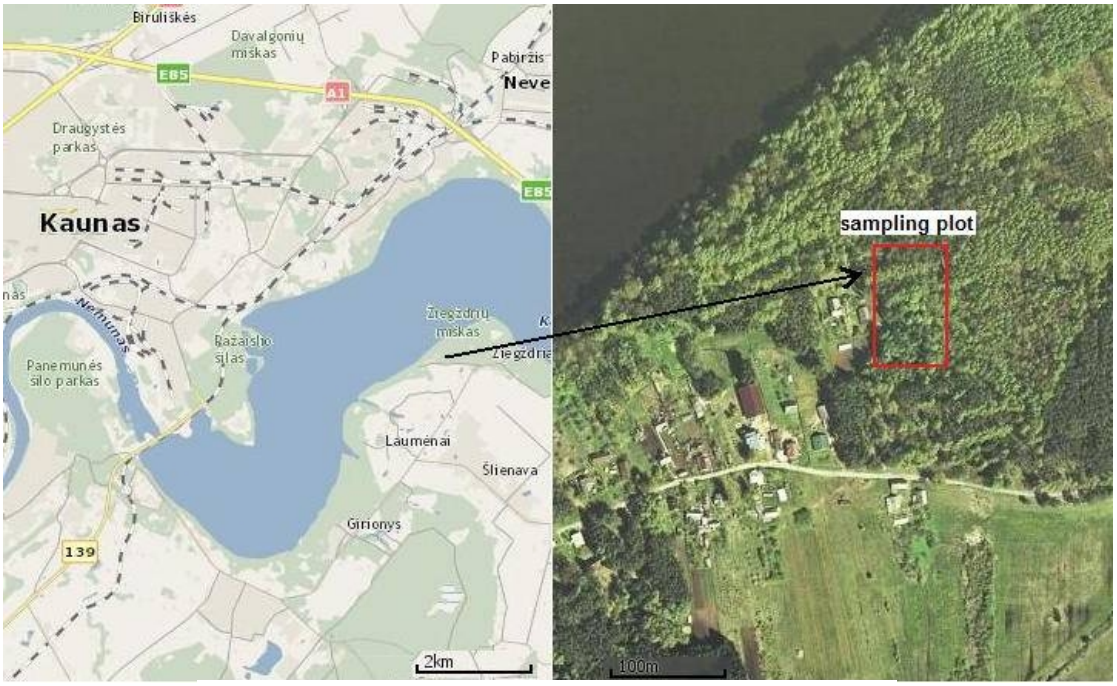

Figure 3. Location of the control study site

Sampling was carried out in early May 2009, during vegetation period when plants are most physiologically active (Fig 2). The contaminated site is located about 200 m from a company. Southwest winds are reported to be dominant (Panevėžys county...2005). Sample trees were at least 10 m away from each other. Ten pine trees were randomly selected in each control and contaminated plots. Tree (*Pinus sylvestris* L.) cores were taken at breast height (1.5 m) from the north–facing side (facing the industry) (Watmough and Hutchinson 2005) using acid washed 10 mm stainless steel increment borer. Samples were immediately sealed in dry, plastic straws and were stored for further analysis.

Soil samples were collected and stored in plastic bags, near the selected trees from depth of 0–20 cm.

Chemical analyses

Each core were burnt for 45 min in E5CK-T muffle furnace (450^0C) and weighted, then mixed with 9 ml HCl (37%) and 3 ml HNO_3 (65%), poured into special vessels and then placed into a Milestone ETHOS digestor and heated for 30 min. The solution was then poured into 50 ml flask and diluted with distilled water to reach the marks of 50 ml (Butkus and Baltrėnaitė 2007).

Soil samples were air dried at room temperature ($20–22^0$C) for 24 hours, sieved (2 mm mesh) and weighing 0.2 g. Then poured into mineralization vessels and the same methods described in pinewood analysis were used. The total concentrations of metals in soil and wood samples were determined by flame atomic absorption spectrophotometry (FAAS). A graphite furnace (GFAAS) was employed to determine metal concentrations when they were too low to be detected accurately by FAAS (Butkus and Baltrėnaitė 2007).

Soil extractable metals were assessed by water extraction of 20 g soil in 100 ml of distilled deionised water. Soil-water samples were shaken in *Gerhardt, Rotoshake RS 12* for 1 hour and left for settle. Afterwards extracts were collected by filtration through filter paper and analysed for Pb, Cd, Zn, Cu, K, Mg concentrations by FAAS or GFAAS.

Soil pH (sieved only) was measured using a soil water ratio 1:5 and a glass electrode pH meter. 20 g of the soil was mixed with 100 ml distilled deionised water and was shaken for 1 hour using mechanical shaker *Gerhardt, Rotoshake RS 12*. The mixture was allowed to stand for 60 minutes to allow it to settle. The electrode of pH meter – *pH 538 WTV* was put into the slurry and measured 3 times in one solution.

TF for metals Pb, Cd, Zn, Cu, Mg, K were determined by dividing the mean metal concentration in pinewood (stem) for the average total metal concentration in the soil (Alloway 1995; Adriano et al 2001; Butkus and Baltrėnaite 2007):

$$TF = \frac{C_{pinewood}}{C_{soil}}, \qquad (1)$$

where $C_{pinewood}$ – mean metal concentration in pinewood stem, mg kg^{-1} DW; C_{soil} – mean total metal concentration in soil mg kg^{-1} DW.

Partition coefficient log K_d of soil was calculated as:

$$\log K_d = \log \frac{C_{TotalMetal}}{C_{DissolvedMetal}}, \quad (2)$$

where $C_{Total\ Metal}$ – mean total metal concentration in the soil, mg kg^{-1} DW; $C_{Dissolved\ Metal}$ – the mean metal concentration in soil solution, (mg kg^{-1} DW) (MacDonald and Hendersshot 2006).

Total organic carbon (TOC) was determined using apparatus TOC-V by SHIMADZU at 900^0 C temperature. TOC content was recalculated using Equation 3:

$$W_{C,t} = 1000 \times \frac{m_2}{m_1} \times 0.272, \quad (3)$$

where Wc,t – TOC on basis of air–dried soil, g kg^{-1}; m_1 – mass (g) of test portion, g; m_2 – mass of released CO_2, g; 0.2727 – conversion factor for CO_2 to C (ISO 10694:1995).

Data analysis

Some descriptive statistics were performed, average and standard deviation (SD), moreover, Pearson correlation coefficient was calculated between soil pH and metals accumulation in the contaminated site. Statistical significance between metals concentrations between contaminated and control plot were assessed with a student *t*. A multivariate analysis of the results was done using principal component analysis (PCA). The differences were considered significant at $p<0.05$. All calculations were performed using the statistical packages Statistica 6.0 (Statsoft.Inc).

Results and discussion

Total elements in soil

Soil pH, total organic carbon (TOC) and total and bioavailable metals in control and contaminated soil plots are presented at Table 1 showing the differences between investigated plots.

The pH of the soils varied from 5.69 to 7.78 and 4.62 to 6.04 in contaminated and control sites, respectively, indicating moderately acid to slightly alkaline soil at contaminated site, strongly acid to moderately acid at control. The total organic carbon (TOC) was ranging from 1.52 to 9.98 g/kg at contaminated and 0.39 to 9.86 g/kg at control site. The averages of soil pH and TOC in depth 0-20 of soil profile at contaminated and control sites were summarized in Table 1. Soil organic matter is, together with soil pH, the most important parameter controlling heavy metal behaviour in soils (Borůvka and Drábek 2004). Soil pH acts significantly in the soil oxidation-reduction reactions and also in the formation of bioavailable metal forms (Grigalavičienė et al. 2005).

According to Watmough et al. total metal concentrations in the upper (0 – 5 cm) mineral soil were ranging from 0.14 – 1.93 mg kg^{-1} for Cd, 12.5 – 128 mg kg^{-1} for Zn and 7.0 – 55.9 mg kg^{-1} for Pb.

Total metal concentrations in depth (0-20 cm) of soil under the sampled trees at contaminated plot ranged from 8.42-37.4 mg kg^{-1} for Pb; 0.167-0.483 mg kg^{-1} for Cd; 12.7-31.7 mg kg^{-1} for Cu; 18.5-114.5 mg kg^{-1} for Zn. K was ranging from 617.7-2096.7 mg kg^{-1}; Mg from 271.7- 1986.6 mg kg^{-1}. The concentrations for Cd, Zn and particularly for Cu and Pb were higher than the background values at contaminated plot, though limit values were not exceeded for all investigated metals. Pb, Cd, Cu and Zn background and limit values from standard are given on Table 2 (HN 60:2004)

Table 2 Heavy metals background values and limit values concentration in moderate sandy soil (HN 60:2004)

Metal	Background values, mg/kg	Limit values mg/kg
Pb	15	100
Cd	0.15	3
Cu	8.1	100
Zn	26	300

Total metal concentrations (0-20 cm) of soil under sampled trees at control plot ranged from 1.56-5.03 mg kg^{-1} for Pb; 0.02-5.16 mg kg^{-1} for Cd; 0.006-0.03 mg kg^{-1} for Cu; 22.5-96.5 mg kg^{-1} for Zn. K was ranging from 608.8-2060.0 mg kg^{-1}; Mg from 375.7-632.7 mg kg^{-1}. The total concentrations of Pb and Cu (except Zn and Cd) under trees in control plot were below their environmental background values (Fig. 3.2), indicating that this area received minimal atmospheric heavy metals input (Kuang *et al.* 2007).

Total Pb and Cu concentrations in contaminated plot were statistically ($p<0.001$***, n=40) higher than those at control, and indicate contamination of this plot by these heavy metals (Table 1).

Bioavailable metals

According to Watmought *et al.* bioavailbale metal concentrations in the upper mineral soil were ranging

from 0.05 – 0.9 μg L^{-1} for Cd, 2.0 – 119 μg L^{-1} for Zn and 0.13 – 27.0 μg L^{-1} for Pb.

Bioavailable heavy metal concentrations in the contaminated plot were ranging from 0.05 – 0.23 mg L^{-1} for Pb, 0.003 – 0.02 mg L^{-1} for Cd, 0.01 – 0.21 mg L^{-1} for Cu, 0.14 – 0.93 mg L^{-1} for Zn. For K were ranging from 7.83 – 52.33 mg L^{-1} and for Mg from 2.72 – 29.68 mg L^{-1}. In the control plot heavy metal concentrations were 0.002 – 0.03 mg L^{-1} for Pb, 0.00003 – 0.0002 mg L^{-1} for Cd, 0.0001 – 0.0008 mg L^{-1} for Cu, 0.079 – 0.58 mg L^{-1} for Zn. Macronutrients in the control plot were ranging from 3.47 – 27.23 mg L^{-1} for K and from 0.6 – 7.71 mg L^{-1} for Mg.

Average concentrations of Pb, Cd, Cu, Zn, K and Mg in control site were significantly (p<0.001) lower than in contaminated site (Table 1).

Table 1 Soil pH, TOC and total and bioavailable metals, in control and contaminated soils. Significant differences between plots, at a p<0.001***. n.s (non significant). Data in mg kg^{-1} DW in total elements and in mg L^{-1} in bioavailable concentrations

	Control (*N*=10)	Contaminated (*N*=40)	*p*
pH	5.29±0.09	6.59±0.06	***
TOC	2.47±0.48	4.22±0.34	***
Mg^{tot}	497.32±73.19	497.72±72	n.s
K^{tot}	1282.12±87.23	1106.60±61.68	n.s
Pb^{tot}	2.99±3.24	25.63±2.29	***
Cd^{tot}	0.719±0.19	0.278±0.13	n.s
Cu^{tot}	0.01±0.80	23.18±0.56	***
Zn^{tot}	40.47±5.45	36.88±3.58	n.s
Mg^{bioav}	2.40±1.17	8.44±0.83	***
K^{bioav}	7.81±2.15	24.42±1.52	***
Pb^{bioav}	0.007±0.006	0.11±0.004	***
Cd^{bioav}	0.00004±0.001	0.009±0.0007	***
Cu^{bioav}	0.0002±0.007	0.076±0.005	***
Zn^{bioav}	0.22±0.03	0.51±0.02	***

Table 2 shows the percentage of bioavailable metal of total metals in control and contaminated plots.

Table 2 % of bioavailable metals in control and contaminated soils. Significant differences between plots, at a p<0.001*. n.s (non significant). Data in %.

	Control (*N*=10)	Contaminated (*N*=40)	*p*
Mg	0.45±0.15	1.766±0.11	*
K	0.68±0.18	2.24±0.13	*
Pb	0.25±0.07	0.61±0.05	*
Cd	0.03±0.44	3.70±0.31	*
Cu	2.11±0.35	0.36±0.24	*
Zn	0.66±0.17	1.77±0.12	*

Total elements in wood

Concentrations of heavy metals in a pinewood in contaminated area varied: Pb – 15.5-68.1 mg/kg; Cd – 0.002-0.013 mg/kg; Cu – 0.097-0.57 mg/kg; Zn – 0.775-2.182 mg/kg; macroelements varied: K – 24.13-72.76 mg/kg; Mg – 30.53-65.83. Concentrations of metals in control area varied: Pb – 0.009-0.036 mg/kg; Cd – 0.001-0.007 mg/kg; Cu – 0.07-0.65; Zn – 0.47-1.64 and macroelements: K – 22.91-55.49 mg/kg; Mg – 11.29 – 55.57mg/kg.

Heavy metal concentrations in sampled pine wood at two sites are shown in Table 3.5. Pb, Cu and Zn, except Cd, concentrations in pinewood in contaminated site was statistically higher (p>0.05* and p<0.001**) than those at control plot.

Table 3 Concentration of elements in wood in control and contaminated plots. Significant differences between plots, at a p>0.05* and p<0.001**. n.s (non significant)

	Control (*N*=10)	Contaminated (*N*=40)	*p*
Mg	20.56±2.99	39.51±2.11	**
K	32.18±2.55	41.95±3.61	*
Pb	0.01±4.10	34.49±2.90	**
Cd	0.003±0.0006	0.004±0.0004	n.s
Cu	0.172±0.03	0.258±0.02	*
Zn	0.93±0.11	1.36±0.08	**

The concentration of Pb in contaminated pine wood showed the highest increase compared to control samples. The mean of Pb concentrations were 39.51(±2.11) in contaminated and 0.01(±4.10) in the control site. Pb is not an essential element, however, is easily absorbed and accumulated in different tree parts (Sharma and Dubey 2005). Mean concentration of Zn in contaminated wood was 1.5 times higher than in control wood. In all tree species Cu was taken up to a higher degree than Cd (Bräker et al 1994). The mean concentrations of Cd of 0.005(±0.0035), Cu 0.286(±0.176) and Zn 1.364(±0.611) were slightly higher at contaminated than those of Cd (0.004±0.002), Cu (0.172±0.17) and Zn (0.930±0.333) at control.

The mean heavy metal concentration values following decreasing order: Pb>Zn>Cu>Cd in contaminated site and Zn>Cu>Pb>Cd in control site. The close relationship between Pb concentration and Pb anomaly, formed from manufacturer has been visible in pinewood, concentration of Pb ranging from 13.14 to 114.65 mg/kg. In most environmental conditions, Cd enters first the roots, and only small amount are transported to the shoots, the content decreases in order: roots>stems>seeds (Benavides *et al* 2005). The average concentration of Cd was 0.005±0.003 mg/kg and 0.004±0.002 mg/kg in contaminated and control sites respectively. Cu content in

stemwood, generally, was very low, even with an extremely high soil contamination (Trüby 2005).

K is the only macroelement that does not have a structural role in the tree, however, its needed in relatively large quantities to serve its various regulatory functions (Davey 2005). Pinewood is characterized by the lower contents of macronutrients in comparison with the other organs (Shcherbenko *et al* 2008). As a consequence, the mean concentrations of macronutrients K 41.96(±18.77) and 32.19(±10.01), Mg 39.51(±13.89) and 20.57(±13.11) at contaminated and control sites respectively in both sites were low.

In general, Cd is effectively absorbed by plant roots and accumulated in aboveground organs, having thus a comparatively high transfer soil-tree factor. Zinc has relatively high transfer factor from soil to tree and most plants can tolerate high Zn levels. Pb is rather immobile in soil and easily forms organic complexes with fulvic acids. In addition, it concentrates primarily in the roots and is poorly translocated to the tree parts, resulting in a comparatively low transfer factor from soil to tree (Madejon et al 2004). Heavy metals such as Zn, Cd are readily translocated to the top of tree, Cu is intermediate and Pb is translocated to the least extent (Alloway 1995).

Principal components analysis (PCA)

PCA is a useful tool in the examination of multivariate data (Topalian *et al.* 1999). The aim of using PCA was to ascertain any patters in the all samples in relation to chemical characteristics and make a preliminary conclusion to the possible relationship among metals in soil, wood and soil properties (Jia *et al.* 2010).

The results of the current study show that, with the exception of total Mg, K, Cd and Zn in soil and Cd in pinewood, the concentrations of most elements were significantly higher in the contaminated plot (Table 3.1; Table 3.4). PCA was used to compare soil and wood samples at both plots. PCA incorporates the data from all metals in all the samples for an unified comparison. The aim of this statistical analysis is, beginning from numerous set of variables, to get another substantially minor set of variables, which preserves the maximum information of the original set (Granero and Domingo 2002). This analysis provided a single two-dimensional model, which explains 61.5 % of the variance in the data (component 1 – 47.4%; component 2 – 14.1%). Figure 3.5 shows the scatterplot of all components. Two clusters, which separate in a clear from both sampling plots, contaminated and control, can be identified.

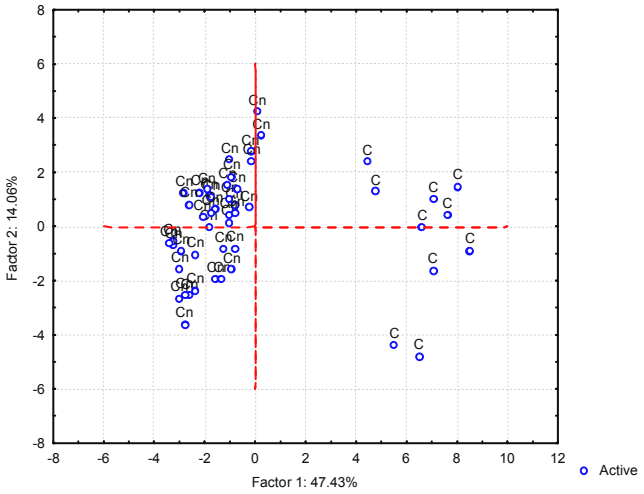

Figure 4 Relation between Factor 1 and Factor 2 (Cases). Principal component plot of all samples collected in contaminated (Cn) and control plots

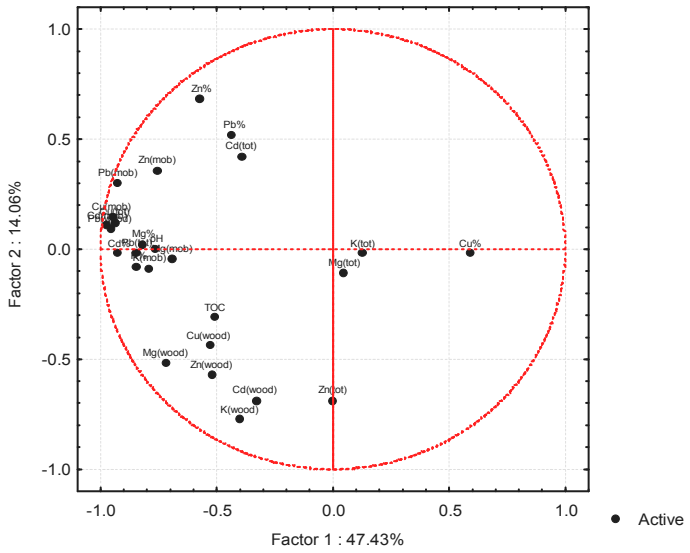

Figure 5 Relation between Factor 1 and Factor 2 (Variables)

Figure 3.6 shows the relation among pH, TOC, mobile and total metals and wood metals, figure shows three separate clusters from two sampling plots. In the first cluster the correlation of mobile metal forms and soil pH is visible, while in the second one is correlated TOC and metals in pinewood. This demonstrates that soil organic matter with soil pH is important parameters controlling heavy metal behaviour.

Acknowledgement

We gratefully acknowledge the colleagues from the Department of Environmental Protection at Vilnius Gediminas Technical University chemical analysis as well as Giedrė Raginytė and Laimonas Cvirka for assistance in the field and laboratory work.

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