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**Contents and forms of potentially toxic elements in reclaimed
dumpsite soils after brown-coal mining in Northern Bohemia**

Diploma Thesis

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Declaration

I declare that the Master Thesis Contents and forms of potentially toxic elements in reclaimed dumpsite soils after brown-coal mining in Northern Bohemia is my own work and all the sources I cited in it are listed in Bibliography.

Prague, 10.4.2015

Anna Vasilkova

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Summary

It is an ordinary practice to cover the areas after brown-coal mining with natural topsoil cover (topsoiling). Topsoiling is removal one topsoil from agricultural land, forest or area with vegetation and excavating to another place with poor organic matter content or in our case the brown-coal mining dumpsite. Advantages of topsoiling include higher organic matter and greater available water-holding capacity and nutrient content. Content of potentially toxic elements is very low. Ammonia nitrate (NH_4NO_3) extraction, BCR sequential analysis and aqua regia determination were applied in this study to prove that the proportion of bioavailable forms of PTE in reclaimed soils is also low. Amounts of potentially toxic elements were compared between different types of reclamation: an agricultural shown higher value for Pb and Cd, forestry has only one contaminant – Cd. The research shows that toxicity of soil is low and has no dangerous influence for agricultural application.

Keywords: brown-coal mining dumpsites, topsoiling, potentially toxic elements

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1. Introduction

Large-scale open-cast mining of brown coal is a frequently applied method of mining all over the world. It leads to formation of permanent dumps of sterile rock. Brown-coal mining dumpsites are a problem of our days. In Northern Bohemia, dumpsites account for a large area (more than 8000 ha). The issue is that the works in mining are over the soils leave there with very low content of organic matter or even without. It means that soil after mining is getting useless: it cannot produce agricultural goods nor have a forest to be helpful for the all creatures, it has no vegetation and the land becomes deserted.

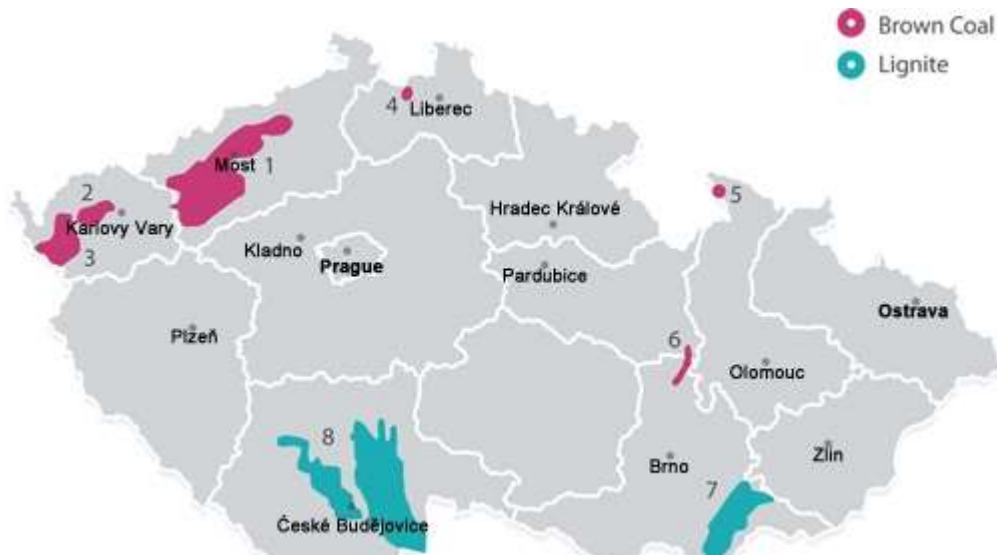
There are a lot of reclamation measures to give the areas, soils the second life. The reclamation measures which were used in the dumpsites I observe are agricultural, forestry, topsoiling. Topsoiling is removal one topsoil from agricultural land, forest or area with vegetation and excavating to another place with poor organic matter content or in our case the brown-coal mining dumpsite. Advantages of topsoiling include higher organic matter and greater available water-holding capacity and nutrient content.

The aim of this study is determination the content and forms of potentially toxic elements (PTE) in selected reclaimed dumpsite soils after brown coal mining in Northern Bohemia, as related to reclamation method with the help of different laboratory methods of determination like ICP-analysis and BCR sequential extraction and more advanced standardized aqua regia extraction. Another aim is to understand how useful application of topsoiling reclamation measure.

2. Literature review

2.1. General information about brown-coal mining dumpsites

Borůvka et al., 2012 demonstrated that large-scale open-cast mining of brown coal is a commonly used method of mining in many parts of the world. It leads to formation of permanent dumps of sterile rock. Gholizadeh et al., 2015 presented that mining is one of the anthropogenic activities that causes some of the most dramatic disturbances to the earth. Fertile, cultivated land is transformed into wasteland, as mining activities generate a vast amount of solid wastes, which are deposited at the surface and typically occupy a huge area. Among the various geo-environmental impacts of mining, contamination of soil is by far the most significant. Elevated concentrations of Potential Toxic Elements (PTEs) in soils do not only impact the soil quality, but due to their persistent nature and long biological half-lives, can accumulate in the food chain and can eventually influence human health. Boruvka et al., 2012 shown that the brown-coal mining dumpsites are often very clayey, with no or very low organic matter content, and sometimes also with unfavorable soil reaction. In Northern Bohemia, these dumps account for a large area (more than 8000 ha). In agreement with the Czech legislation, an effort is concentrated on landscape reclamation and restoration. One reclamation measure consists in soil covering with natural topsoil. It should increase mainly organic matter content and improve nutrients status. Physical properties, particularly soil structure, are often improved. Moreover, topsoiling should increase biodiversity of the newly created soils and accelerate vegetation succession favoring earlier development of a native shrub community. However, the topsoil removal, handling and storage prior to its use for reclamation must be performed with care to keep its favorable properties. The spatial heterogeneity of the anthropogenic soils is caused by the heterogeneity of the deposited material. It includes sterile rock originating from different depths, remains of brown coal carbon, and possibly added material rich in organic matter. The variability of anthropogenic soils did not develop naturally as a result of pedogenic processes and natural spatial distribution, as it is the case in natural soils, but it is the result of human activities. The time-scale of the reclaimed dumpsite soils development is too short for the soil-forming factors to manifest fully. Nevertheless, temporal changes of reclaimed soils even at the initial stages of their development are very important.



Picture 1. The area of research. Violet color №1. (Source: Technical University of Ostrava, 2014).

2.2. Classification of lands and types of reclamation

The most common type of land reclamation involves land with unfavorable water conditions (The Great Soviet Encyclopedia, 1979). In swamps and excessively wet lands reclamation is aimed at increasing aeration of the soil, improving its temperature, and stimulating the aerobic decay of organic matter. These goals are achieved by draining the land—that is, by removing excess water from the soil cover by means of ditches or pipes that run into streams or other bodies of water. In arid farming regions where there is little precipitation and the rate of evaporation is high, reserves of soil moisture are supplemented by water brought to the fields by artificial means (irrigation ditches or pipes). In many cases this technique is combined with selective oasis irrigation (in deserts, for example). Where there is little water, management of water resources is improved by seasonal and long-term regulation of river flows, which may be accomplished by building a reservoir, by changing the flow within a basin, or by excavating a new channel. In places where rivers have insufficient carrying capacity their channels are regulated. Low-lying areas are improved by siltation. The set of measures designed to improve the unfavorable water conditions of a region is referred to as hydro mechanical land reclamation.

Land with unfavorable chemical and physical characteristics is improved by agricultural technology and chemical reclamation measures. In steppe and desert regions saline soils and solonchaks containing an excess of salts, which are harmful to most agricultural crops, are improved by leaching, by applying gypsum, and by deep tillage. Chemical reclamation agents such as gypsum, calcium chloride, iron sulfate, and sulfuric acid help remove soda, the salt most

toxic to agricultural plants, from the soil. Liming increases the fertility of acid soils. On sandy soils large quantities of organic fertilizers are applied, legumes are planted, and clay is spread. Sand is applied to heavy soils. The plowing horizon is made deeper on compacted soils. Uneven surfaces are graded.

The reclamation of lands subject to the harmful mechanical action of wind or water entails preventing the erosion of soils by surface water and wind and combating moving sands, landslides, and gullies. On eroded land, reclamation measures aim at reducing the amount and the speed of surface runoff, increasing the soil's resistance to movement and to water and wind erosion, and establishing obstacles to soil movement and the action of water and wind. Hydraulic engineering methods are applied to achieve these ends. Man-made terraces, water retention ridges, and ditches are built to eliminate soil erosion on slopes, diversion canals are dug along the edges of gullies, hydraulic engineering structures are built to regulate flow and prevent gullying, and shelterbelts are planted (The Great Soviet Encyclopedia, 1979).

The type of Bohemian dumpsites reclamation is topsoiling. The entire characteristics see further.

2.3. Topsoil

Topsoil is the upper, outermost layer of soil, usually the top is from 5.1 cm to 20 cm. It has the highest concentration of organic matter and microorganisms and is where most of the Earth's biological soil activity occurs. Plants generally concentrate their roots in and obtain most of their vital nutrients from this layer. The actual depth of the topsoil layer can be measured as the depth from the surface to the first densely packed soil layer known as subsoil.

As has been shown (Tucker et al., 1995) topsoil often needs amending with lime, fertilizer or organic matter. Use of topsoil is increasing in rapidly developing areas where the native soil is predominantly clay. Concerns have been raised about using clay-based soils for landscaping or lawns.

2.4. Deciding when to use topsoil

To use topsoil effectively, you must know two things: what kind of soil you are amending and what kind of result you hope to achieve. If your goal is to improve drainage, your strategy will be different than if your goal is to increase water-holding capacity. Applying appropriate amendments can help alleviate either problem. For example, in North Carolina, topsoil is often applied to "improve" existing clay-based soils. The topsoil chosen for this purpose is likely to be sandy. This scenario sets the stage for increased nutrient deficiencies,

acidity problems and moisture stress. The very qualities of sandy soils that improve drainage can trigger these other problems. In such cases, the soil is better amended with a combination of topsoil and organic matter. Amendments that include compost, rotten sawdust, manure, peat moss or aged tree bark can improve drainage, soil porosity, nutrient retention and soil pH. They can also increase biological activity and promote root growth. Your decision to apply topsoil will be based on the qualities of the topsoil and the qualities of the soil you want to amend (Tucker et al., 1995).

2.5. Evaluating topsoil quality

A soil test is the most reliable way to determine the quality of topsoil. Typical test results from a bulk soil and a bagged soil are given in Table 1. Most native bulk soils tested have low pH and nutrient content, both of which can be corrected with appropriate amendments. The addition of amendments, such as lime and fertilizer, also improves granulation of soil particles (Tucker et al., 1995).

Table 1. Typical soil test results from bulk and bagged topsoil

Topsoil	HM%	BS%	pH	P-I	K-I	Ca%	Mg%
Bulk	0,3	69	6,2	9	26	45	10
Bugged	0,7	78	6,8	166+	178	56	12,3

Table 2 presents some guidelines for evaluating topsoil quality. The parameters shown are within ranges that should produce good plant growth. They apply to both bulk and bagged topsoils.

Table 2. Desired levels of soil nutrients

pH	5,8-6,2
phosphorus index (P-I)	50
potassium index (K-I)	50
calcium (Ca%)	40–60% of CEC*
magnesium (Mg%)	8–10% of CEC*
base saturation (BS%)	60–80% of CEC*
manganese index (Mn-I)	> 25
zinc index (Zn-I)	> 25
copper index (Cu-I)	> 25

*CEC = Cation Exchange Capacity = Ca + Mg + K + Acidity; CEC is a measure of the quantity of nutrients a soil will hold. Ca% = [(Ca/CEC) × 100] Mg% = [(Mg/CEC) × 100].

2.6. Optimizing water movement

The mechanics of water movement through soil is often misunderstood. If a layer of sand is placed on top of a clay-based soil, water moves readily through the sand and is absorbed by the clay. In contrast, if sand is placed below the clay, water moves into the sandy layer only when the clay soil is totally saturated. Therefore, placing a layer of sand on a poorly drained clay-based soil has no effect on drainage of the clay. Drainage of soils can be improved with any treatment that enhances granulation or aggregation of soil particles. Such treatments include lime, gypsum (calcium sulfate), organic matter, sand or a combination of all of the above. When adding topsoil or other treatment to an existing soil, mix the two thoroughly for best results (Tucker et al., 1995).

2.7. Topsoiling

As Boutiette et al., 1994 demonstrating: preserving and using topsoil in need to provide a suitable growth medium and enhance final site stabilization with vegetation (Boutiette et al., 1994).

Practice Applies:

- Where a sufficient supply of quality topsoil is available.
- Where slopes are 2:1 or flatter.
- Where the subsoil or areas of existing surface soil present the following problems:
 1. The structure, pH, or nutrient balance of the available soil cannot be amended by reasonable means to provide an adequate growth medium for the desired vegetation.
 2. The soil is too shallow to provide adequate rooting depth or will not supply necessary moisture and nutrients for growth of desired vegetation.
- The soil contains substances toxic to the desired vegetation.
- Topsoiling is strongly recommended where ornamental plants or high maintenance turf will be grown.

Advantages of topsoil include higher organic matter and greater available water-holding capacity and nutrient content. Topsoil stockpiling ensures that a good growth medium will be available for establishing plant cover on graded areas. The stockpiles can be used as noise and view baffles during construction.

Disadvantages/Problems: Stripping, stockpiling, and re-applying topsoil, or importing topsoil may not always be cost-effective. It may also create an erosion problem if improperly secured. Unless carefully located, storage banks of topsoil may also obstruct site operations and therefore

require double handling. Topsoiling can delay seeding or sodding operations, increasing exposure time of denuded areas. Most topsoil contains some weed seeds (Boutiette et al, 1994).

Planning Considerations:

Topsoiling may be required to establish vegetation on shallow soils, soils containing potentially toxic materials, very stony areas, and soils of critically low pH. Topsoil is the surface layer of the soil profile, generally characterized as being darker than the subsoil due to the presence of organic matter. It is the major zone of root development and biological activities for plants, carrying much of the nutrients available to plants, and supplying a large share of the water used by plants. It should be stockpiled and used wherever practical for establishing permanent vegetation. The need for topsoiling, should be evaluated. Take into account the amount and quantity of available topsoil and weigh this against the difficulty of preparing a good seedbed on the existing subsoil. Where a limited amount of topsoil is available, it should be reserved for use on the most critical areas. Make a field exploration of the site to determine if there is surface soil of sufficient quantity and quality to justify stripping.

More topsoil (more than 10 cm) will be needed if the subsoil is rocky. Topsoil should be friable and loamy (loam, sandy loam, silt loam, sandy clay loam, and clay loam). Areas of natural ground water recharge should be avoided. Allow sufficient time in scheduling for topsoil to be spread and bonded prior to seeding, sodding, or planting. Do not apply topsoil if the subsoil has a contrasting texture. Sandy topsoil over clayey subsoil is a particularly poor combination; water can creep along the junction between the soil layers and causes the topsoil to slough (Boutiette et al., 1994).

Stripping:

Stripping should be confined to the immediate construction area. A 4(10, 16 cm) to 6(15, 24 cm) inch stripping depth is common, but depth may vary depending on the particular soil. All surface runoff control structures should be in place prior to stripping.

Disadvantages/Problems:

- Locate the topsoil stockpile so that it does not interfere with work on the site.
- Side slopes of the stockpile should not exceed 2:1.
- Surround all topsoil stockpiles with an interceptor dike with gravel outlet and silt fence.
- Either seed or cover stockpiles with clear plastic or other mulching materials within 7 days of the formation of the stockpile.

Placement:

- Topsoil should not be placed while in a frozen or muddy condition, when the subgrade is excessively wet, or when conditions exist that may otherwise be detrimental to proper grading or proposed sodding or seeding.

- Do not place topsoil on slopes steeper than 2:1, as it will tend to slip off.
- If topsoil and subsoil are not properly bonded, water will not infiltrate the soil profile evenly and it will be difficult to establish vegetation. The best method is to actually work the topsoil into the layer below for a depth of at least 6 inches.

Maintenance:

- Maintain protective cover on stockpiles until needed (Boutiette et al, 1994).

2.8. Potentially toxic elements (PTE)

Kicku et al, 2000 found that potentially toxic elements (PTE) like iron (Fe), zinc (Zn), copper (Cu) and manganese (Mn) are essential trace elements to plant life while lead (Pb), chromium (Cr), nickel (Ni) and cadmium (Cd) are toxic even in a very low concentrations. However, all these metals are toxic beyond a certain threshold value that may vary with nature and species of element and plant. The accumulation of PTE may vary from plant to plant from soil to soil.

Keil et al, 2011 considered four toxic elements: arsenic As, cadmium Cd, lead Pb, and mercury Hg.

Arsenic is widespread in the environment. Arsenic's toxicity depends largely on the valence state, solubility, and rate of absorption and elimination. The 3 major groups for arsenic include arsine gas (-3 oxidation state), inorganic, and organic forms. Arsine gas is the most toxic arsenical. Inorganic arsenic compounds that also have high toxic potential include arsenite (trivalent), arsenate (pentavalent), arsenic oxide, and gallium arsenide. Metabolites of inorganic arsenic compounds include methyl and phenyl derivatives of arsenic such as monomethylarsonic acid (MMA) and dimethyl arsenic acid (DMA) and have moderate toxic potential. The methylated metabolites may arise from the environment or by metabolism of inorganic arsenicals. Arsenobetaine and arsenocholine are the most common organic forms, sometimes called "fish arsenic," and are relatively nontoxic to humans.

Cadmium is often found near sites of metal mining and refining, production and application of phosphate fertilizers, waste incineration, and disposal. Occupational exposure to cadmium is a serious consideration in the battery, smelting, and electroplating industries. Soluble forms are transported easily by water and accumulate in aquatic organisms. Cadmium may also be transported as a particle or vapor for long distances in the atmosphere, depositing on soil and water surfaces. Cadmium binds strongly to organic matter where it is immobilized in soil and taken up by plant life and agricultural crops.

Lead is found in the earth's crust that has been mobilized in the environment by recent anthropological activities. Lead is malleable, corrosion-resistant, ductile, and is present primarily in its divalent form (Pb^{2+}). These properties allow for easy smelting and the addition of lead in the production of batteries, ammunition, paints, dyes, ceramic glazes, gasoline, and medical equipment.

When lead is deposited in soil from anthropogenic sources, it does not biodegrade or decay and is not rapidly absorbed by plants, so it remains in the soil at elevated levels. Lead is estimated to have a half-time of residence in soil of 1,000 years (Benninger et al., 1975).

Mercury exists as metallic mercury, inorganic mercuric salt, and organic mercury. Metallic mercury is a liquid at room temperature. Mercury binds to chlorine, sulfur, or oxygen to form inorganic mercurous (Hg^+) or mercuric (Hg^{2+}) salts. The primary organometallic forms include methylmercury (MeHg) and ethylmercury. The risk of mercury toxicity depends very much on the form of mercury and route of exposure. Metallic mercury exposure can occur by inhalation of mercury vapor. Mercury vapor in the atmosphere is typically low and not considered a major route of exposure. However, mercury vapor is a potential occupational exposure in gold mining where mercury is used to form an amalgam with gold during its extraction, in dentistry for tooth restoration, and in the manufacture of scientific instruments and electrical control devices. Amalgam fillings can provide an exposure to mercury vapor, and it is estimated that 10 amalgam surfaces would raise urinary mercury concentrations by $1 \mu\text{g/L}$ (Keil et al., 2011).

2.9. Potentially toxic elements pollution

By Nriagu, 1996 air pollution is often regarded as the product of modern technological development. In fact, environmental pollution caused by potentially toxic elements began with the domestication of fire: The deposition of small amounts of trace metals released during the burning of firewood altered the metal levels in the cave environment. With the discovery of mining and metal-working techniques in ancient times, the close link between metals, metal pollution, and human history was formed. Mining and trade of mineral resources became a key feature of the early economy, and metal recovery techniques attained status as a barometer of technological advancement for ancient cultures. During the time of the Roman Empire, large quantities of potentially toxic elements, especially Pb (80,000 to 100,000 metric tons per year), Cu (15,000 tons/year), Zn (10,000 tons/year), and Hg (>2 tons/year), as well as Sn and Zn, were required to sustain the high standard of living. Although the mines were operated on a small scale, uncontrolled smelting of large quantities of ores in open fires resulted in substantial emissions of trace metals to the atmosphere. Emissions of toxic metals were serious enough to

draw the attention of a number of ancient authors and may have been responsible for the interdiction of mining operations in Italy and near some ancient cities. The Industrial Revolution brought about unprecedented demand for metals and an exponential increase in the intensity of metal emissions, both in absolute masses and in the number and type of potentially toxic elements compounds released. The emissions may be compared with mine productions of Cd, Cu, Pb, Ni, and Zn; about 90% of the mine outputs were consumed in this century. Profiles of Pb levels in ice layers from northwest Greenland to deduce that extensive contamination of Arctic atmosphere with Pb began before the Industrial Revolution. Subsequent studies found that the Pb contents of ice layers deposited in Greenland between 500 B.C. and A.D. 300 were about four times that of background, implying widespread pollution of the Northern Hemisphere by emissions from Roman mines and smelters. The Pb content returned to baseline levels (~0.5 pg/g) after the eclipse of the Roman Empire and then began a steady rise with the mining renaissance in Europe, reaching values of 10 pg/g in the 1770s and 50 pg/g in the mid-1990s . Since the 1970s, a sharp (approximately sevenfold) decrease in the Pb content of Arctic snow fields has been documented, which can be attributed to the phase-out of leaded gasoline in North America and Europe. Studies of other types of deposits have confirmed the global nature of Pb pollution dating back to ancient times. Analysis of lake sediments from various parts of Sweden found a peak in Pb deposition around 2000 years before present. Advances in mining technology are driven by the need to exploit new ore minerals or to improve the recovery efficiency. Either impetus has a major impact on metal emission rate. Retrospective geochemical monitoring hence represents a potential tool for evaluating historical developments in mining technology. For instance, the development of the patio process (or mercury amalgamation process) into an industrial-scale operation stimulated massive production of silver in South and Central America and left behind an unparalleled legacy of Hg pollution in the area.

2.10. PTE in the region of brown-coal mining dumpsites in Czech Republic

The soils formed after open-cast brown coal mining are formed by different reclamation procedures, including layering of mineral materials, covering with natural topsoil, planting with agricultural crops or forests, and other methods (Štrudl et al., 2006).

One of the most important criteria of the exploitability of these soils for the agricultural production is the content of potentially toxic elements. The input of the potentially toxic elements into the reclaimed soils can be potentially increased, as the related industry is often concentrated in the mining areas. On the other hand, as the soils have been just recently exposed on the surface, the effect of the atmospheric deposition should be low, except for the soils where the natural topsoil cover with the previous accumulation of deposited substances was used. Most

of the elements present in these soils should therefore originate from the mineral materials. A higher content in the coal mining deposits is often reported for As. The lack of organic matter as a sorption medium can lead to a greater risk of the element release after weathering and their increased mobility and bioavailability. However, reported that only a small fraction of the metals released during the natural weathering of coal mine spoils is released to the environment. Nevertheless, the vulnerability of the reclaimed soils to the potential pollution can be strong. It is therefore necessary to assess the risk and potential threat. The contents in the anthropogenic soils of the potentially toxic elements studied were in most cases under the limit values for agricultural soils. In some cases, as with Cu and Cr, they were very low compared to the limit values. Arsenic is the only element that exceeded the limit value. This happened on three sites in Stare Sedlo, once in Nove Sedlo, and once in Locket; all these sites are natural soils. All reclaimed areas were in this respect under the limit. Very small concentrations of potentially toxic elements in lignite mine soils. The comparison between the natural and the reclaimed soils showed that the natural soils have significantly higher concentrations of As, Cd, Cr, and Pb than the reclaimed soils. They can be influenced by atmospheric deposition, especially in the case of Cd and Pb. Although the region under study represents an area with a small to moderate level of deposition, a long-term exposure of the natural soil surface to deposition could increase the element contents in the topsoil as compared to deeper layers. In contrast, the concentration of Cu was significantly higher in the reclaimed soils in comparison to the natural ones. This suggests a low input of this element to soil from atmospheric deposition and the prevalence of lithogenic origin. The concentrations of Ni, V, Zn, and Mn in the reclaimed soils were also slightly higher than those in the natural ones; however, this difference was not significant (Štrudl et al., 2006).

2.11. Occurrence of potentially toxic elements (PTE) in soil

From theory on bounded rationality (McLean et al, 1992) metals are defined as any element that has a silvery luster and is a good conductor of heat and electricity.

As has been shown (Callender et al., 2003) there are a variety of natural and anthropogenic sources of the most common potentially toxic elements (Pb, Zn, Cd, Cr, Cu, Ni) in the environment.

a) Natural Occurrence

The principal natural source of potentially toxic elements in the environment is from crustal material that is either weathered on (dissolved) and eroded from (particulate) the Earth's surface or injected into the Earth's atmosphere by volcanic activity. These two sources account for 80% of all the natural sources; forest fires and biogenic sources, account for 10% each (Nriagu, 1996). Particles released by erosion appear in the atmosphere as windblown dust. In

addition, some particles are released by vegetation. The natural emissions of the potentially toxic elements are 12,000 (Pb); 45,000 (Zn); 1,400 (Cd); 43,000 (Cr); 28,000 (Cu); and 29,000 (Ni) metric tons per year, respectively (Nriagu 1996). Thus, we can conclude that abundant quantities of metals are emitted into the atmosphere from natural sources. The quantity of anthropogenic emissions of these metals is given in the next section (Callender et al., 2003).

b) Anthropogenic Occurrence

There are a multitude of anthropogenic emissions in the environment. The major source of these metals is from mining and smelting. Mining releases metals to the fluvial environment as tailings and to the atmosphere as metal-enriched dust whereas smelting releases metals to the atmosphere as a result of high-temperature refining processes. In the lead industry, Pb–Cu–Zn–Cd are released in substantial quantities; during Cu and Ni smelting, Co–Zn–Pb–Mn as well as Cu–Ni are released; and in the Zn industry, sizeable releases of Zn–Cd–Cu–Pb occur. Table 3 shows that the world metal production during the 1970s and the 1980s has remained relatively constant except for Cr production that substantially increased during the 1980s due to the technological advances and increased importance. Table 3 shows that metal emissions to soil are high, suggesting that land disposal of mining wastes, chemical wastes, combustion slags, municipal wastes, and sewage sludges are the major contributors of these emissions (Callender et al., 2003).

Table 3. Global primary production and emissions of six potentially toxic elements during the 1970s - 1980s.

Metal	Metal production		Emissions to soil 1980s
	1970s	1980s	
Pb	3400	3100	796
Zn	5500	5200	1372
Cr	17	15	22
Cd	6000	11250	896
Cu	6000	7700	954

Source: Nriagu (1980a), Pacyna (1986), and Nriagu and Pacyna (1988).

All values are thousand metric tons.

2.12. Behavior of potentially toxic elements in soil

Metals associated with the aqueous phase of soils are subject to movement with soil water, and may be transported through the vadose zone to ground water. Metals, unlike the hazardous organics, cannot be degraded. Some metals, such as Cr, As, Se, and Hg, can be transformed to other oxidation states in soil, reducing their mobility and toxicity.

Immobilization of metals, by mechanisms of adsorption and precipitation, will prevent movement of the metals to ground water. Metal-soil interaction is such that when metals are introduced at the soil surface, downward transportation does not occur to any great extent unless the metal retention capacity of the soil is overloaded, or metal interaction with the associated waste matrix enhances mobility. Changes in soil environmental conditions over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes, also may enhance metal mobility. The extent of vertical contamination is intimately related to the soil solution and surface chemistry of the soil matrix with reference to the metal and waste matrix in question (McLean et al., 1992).

2.13. Fate of potentially toxic elements in the Soil Environment

In soil, metals are found in one or more of several "pools" of the soil, as described by Shuman, 1991:

- 1) dissolved in the soil solution;
- 2) occupying exchange sites on inorganic soil constituents;
- 3) specifically adsorbed on inorganic soil constituents;
- 4) associated with insoluble soil organic matter;
- 5) precipitated as pure or mixed solids;
- 6) present in the structure of secondary minerals; and/or
- 7) present in the structure of primary minerals.

In situations where metals have been introduced into the environment through human activities, metals are associated with the first five pools. Native metals may be associated with any of the pools depending on the geological history of the area. The aqueous fraction, and those fractions in equilibrium with this fraction, i.e., the exchange fraction, are of primary importance when considering the migration potential of metals associated with soils.

Metals in the soil solution are subject to mass transfer out of the system by leaching to ground water, plant uptake, or volatilization, a potentially important mechanism for Hg, Se, and

As. At the same time metals participate in chemical reactions with the soil solid phase. The concentration of metals in the soil solution, at any given time, is governed by a number of interrelated processes, including inorganic and organic complexation, oxidation-reduction reactions, precipitation/dissolution reactions, and adsorption/desorption reactions. The ability to predict the concentration of a given metal in the soil solution depends on the accuracy with which the multiphase equilibria can be determined or calculated.

Most studies of the behavior of metals in soils have been carried out under equilibrium conditions. Equilibrium data indicate which reactions are likely to occur under prescribed conditions, but do not indicate the time period involved. The kinetic aspect of oxidation/reduction, precipitation/dissolution, and adsorption/desorption reactions involving metals in soil matrix suffers from a lack of published data. Thus the kinetic component, which in many cases is critical to predict the behavior of metals in soils, cannot be assessed easily. Without the kinetic component, the current accepted approach is to assume that local equilibrium occurs in the soil profile. Equilibrium thermodynamic data can then be applied not only to predict which precipitation/dissolution, adsorption/desorption, and/or oxidation/reduction reactions are likely to occur under a given set of conditions, but also to estimate the solution composition, i.e., metal concentration in solution, at equilibrium (McLean et al, 1992).

Czech Law from Environmental Ministry. Standards of PTE in soils (13/1994 Sb. Vyhláška Ministerstva životního prostředí):

All the limits are in mg/kg.

Elements	Other Soils
As	30
Cd	1
Cu	100
Pb	140
Zn	200

2.14. Forms of elements in soil

Brady and Weil, 1996 demonstrated that soil elements may be dissolved in soil solution as ions (molecules with a positive or negative charge). They may be bound in insoluble forms, often through association with parent minerals. The parent materials slowly release the elements over time as part of the natural weathering process. As molecules of an element move between their various forms, they come to a dynamic equilibrium that shifts according to certain soil

conditions, including: pH, texture, aeration of the soil, and the presence of other ions.

The North Haven soil is acidic, sandy, and dry. The elements we analyzed are usually present as cations (ions with a positive charge). Cations are most likely to be found in their dissolved ionic form in acidic sandy soils, because the H^+ ions in acid replace the positively charged ions on the parent material and other soil exchange sites. In sandy acidic soils, these ions can leach out with groundwater or runoff, and for this reason often are deficient.

Uptake by plants is a significant part of the cycles of some of these elements. Plants absorb the molecules when they are in ionic form and then release them upon decomposition.

The macronutrients are essential elements that comprise between 0.1 - 1.0 % of a plant. They generally are important to the structural molecules of a plant, including carbohydrates, proteins, chlorophyll, cell walls, DNA, RNA, sugar phosphates and phospholipids.

Potassium is crucial to most ionic functions of a plant, including stomatal control, the maintenance of turgor pressure, and charge balance during selective ion uptake across root membranes. It is also a coenzyme in many biochemical reactions. It comprises 1.0% of a plant. Potassium is highly mobile and leaches easily from leaves and then is taken up in high quantities by microbes and plants. The primary movement of potassium in the system is between plants and the soil solution, where it resides as an ion that easily leaches from the ecosystem.

The primary source of potassium in soil solution is the weathering of parent rocks. Within an acidic soil, potassium may be tightly bound in insoluble minerals (micas and feldspars), slowly available when associated with 2:1 type minerals, moderately available when associated with clay and humus colloids, and easily available when in soil solution. The small amount of potassium dissolved in soil solution as an ion is highly leachable, although losses of potassium from runoff and erosion is not a significant problem in forests, compared to some elements.

Plants use calcium to build cell walls. It also helps keep P available in the root zone by binding with other competitor ions. It commonly comprises 0.5 % of a plant. Because it is bound within cell walls, it does not leach from the leaves nor circulate within the plant. However, it can easily leach through soil layers. Its primary source is from weathering, and then it is stored as a cation (a positively charged ion) on soil exchange sites (negatively charged)

Magnesium is the central atom of the chlorophyll molecule. It also is an important co-enzyme. It is very mobile in plants as a cation. It generally makes up 0.2 % of plants.

Phosphorous is required for the formation of energy transfer and storage molecules (ADP, ATP). Because it forms the backbone of DNA and RNA molecules, it also regulates cell division, root development, and protein formation. On average, phosphorous comprises between 0.2% - 0.4 % of the dry matter in the leaves of a healthy plant. It is crucial to many functions of plants, a key component of most fertilizers, and often deficient in non-fertilized soils.

It is mobile as an anion in plants. The primary source of potassium in soil solution is the weathering of parent rocks. Within most soils are large amounts of potassium bound in unavailable forms. In acidic soils, the largest proportion of potassium is bound in iron- and aluminum- bound insoluble minerals. They may also bind with manganese. In its ionic (available) form, phosphate strongly adsorbs to soil particles and does not quickly flush out of the system. Still, losses in runoff are important.

The micronutrients are essential elements that comprise less than .01 % (100 ppm) of a plant. They generally are metabolically active in plants as important coenzymes.

Iron primarily originates from chemical weathering of the parent material and is not absorbed by plants in appreciable quantities; the amount found in plants is several orders of magnitude lower than the amount in mineral soil. Its movement in soil horizons is due mainly to chemical processes within the soil, rather than association with organic matter or uptake by biomass. Therefore, its distribution patterns exemplify the chemical redistribution occurring as the soil re-stratifies into horizons. In fact, the distinctive color of the soil horizons are caused by iron. Its presence gives the reddish tint to the B_{hs} and B_s horizons, and its absence leaves the E horizon a light gray color. Iron generally makes up 100 ppm (0.01 %) of plants. It serves important roles, especially as an electron carrier in enzymes. It also plays a role in nitrogen fixation and chlorophyll formation.

Manganese is generally plentiful in acid soil and may reach toxic levels below a pH of 6.5 (as in the pitch pine site). It generally leaches out of acidic soils and deposits in alkaline soil layers. Most plants contain around 50 ppm manganese. It is key to many plant functions, including photosynthesis, respiration, and nitrogen metabolism, because it forms bridges between enzymes and their substrates.

In soils, zinc is tightly adsorbed to magnesium. On average, plants contain around 20 ppm of zinc. Zinc is a key component of growth control hormones and aids in protein synthesis.

Copper is especially plentiful in acidic, sandy soils. Though it only comprises 0.1 ppm of the plant, it is an important enzyme activator found mostly in the chloroplasts of leaves.

Aluminum is an element that is not used in significant amounts by plants. In soils, it immobilizes phosphorous and generally increases the acidity and concentration of cations (including the other elements analyzed in this study). Like most elements, aluminum becomes toxic above certain concentrations; it is poisonous to some plants above 1 ppm and to most plants above 15 ppm.

Lead complexes with organic matter in the soil and accumulates in certain organic tissues of plants (Brady and Weil, 1996).

3. Aims and Hypothesis

Aim:

The aim of the thesis will be to determine and assess the content and forms of potentially toxic elements (PTE) in selected reclaimed dumpsite soils after brown coal mining in Northern Bohemia, as related to reclamation method, soil properties and other factors.

Hypotheses:

The content of PTE in reclaimed soils without topsoiling is lower than in soils with natural topsoil cover because the former ones were not exposed to atmospheric deposition for so long time. The content and form of PTE in reclaimed soils depend on the type of reclamation (topsoiling, agricultural vs. forest reclamation, etc.). The proportion of bioavailable forms of PTE in reclaimed soils is low.

4. Methodology

4.1. Soil sampling

Boruvka et al., 2012 intend two dumpsites of the Severoceske doly, a. s., mining company were selected: Libous and Pokrok. Both are formed by clays. On a part of each dumpsite, cover with natural topsoil was spread in an amount of approximately 2500 to 3000 t per ha one year before sampling. The topsoil material originated from humic horizons of natural soils of the region, particularly Vertisols, partly also Chernozems (clayish and haplic). The topsoil was not mixed with the dumpsite material. Individual soil properties differed a little between the two dumpsites. Disturbed and undisturbed soil samples were collected on both dumpsites. The size of the sampled square area was 90×90 m at the Libouš dumpsite and 120×120 m at the Pokrok dumpsite. The total size of the sampled area was thus 8100 m² at the Libouš dumpsite and 14,400 m² at the Pokrok dumpsite. The sampling scheme was placed on each dumpsite on the border between areas with and without topsoil cover. Forty five soil samples were collected on the Libouš dumpsite and fifty samples were collected on the Pokrok dumpsite. Approximately half of the sampling points were located on the area with natural topsoil cover, half of the points were on the area without the cover. Sampling was made in the 0 to 20 cm layer. This depth corresponds to common depth of ploughing soil layer, as these soils should be used as arable land in future. The depth of the topsoil cover, where it was applied, was also at least 20 cm.

4.2. List of samples

№	Mine	Source	Year	Crop	Reclamation	Topsoiling	pHH ₂ O	pHKCl	Cox
1.	DNT	Brezno 11	2012	No		With cover	6.99	6.27	2.2
2.	DNT	Brezno 11	2012	No		With cover	7.15	6.7	1.9
3.	DNT	Brezno 11	2012	No		With cover	7.22	6.69	1.8
4.	DNT	Brezno 11	2012	No		With cover	7.72	7.26	1.5
5.	DNT	Brezno 11	2012	No		With cover	7.5	7.03	1.8
6.	DNT	Brezno 11	2012	Yes	agricultural		7.29	6.55	2

7.	DNT	Brezno 11	2012	Yes	agricultural		7.91	7.22	1.9
8.	DNT	Brezno 11	2012	Yes	agricultural		7.78	6.94	1.9
9.	DNT	Brezno 14	2012	No		With cover	7.75	7.43	1.5
10.	DNT	Brezno 14	2012	No		With cover	7.44	6.95	1.9
11.	DNT	Brezno 14	2012	No		With cover	7.48	7.12	1.8
12.	DNT	Brezno 14	2012	No		With cover	6.77	6.39	1.9
13.	DNT	Brezno 14	2012	No		With cover	7.71	7.27	1
14.	DNT	Brezno 14	2012	No		With cover	7.11	6.5	1.7
15.	DNT	Merkur 19	2012	Yes	agricultural	With cover	7.1	6.45	1.8
16.	DNT	Merkur 19	2012	Yes	agricultural	With cover	6.94	6.4	1.7
17.	DNT	Brezno 18	2012	No		With cover	6.86	6.34	2
18.	DNT	Brezno 18	2012	No		With cover	7.34	7.24	1.9
19.	DNT	Brezno 18	2012	No		With cover	7.21	6.71	1.6
20.	DNT	Brezno 18	2012	No		With cover	7.19	6.64	1.6
21.	DNT	Brezno 18	2012	No		With cover	7.46	6.96	1.5
22.	DNT	Brezno 7	2012	Yes	agricultural	With cover	6.37	5.83	2.2
23.	DNT	Brezno 7	2012	Yes	agricultural		5.76	5.28	2.3
24.	DNT	Brezno 7	2012	Yes	agricultural		6.82	6.12	2.4
25.	DNT	Brezno 7	2012	Yes	agricultural		6.96	6.15	2.5
26.	DNT	Brezno 7	2012	Yes	agricultural		6.59	5.87	2.3

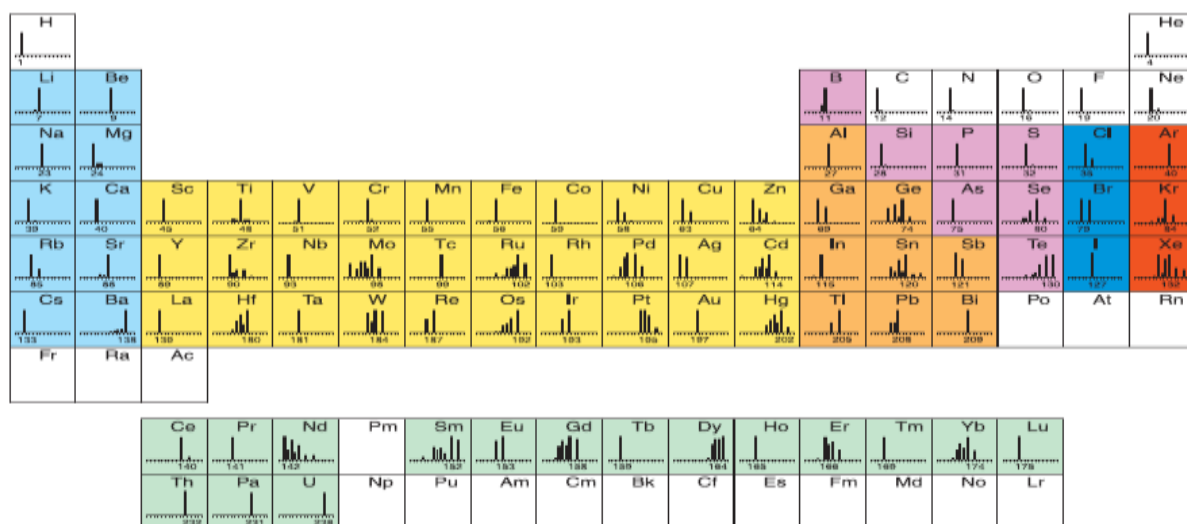
27.	DNT	Brezno dep.	2012	Yes	agricultural		7.61	6.74	1.12
28.	DNT	Brezno dep.	2012	Yes	agricultural		7.93	7.56	1.24
29.	DNT	Brezno dep.	2012	Yes	agricultural		7.02	6.28	1.65
30.	DNT	Brezno dep.	2012	Yes	agricultural		7.3	6.58	2.1
31.	DNT	Prunerov 1	2010		agricultural		2.93	2.67	3.01
32.	DNT	Prunerov 1	2010		agricultural		3.47	3.1	0.95
33.	DNT	Prunerov 1	2010		agricultural		6.92	6.32	2.5
34.	DNT	Prunerov 1	2010		agricultural		7.8	7.12	3.58
40.	DNT	Prunerov 1	2010		agricultural		7.02	6.61	1.85
41.	DNT	Merkur 16	2010			With cover	7.42	7.01	1.65
42.	DNT	Merkur 16	2010			With cover	7	6.58	1.48
43.	DNT	Merkur 16	2010			With cover	7.35	6.93	1.88
45.	DNT	Merkur 16	2010			With cover	7.08	6.64	2.12
48.	DNT	Merkur 16	2010			With cover	7.43	6.98	1.74
49.	DNT	Prunerov 8	2010		forestry		7.18	6.73	1.87
50.	DNT	Prunerov 8	2010		forestry		6.52	6.09	1.45
51.	DNT	Prunerov 8	2010		forestry		6.11	5.39	2.21
52.	DNT	Prunerov 8	2010		forestry		6.35	5.95	2.58
53.	DNT	Prunerov 9	2010		forestry		4.24	3.9	2.05
55.	DNT	Prunerov 9	2010		agricultural		7.78	7.21	1.12
57.	DNT	Tumerity	2010		forestry		6.54	6.11	1.61
59.	DNT	Tumerity	2010		forestry		7.33	6.78	1.55
60.	DNT	Tumerity	2010		forestry		7.21	6.8	1.08
61.	DNT	Tumerity	2010		forestry		6.97	6.44	0.95
62.	DNT	Tumerity	2010		forestry		7.1	6.56	0.76
63.	DNT	Tumerity	2010		forestry		6.26	5.82	0.83
64.	DNT	Tumerity	2010		forestry		6.25	5.8	1.19
65.	DNT	Tumerity	2010		forestry		6.55	6.11	1.68
66.	DNT	Tumerity	2010		forestry		6.81	6.27	1.45

4.3. ICP-OES.

It has been 25 years since ICP optical emission spectrometer (ICP-OES) began to be widely used, and is now one of the most versatile methods of inorganic analysis.

ICP, abbreviation for Inductively Coupled Plasma, is one method of optical emission spectrometry. When plasma energy is given to an analysis sample from outside, the component elements (atoms) are excited. When the excited atoms return to low energy position, emission rays (spectrum rays) are released and the emission rays that correspond to the photon wavelength are measured. The element type is determined based on the position of the photon rays, and the content of each element is determined based on the rays' intensity.

To generate plasma, first, argon gas is supplied to torch coil, and high frequency electric current is applied to the work coil at the tip of the torch tube. Using the electromagnetic field created in the torch tube by the high frequency current, argon gas is ionized and plasma is generated. This plasma has high electron density and temperature (10000K) and this energy is used in the excitation-emission of the sample. Solution samples are introduced into the plasma in an atomized state through the narrow tube in the center of the torch tube (<http://www.hitachi.com/>).



Picture 2. Elements analyzed by ICP (in color) (<http://www.perkinelmer.com/>).

The following features of ICP-OES distinguish it from atomic absorption spectrometer used for similar purposes:

1. Simultaneous, sequential analysis of multiple elements possible
2. Wide linear region of analytical curve
3. Few chemical interference or ionization interference, making analysis of high-matrix samples

possible

4. High sensitivity (low limit of detection for majority of elements is 10ppb or lower)
5. High number of measurable elements - elements that are difficult to analyze in atomic absorption spectrometry such as Zr, Ta, rare earth, P and B can be easily analyzed
6. Stable

The majority of the above features are derived from the structure and characteristics of the light source plasma (<http://www.hitachi.com/>).

4.4. Statistical analyses

Statgraphics XVI.I. Centurion (www.statgraphics.com) was used for basic statistical analyses.

4.5. Extraction of bioavailable potentially toxic elements (PTE)

1. Take from each sample 10 g ($\pm 0,005$ g) of soil. Each soil sample is in duplicate.
2. Prepare the solution. For 2 L bottle take 160, 08 g ($\pm 0,005$ g) of 1M ammonia nitrate (NH_4NO_3).

Ammonia nitrate composed of nitric acid and salt of ammonia. Ammonium nitrate appears in a white crystalline form and it is also colorless (<http://www.ammoniumnitrate.org/>). This solution is weak extractant and is popular for estimating immediate bioavailability (landfood.ubc.ca/labmodules/trace-elements/extractable-forms).

3. 10 g of soil + 25 ml of dissolved solution (1M NH_4NO_3).
4. Shaking for 2 hours with the speed 120 times/per min
5. Put in centrifuge with the speed 4000 times/per min for 5-10 min.
6. Store samples in the fridge.
7. Take from each sample 1 ml of solution.
8. 1 ml of solution mix with 9 ml of 2% nitric acid (HNO_3).
9. Then we get 10 times diluted samples.
10. Solutions check by ICP-OES.

4.6. BCR sequential extraction

Fernandez et al., 2004 demonstrated that the determination of element concentrations using extraction methods shows greater uncertainties than do the procedures in which their total contents are determined in a direct manner. This is due to: (1) the difficulties in isolating the

compounds to be studied from their substrates; (2) the possibility of upsetting the equilibrium between the different chemical species present in the system; (3) the inadequate analytical sensitivity of some of the techniques, especially when trace elements are found at very low concentrations; and (4) the frequent lack of certified reference materials. The proposal of the European Community Bureau of Reference, usually called the BCR method, seeks to minimize errors in the treatment and analysis of samples, to identify the most appropriate analytic procedure and to supply reference materials for comparisons of the results between different laboratories. This method appears to be more operationally effective than others proposed previously. Nevertheless, the dissolution or selective destruction of the soil components seems to be implicit in any sequential extraction technique, as does the non-specificity of the reagent or the possibility of the redistribution of metals during the extraction. Recent years have shown growing interest in the BCR method, both in polluted as well as non-polluted soils. The method has been used not only in laboratory experiments, with mineralogically uniform samples (humic acids, calcium carbonate, iron oxides or manganese, illite, montmorillonite, etc.) and with controlled quantities of added metals but also in natural substrates, fundamentally sediments from estuaries. The use of simple substrates eliminates the problem of the redistribution of the metal into the constituents of the substrate, and the samples reach equilibrium better in sea-water solutions, such as the estuary substrates.

4.7. Standardized procedure BCR sequential extraction

For BCR analyses weight 20 samples (each is duplicated) for 1 g ($\pm 0,005$ g). Each solution will have blanks without soil.

Determine (Rauret et al., 2000) the extractable contents of Cd, Cr, Cu, Ni, Pb, and Zn using the procedure described below. Carry out all the extractions on the sediment as received in the glass bottle. Before subsampling the sediment, shake the contents of the bottle manually for 3 min. Take the sample using a suitable plastic spatula. For each batch of extractions, dry a separate 1 g sample of the sediment in a layer of about 1 mm depth in an oven (105 ± 2 °C) until constant weight. From this, a correction "to dry mass" is obtained which shall be applied to all analytical values reported (i.e., results shall be quoted as quantity of metal per g dry sediment). Perform the extractions by shaking in a mechanical, endover-end shaker at a speed of 30 ± 10 rpm and a room temperature of 22 ± 5 °C. The sediment sample should be in suspension during shaking. Measure and report the temperature of the room at the start and at the end of each step of the extraction procedure.

1. Add 40 mL of Solution A to 1 g sediment in an 80 to 100 mL centrifuge tube, stopper and extract by shaking for 16 h at 22 ± 5 °C (overnight). No delay should occur between

the addition of the extractant solution and the beginning of the shaking. Separate the extract from the solid residue by centrifugation at 3000g for 20 min and decantation of the supernatant liquid into a polyethylene container. Stopper the container and analyze the extract immediately, or store in a refrigerator at about 4 °C prior to analysis. Wash the residue by adding 20 mL distilled water, shaking for 15 min on the end-over-end shaker and centrifuging for 20 min at 3000g. Decant the supernatant and discard, taking care not to discard any of the solid residue.

Solution A: (acetic acid, 0.11 mol/L). Add, in a fume cupboard, 25±0.1 mL of glacial acetic acid to about 0.5 L of distilled water in a 1 L graduated polypropylene or polyethylene bottle and make up to 1 L with distilled water. Take 250 mL of this solution (acetic acid, 0.43 mol/L) and dilute to 1 L with distilled water to obtain an acetic acid solution of 0.11 mol/L.

2. Add 40 mL of a freshly prepared Solution B to the residue from Step 1 in the centrifuge tube. Resuspend by manual shaking, stopper and then extract by mechanical shaking for 16 h at 22±5 °C (overnight). No delay should occur between the addition of the extractant solution and the beginning of the shaking. Separate the extract from the solid residue by centrifugation and decantation as in Step 1. Retain the extract in a stoppered polyethylene container, as before, for analysis. Wash the residue by adding 20 mL distilled water, shaking for 15 min on the end-over-end shaker and centrifuging for 20 min at 3000g. Decant the supernatant and discard, taking care not to discard any of the solid residue.

Solution B: (hydroxylammonium chloride (hydroxylamine hydrochloride), 0.5 mol/L). Dissolve 34.75 g of hydroxylammonium chloride in 400 mL distilled water. Transfer the solution to a 1 L volumetric flask, and add, by means of a volumetric pipette, 25 mL of 2 mol/L HNO₃ (prepared by weighing from a suitable concentrated solution). Make up to 1 L with distilled water. Prepare this solution on the same day the extraction is carried out.

3. Add carefully, in small aliquots to avoid losses due to a possible violent reaction, 10 mL of Solution C to the residue in the centrifuge tube (see recommendations). Cover the vessel loosely with its cap and digest at room temperature for 1 h with occasional manual shaking. Continue the digestion for 1 h at 85±2 °C, with occasional manual shaking for the 30 min; in a water bath, and then reduce the volume to less than 3 ml by further heating of the uncovered tube. Add a further aliquot of 10 mL of Solution C. Heat the covered vessel again to 85±2 °C and digest for 1 h, with occasional manual shaking for the 30 minutes remove the cover and reduce the volume of liquid to about 1 ml. Do not take to complete dryness. Add 50 mL of Solution D to the cool moist residue and shake for 16 h at 22±5 °C (overnight). No delay should occur between the addition of the

extractant solution and the beginning of the shaking. Separate the extract from the solid residue by centrifugation and decantation as in Step 1. Stopper and retain as before for analysis.

Solution C: (hydrogen peroxide, 300 mg/g, i.e., 8.8 mol/L). Use the hydrogen peroxide as supplied by the manufacturer, i.e., acid-stabilized to pH 2-3.

Solution D: (ammonium acetate, 1.0 mol/L). Dissolve 77.08 g of ammonium acetate in 800 mL distilled water. Adjust the pH to 2.0 ± 0.1 with concentrated HNO₃ and make up to 1 L with distilled water (Rauret et al, 2000).

4.8. Standardized procedure aqua regia extraction

The following digestion method, according to the ISO Standard 11466, was adopted as the common method for the interlaboratory trial (Rauret et al., 2000). This international standard has been proposed for the determination of extractable metals in soils and similar materials containing less than about 20% m/m organic carbon according to ISO10694. Materials containing more than about 20% m/m organic carbon will require treatment with additional nitric acid.

Extraction procedure:

Weigh approximately 3 g, to the nearest 0.001 g, of the air-dried material into the reaction vessel. (The water content of the air-dried material should be determined in a different subsample according to ISO 11465.) Add 0.5 mL to 1.0 mL of water to obtain a slurry, and add, while mixing, 21 mL of 12.0 mol/L HCl followed by 7 mL of 15.8 mol/L HNO₃, drop by drop if necessary, to reduce foaming. Add 15 mL of 0.5 mol/L HNO₃ to the adsorption vessel, connect the vessel to the reflux condenser and place both on top of the reaction flask. Allow to stand for 16 h at room temperature to allow for slow oxidation of the organic matter of the soil. Raise the temperature of the reaction mixture slowly until reflux conditions are reached and maintain for 2 h, ensuring that the condensation zone is lower than 1/3 of the height of the condenser. Allow to cool slowly to room temperature. Add the content of the absorption vessel, through the condenser tube, into the reaction vessel and rinse both with 10 mL of 0.5 mol/L HNO₃. Transfer the contents of the reaction vessel quantitatively to a 100 mL graduated flask. Rinse the vessel with 0.5 mol L HNO₃ and transfer as well. Fill the graduated flask with distilled water up to the mark, close with stopper and shake. After the undissolved matter has settled, the supernatant solution shall be used for the final determination of the elements. If the undissolved components settle too slowly or unsatisfactorily, centrifuge or filter with a cellulose-based

membrane filter with a medium pore size of 8 mm after filling the graduated flask up to the mark (Rauret et al, 2000).

After BCR sequential analysis and aqua regia extraction all the samples dilute 10 times with a distilled water and check by ICP-OES.

5. Results

5.1. Extraction of bioavailable potentially toxic elements

Table 4 shows the results from NH_4NO_3 extraction. All results were recalculated into mg/kg (25 ml/10 g of soil x 10 times of dilution). All meanings are low and As is under detection limit.

Table 4. Results from ICP-OES for all samples in mg/kg. Standard deviation in brackets.

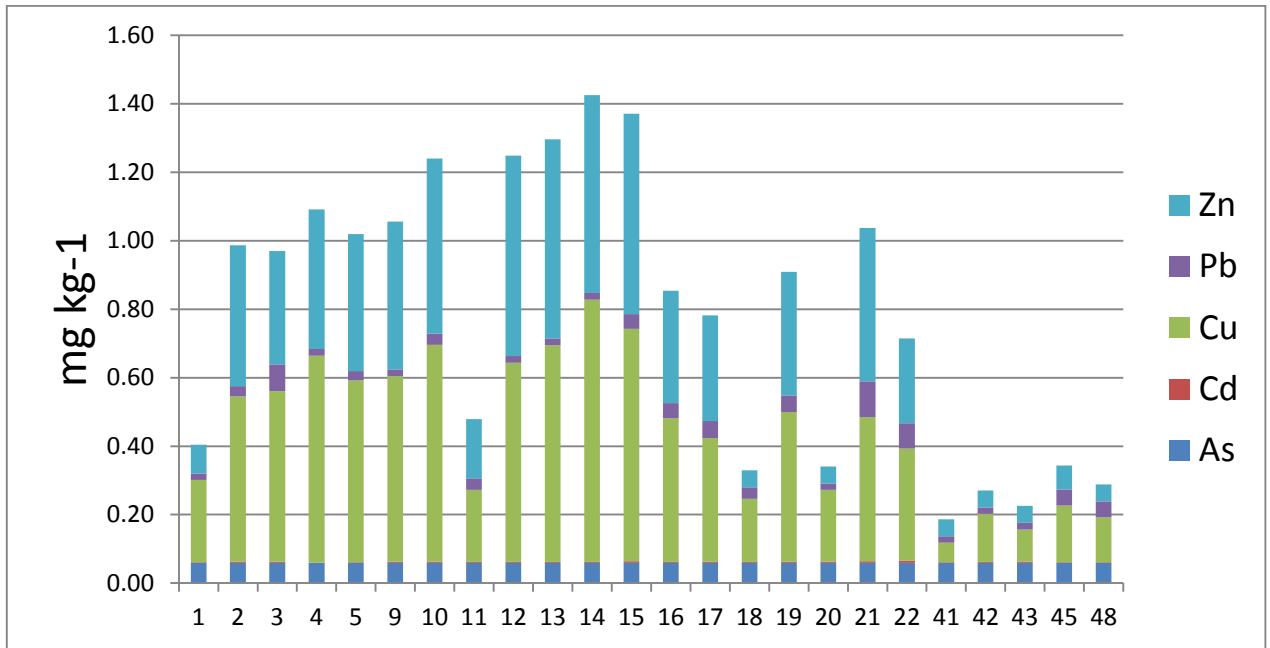
Number	As	As	Cd	Cd	Cu	Cu	Pb	Pb	Zn	Zn
	mg	SD	mg	SD	mg	SD	mg	SD	mg	SD
	kg-1		kg-1		kg-1		kg-1		kg-1	
DL	0.18		0.005		0.13		0.06		0.15	
1/3 DL	0.06		0.002		0.04		0.02		0.05	
1	0.06	(0)	0	(0.001)	0.24	(0.036)	0,02	(0)	0.08	(0.034)
2	0.06	(0)	0	(0)	0.48	(0.025)	0,03	(0.011)	0.41	(0.026)
3	0.06	(0)	0	(0)	0.50	(0.015)	0,08	(0)	0.33	(0.05)
4	0.06	(0)	0	(0)	0.60	(0.099)	0,02	(0)	0.41	(0.037)
5	0.06	(0)	0	(0.001)	0.53	(0.04)	0,03	(0.008)	0.40	(0.016)
6	0.06	(0)	0	(0)	0.58	(0.113)	0,02	(0)	0.52	(0.056)
7	0.06	(0)	0	(0)	0.54	(0.075)	0,02	(0)	0.48	(0.225)
8	0.06	(0)	0	(0)	0.18	(0.056)	0,02	(0)	0.17	(0.123)
9	0.06	(0)	0	(0.001)	0.54	(0.032)	0,02	(0)	0.43	(0.068)
10	0.06	(0)	0	(0.001)	0.63	(0.076)	0,03	(0.014)	0.51	(0.13)
11	0.06	(0)	0	(0)	0.21	(0.008)	0,03	(0.015)	0.17	(0.123)
12	0.06	(0)	0	(0)	0.58	(0.095)	0,02	(0)	0.59	(0.137)
13	0.06	(0)	0	(0.001)	0.63	(0.093)	0,02	(0)	0.58	(0.139)
14	0.06	(0)	0	(0.000)	0.77	(0.119)	0,02	(0)	0.58	(0.094)
15	0.06	(0)	0.01	(0)	0.68	(0.018)	0,04	(0.024)	0.59	(0.065)
16	0.06	(0)	0	(0.002)	0.42	(0.012)	0,04	(0.024)	0.33	(0.095)
17	0.06	(0)	0	(0.001)	0.36	(0.028)	0,05	(0.030)	0.31	(0.018)
18	0.06	(0)	0	(0)	0.18	(0)	0,03	(0.015)	0.05	(0)
19	0.06	(0)	0	(0.001)	0.44	(0.014)	0,05	(0.03)	0.36	(0.057)
20	0.06	(0)	0	(0)	0.21	(0.017)	0,02	(0)	0.05	(0)
21	0.06	(0)	0	(0.001)	0.42	(0.027)	0,10	(0.023)	0.45	(0.052)

22	0.06	(0)	0.01	(0.001)	0.33	(0.055)	0,07	(0.054)	0.25	(0.022)
23	0.06	(0)	0.01	(0)	0.35	(0.025)	0,02	(0)	0.45	(0.006)
24	0.06	(0)	0	(0.001)	0.33	(0.014)	0,02	(0)	0.25	(0.004)
25	0.06	(0)	0	(0)	0.36	(0.048)	0,02	(0)	0.35	(0.054)
26	0.06	(0)	0	(0.001)	0.34	(0.046)	0,04	(0.018)	0.37	(0.010)
27	0.06	(0)	0	(0.001)	0.41	(0.022)	0,29	(0)	0.30	(0.016)
28	0.06	(0)	0	(0.001)	0.44	(0.095)	0,15	(0)	0.33	(0.052)
29	0.06	(0)	0.01	(0)	0.25	(0.049)	0,05	(0.007)	0.14	(0.088)
30	0.06	(0)	0	(0.001)	0.19	(0.007)	0,02	(0)	0.14	(0.088)
31	0.06	(0)	0.02	(0)	0.93	(0.017)	0,32	(0.03)	4.26	(0.027)
32	0.06	(0)	0.04	(0.005)	0.91	(0.12)	0,19	(0.155)	5.69	(0.712)
33	0.06	(0)	0.02	(0.015)	0.16	(0.018)	0,03	(0.008)	0.21	(0)
34	0.06	(0)	0	(0)	0.47	(0.016)	0,03	(0.007)	0.05	(0)
40	0.06	(0)	0.002	(0.001)	0.28	(0.207)	0,02	(0)	0.05	(0)
41	0.06	(0)	0.003	(0.001)	0.06	(0.014)	0,02	(0)	0,05	(0)
42	0.06	(0)	0.003	(0.001)	0.14	(0.006)	0,02	(0)	0,05	(0)
43	0.06	(0)	0.004	(0.001)	0.09	(0.052)	0,02	(0)	0,05	(0)
45	0.06	(0)	0.002	(0.001)	0.17	(0.018)	0,05	(0.028)	0,07	(0.02)
48	0.06	(0)	0.003	(0.001)	0.13	(0.017)	0,05	(0.028)	0,05	(0)
49	0.06	(0)	0.002	(0.001)	0.09	(0.021)	0,03	(0.011)	0,05	(0)
50	0.06	(0)	0.002	(0.001)	0.05	(0.012)	0,03	(0.012)	0,36	(0.024)
51	0.06	(0)	0.01	(0)	0.06	(0.013)	0,03	(0.013)	0,49	(0.007)
52	0.06	(0)	0.01	(0.001)	0.17	(0)	0,02	(0)	1,37	(0.004)
53	0.06	(0)	0.006	(0.002)	0.37	(0.328)	0,03	(0)	0,84	(0.527)
55	0.06	(0)	0.002	(0)	0.37	(0.328)	0,04	(0.017)	0,18	(0.131)
57	0.06	(0)	0.006	(0)	0.07	(0)	0,02	(0)	0,24	(0)
59	0.06	(0)	0.004	(0.002)	0.06	(0.013)	0,03	(0.011)	0,15	(0.098)
60	0.06	(0)	0.002	(0.001)	0.15	(0.008)	0,03	(0.008)	0,05	(0)
61	0.06	(0)	0.004	(0)	0.16	(0.006)	0,06	(0.042)	0,05	(0)
62	0.06	(0)	0.002	(0)	0.14	(0.028)	0,06	(0.042)	0,05	(0)
63	0.06	(0)	0.01	(0.001)	0.20	(0)	0,03	(0.011)	0,33	(0.001)
64	0.06	(0)	0.01	(0.001)	0.28	(0.209)	0,03	(0.014)	0,65	(0.136)
65	0.06	(0)	0.005	(0.003)	0.37	(0.051)	0,12	(0)	0,50	(0.016)
66	0.06	(0)	0.01	(0.001)	0.11	(0.032)	0,04	(0.007)	0,22	(0.038)

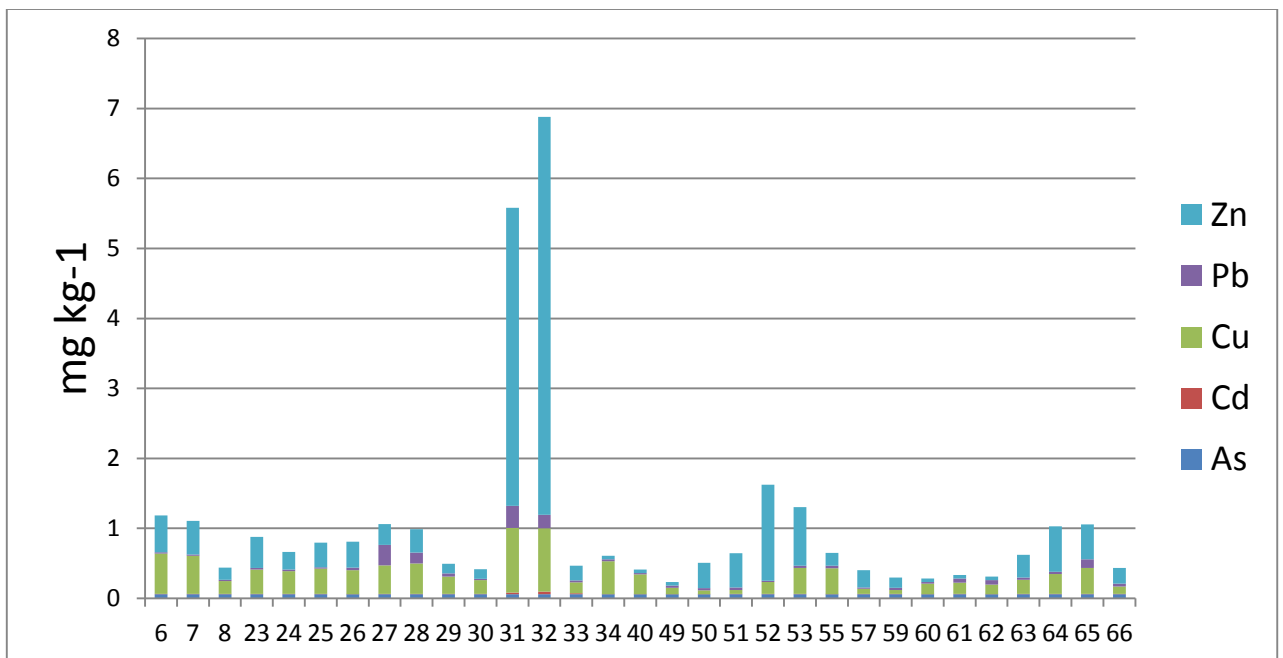
DL – determination limit.

Graph 1 and Graph 2 separated by method of covering land: with topsoil cover and without respectively, all values are results from NH_4NO_3 extraction. . They include all 5 elements which were checking in ICP –OES (As, Cd, Cu, Pb, Zn).

Graph 1. Samples with topsoil cover



Graph 2. Samples without topsoil cover

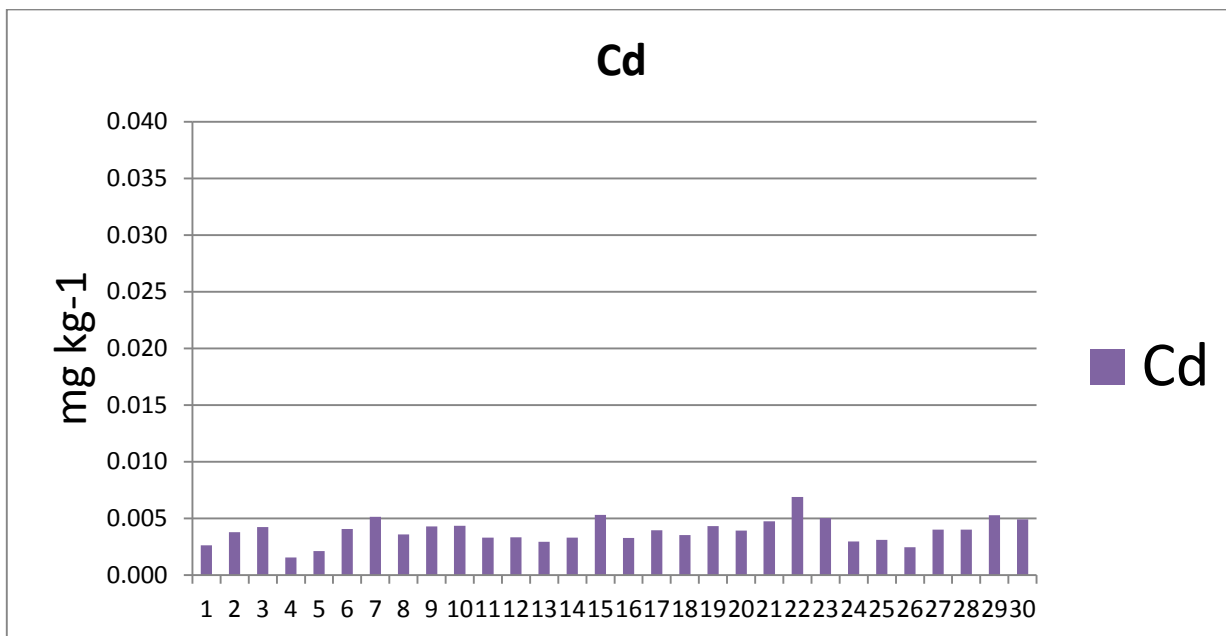


Content of PTE in both graphs is quiet low. Soil which had such reclamation measure as “topsoiling” has values of PTE generally do not reach 1.5 mg/kg. With reference to the second

graph where topsoiling was not applied we can see almost same values of PTE, only 2 samples has meanings higher than 5 mg/kg for all the elements contained in the soil.

Graph 3 below shows the content of Cd after NH_4NO_3 extraction in half of the samples (for better observation).

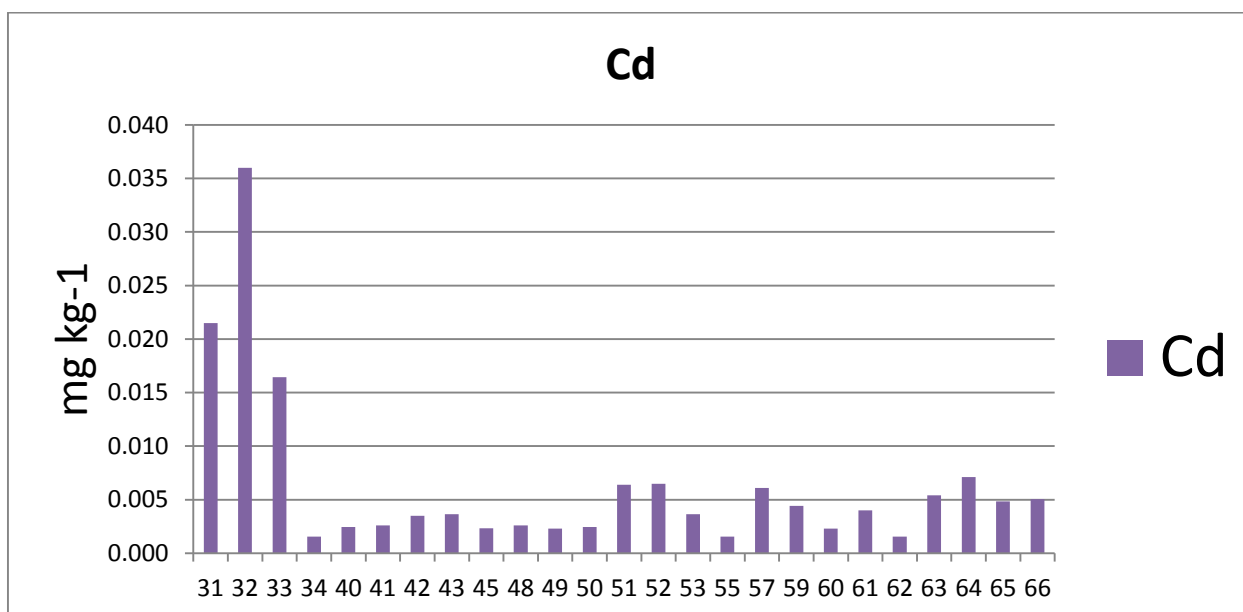
Graph 3. Content of Cd in the samples from 1 to 30.



The Czech Environmental law has the limit for other soils for Cd – 1 mg/kg. Graph 3 displays that all meaning are between 0 and 0,005 mg/kg. Content of Cd is very small. Detection limit for Cd is 0.005 mg/kg.

Graph 4 below displays the content of Cd after NH_4NO_3 extraction in another half of samples (for better observation).Detection limit for Cd is 0.005 mg/kg.

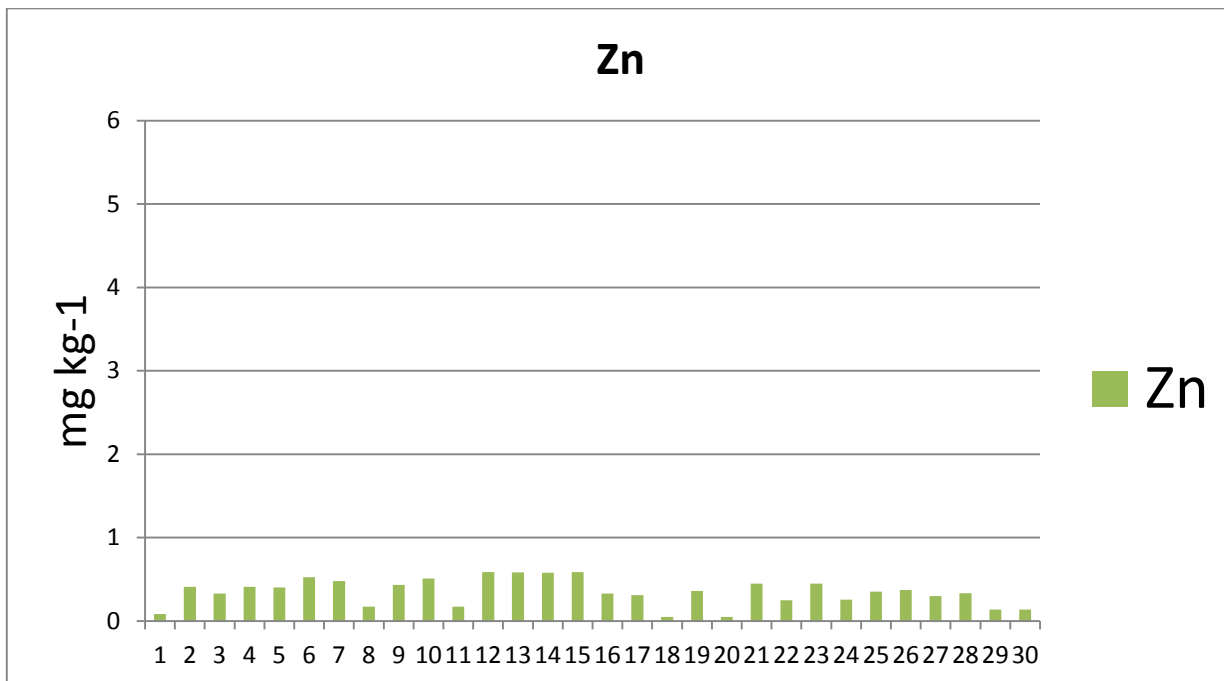
Graph 4. Content of Cd in the samples from 31 to 66.



In spite of we can see higher values (compare with the rest) for samples 31-33, which are without topsoil cover (Graph 2) still they are very far from the Czech Environmental law.

Graph 5 below shows the content of Zn after NH_4NO_3 extraction for the samples from 1 to 30 (for better observation). Detection limit for Cd is 0.005 mg/kg.

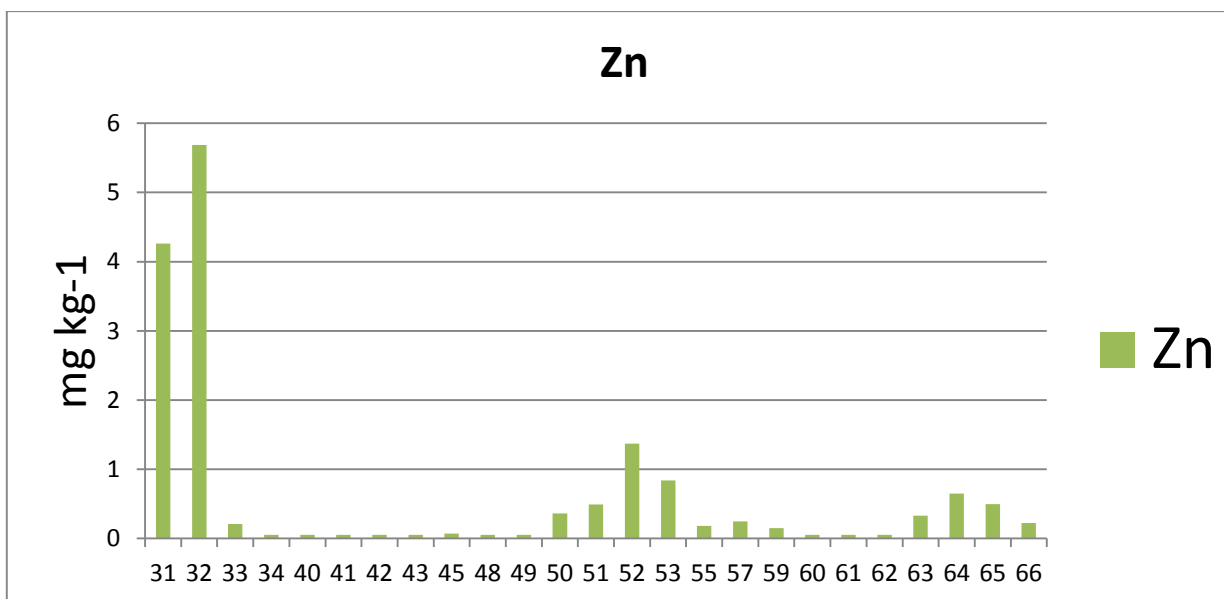
Graph 5. Content of Zn in samples from 1 to 30.



Bioavailable content of Zn is very small, even don't touch a mark of 1 mg/kg. It is defiantly below the Czech Environmental law for the other soils. Detection limit for Zn is 0.15 mg/kg.

Graph 6 demonstrate the composition of Zn after NH_4NO_3 extraction for the samples from 31 to 66 (for better observation). Detection limit for Zn is 0.15 mg/kg.

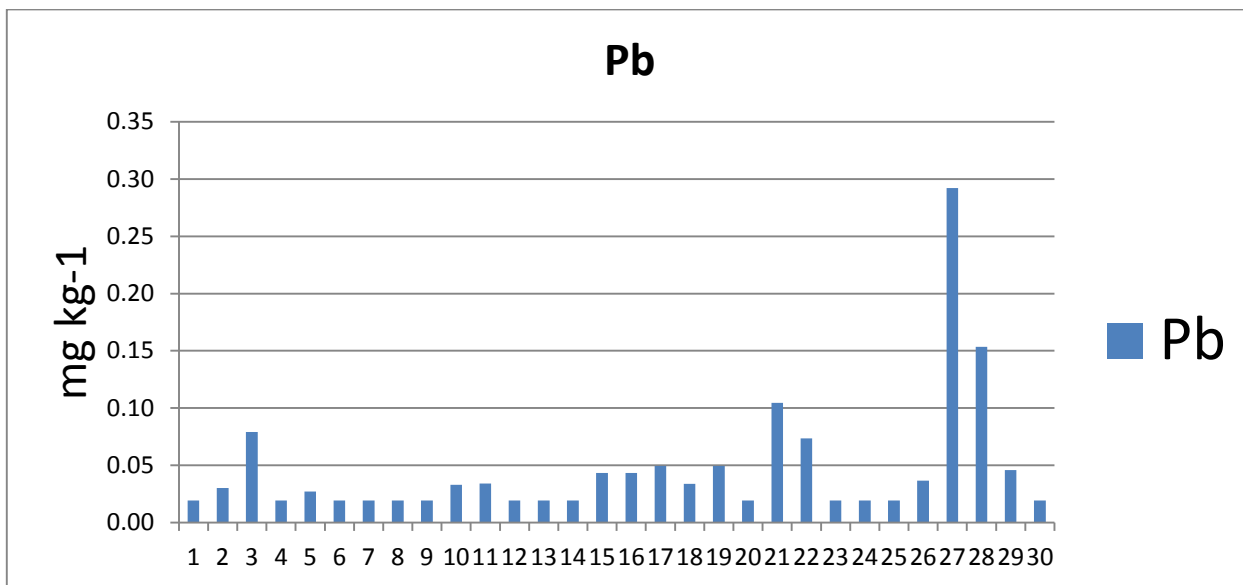
Graph 6. Content of Zn in the samples from 31 to 66.



Samples 31, 32, 52 are more than 1 mg/kg, these samples are without topsoil cover (Graph 2). Despite of the differences in meanings with other samples, the amount of Zn is still very low for all the samples. Detection limit for Zn is 0.15 mg/kg.

Graph 7 below displays the amount of Pb after NH₄NO₃ extraction in half of the samples (for better observation).

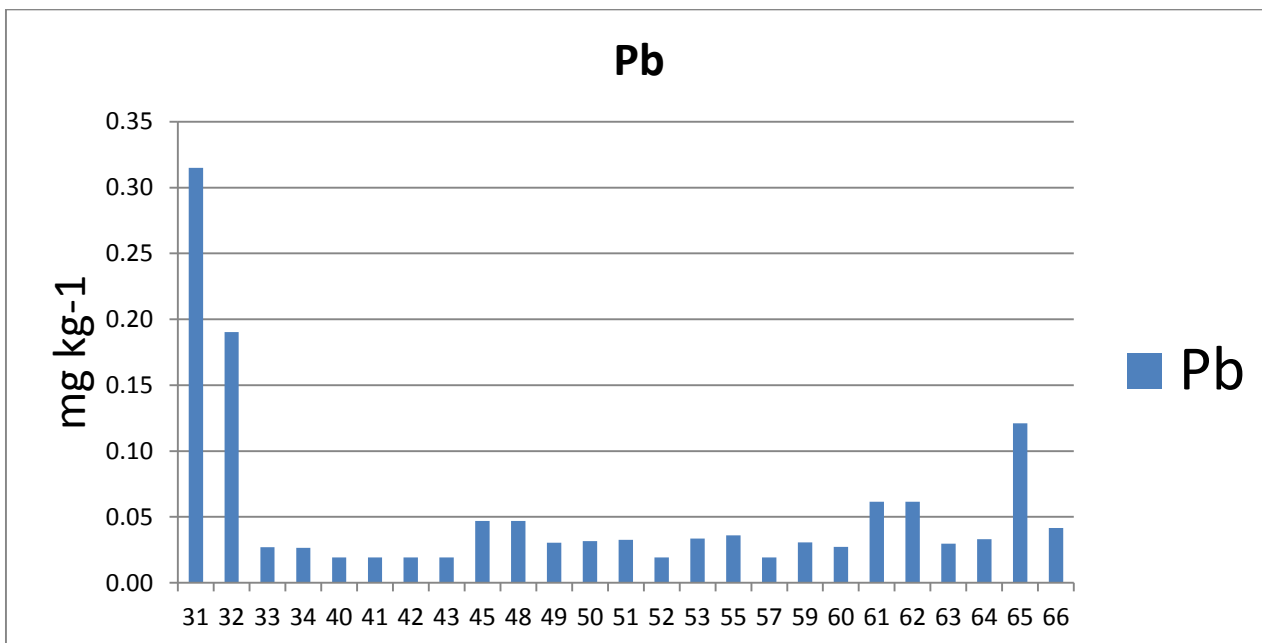
Graph 7. Content of Pb in samples from 1 to 30.



Samples 21,22,27,28 –without topsoil cover (Graph 2) have slightly larger values to compare with the others. Still all samples below the Czech standards. Detection limit for Pb is 0.06 mg/kg.

Graph 8 shows us the composition of Pb after NH₄NO₃ extraction in samples from 31 to 66 (for better observation).

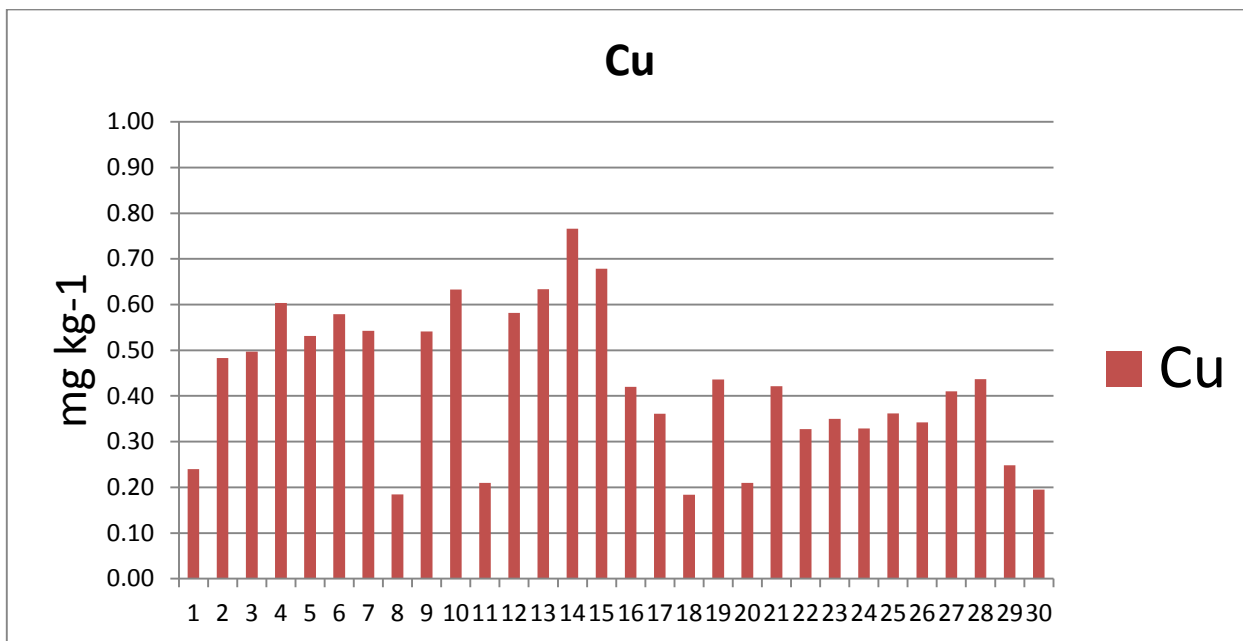
Graph 8. Content of Pb in the samples from 31 to 66.



Samples 31, 32, 65, specimens without topsoil cover (Graph 2) have slightly higher values for Pb but still all of them remain low and much lower than in the law standard. Detection limit for Pb is 0.06 mg/kg.

Graph 9 below shows the Cu contamination after NH₄NO₃ extraction of samples from 1 to 30 (for better observation)

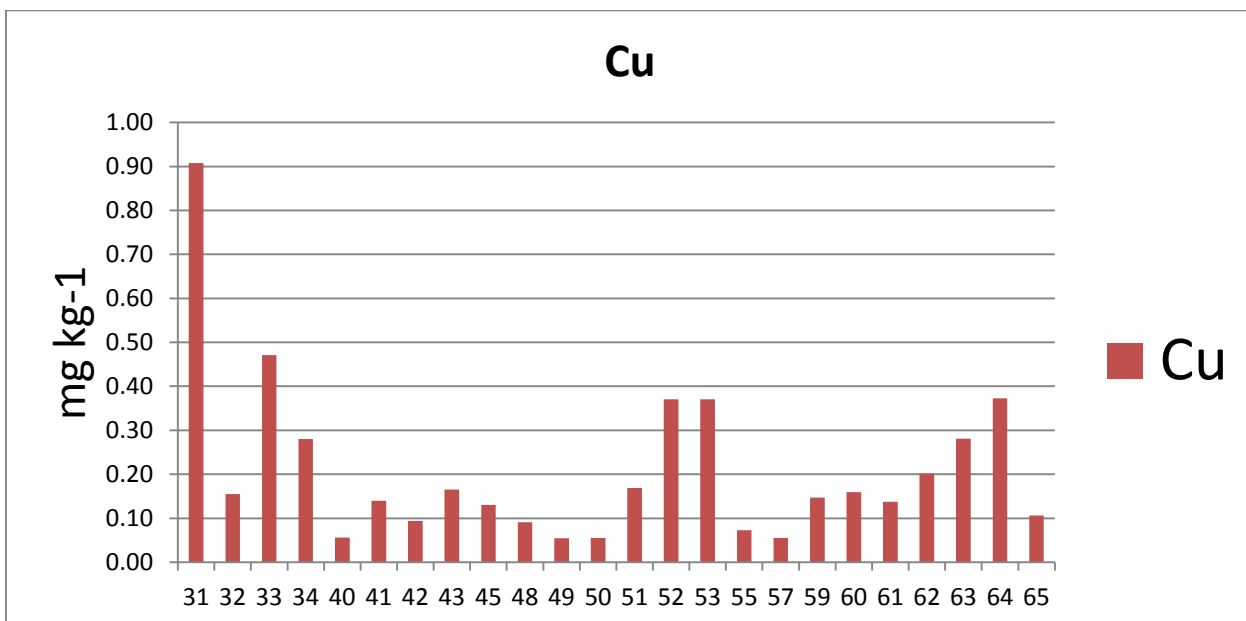
Graph 9. Content of Cu in the samples from 1 to 30.



The Czech Environmental standard is maximum 100 mg/kg of Cu. In this graph values are less than 1 mg/kg, much lower than in the law. Detection limit for Cu is 0.13 mg/kg.

Graph 10 demonstrates the content of Cu after NH₄NO₃ extraction for the samples from 31 to 66 (for better observation).

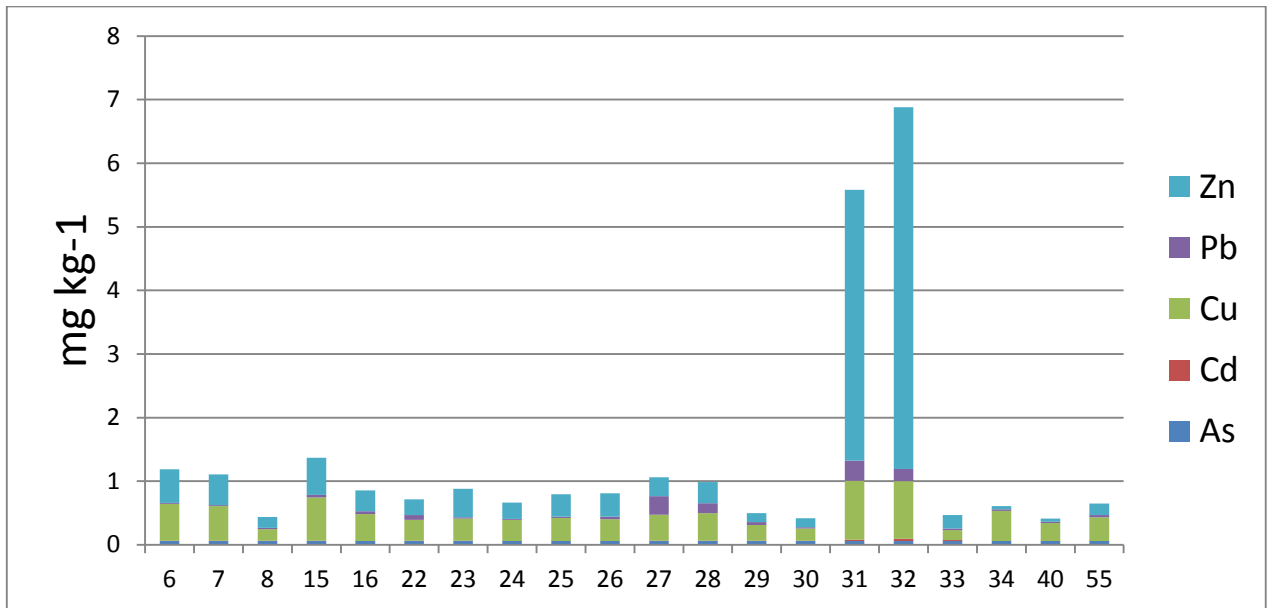
Graph 10. Content of Cu in the samples from 31 to 66.



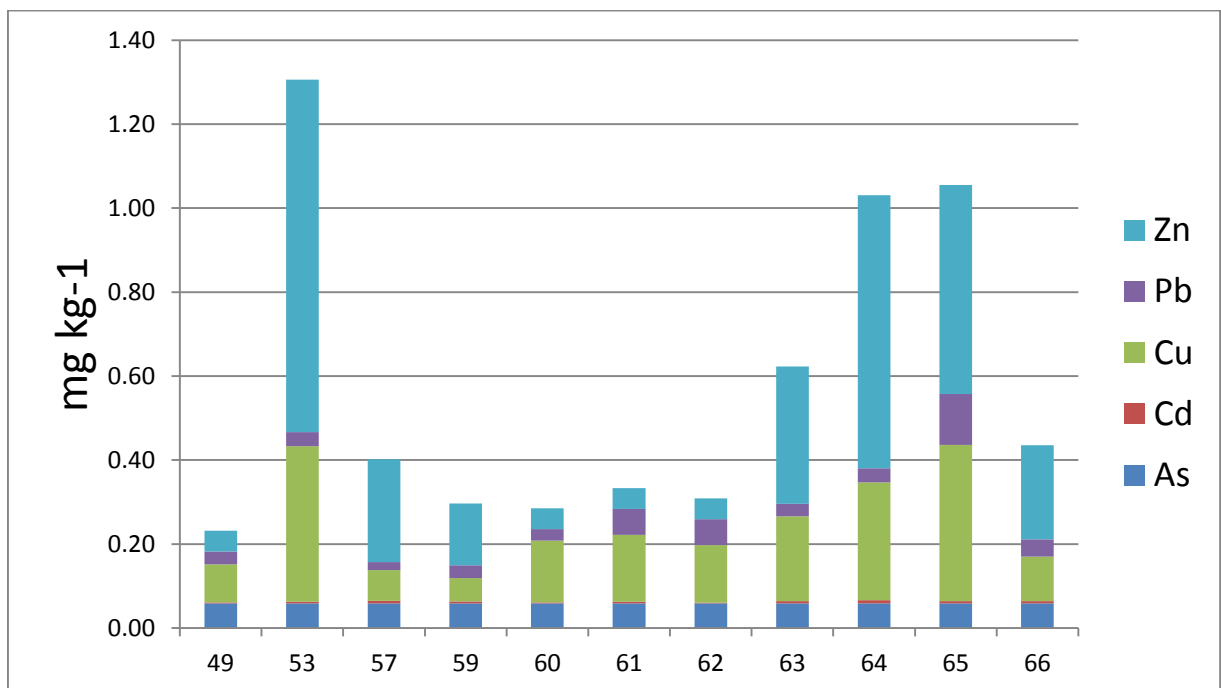
Lightly higher value is for sample 31, without topsoil cover (Graph 2), in comparison to the others – it is almost 2 times more, but still the amount of Cu in that group of samples remain very low. Detection limit for Cu is 0.13 mg/kg.

Graphs 11 and 12 below separated by method of reclamation measures: agricultural and forestry, respectively, after NH₄NO₃ extraction. They include all 5 elements which were checking in ICP –OES (As, Cd, Cu, Pb, and Zn).

Graph 11. Samples with agricultural reclamation



Graph 12. Samples with forestry reclamation



We compare different types of reclamation measure: agricultural and forestry. We can again note that values for a both graphs are quite low and similar. Rates in the graph with agricultural reclamation are about 1 mg/kg for all PTE, only №31 and №32 have higher content of elements. Forestry reclamation shows us really low indicators of all PTE from 1 to 1.3 mg/kg.

5.2. BCR sequential extraction and aqua regia extraction results

Table 5 below demonstrates the values from ICP-OES. Samples were chosen respectively of the reclamation type: 22-26 – agricultural, 57-62 – forestry. Also, topsoiling was applied for sample №22. Table 5 presented 3 steps from BCR sequential analysis and for aqua regia extraction - that's why each number of sample in 4 versions.

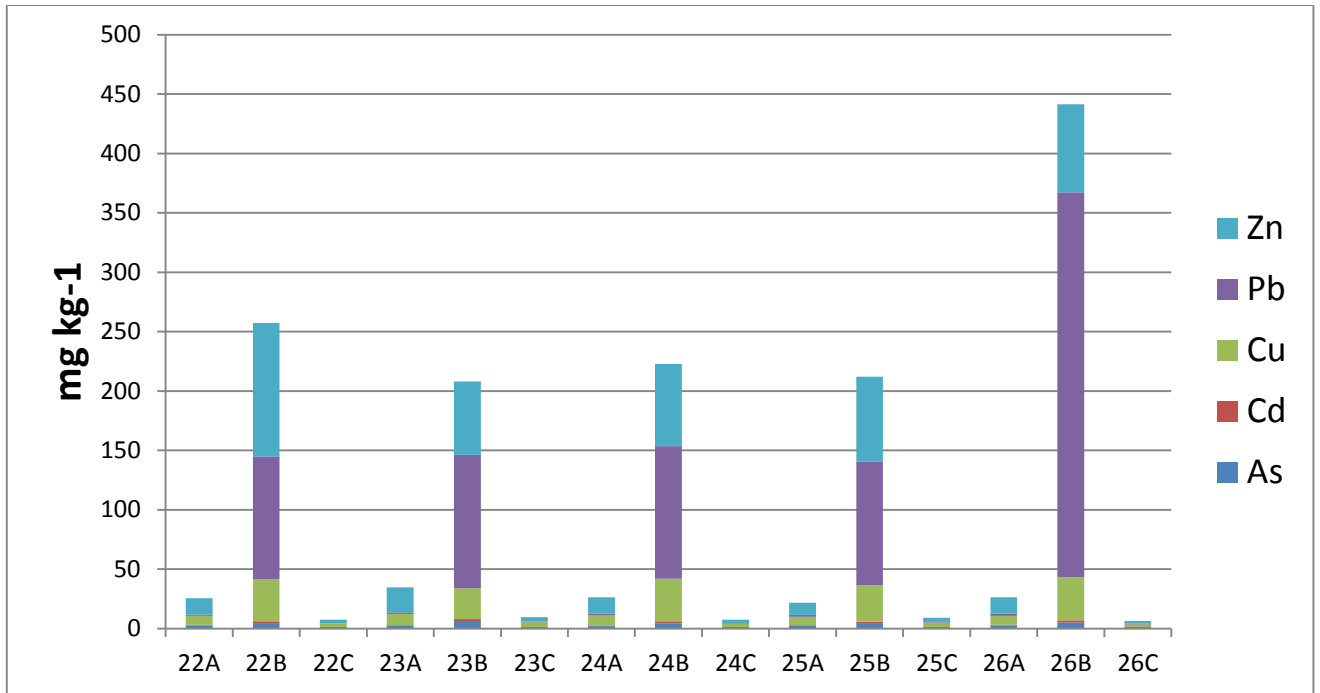
Table 5. Results from ICP-OES for 10 samples in mg/kg. Standard deviation in brackets. A is solution A, B is solution B, C is solution C, Q-aqua regia extraction.

№.	Sol.	As	As	Cd	Cd	Cu	Cu	Pb	Pb	Zn	Zn
		mg	SD	mg	SD	mg	SD	mg	SD	mg kg-	SD
		kg-1		kg-1		kg-1		kg-1		1	
22	A	2.66	(0.09)	0.47	(0)	7.73	(0.17)	1.02	(0.43)	13.68	(0.72)
22	B	4.10	(0.05)	2.13	(0.06)	35.62	(4.14)	103.17	(3.17)	112.46	(3.07)
22	C	1.18	(0)	0.03	(0)	3.01	(2.16)	0.38	(0)	2.97	(2.18)
22	Q	11.2	(0.19)	1.20	(0.02)	59.47	(0.94)	33.56	(0.47)	81.99	(1.07)
23	A	2.34	(0)	0.59	(0.02)	9.37	(1.47)	1.47	(0.06)	20.89	(0.6)
23	B	6.50	(1)	1.43	(0.14)	26.02	(0.69)	112.41	(1.06)	61.80	(2.93)
23	C	1.18	(0)	0.03	(0)	4.22	(0.52)	0.38	(0)	3.81	(0.82)
23	Q	17.5	(0.8)	0.75	(0.03)	33.03	(2.63)	27.82	(0.66)	51.87	(1.58)
24	A	2.04	(0.19)	0.54	(0.01)	8.45	(0.08)	1.60	(0.16)	13.65	(0.4)
24	B	4.38	(0.23)	1.88	(0.05)	35.75	(0.54)	111.69	(0.67)	69.26	(0.26)
24	C	1.18	(0)	0.05	(0.02)	2.80	(1.96)	0.38	(0)	3.06	(0.3)
24	Q	14.4	(1.04)	0.91	(0.01)	34.11	(0.60)	34.89	(0.83)	60.59	(0.57)
25	A	2.38	(0.03)	0.45	(0.01)	7.15	(1.07)	1.55	(0.22)	10.13	(0.11)
25	B	4.00	(0.16)	1.92	(0.06)	30.72	(2.52)	103.68	(4.56)	71.76	(1.99)
25	C	1.18	(0)	0.03	(0)	3.79	(1.51)	0.52	(0.14)	3.46	(0.39)
25	Q	16.4	(1.32)	0.99	(0.07)	33.17	(0.21)	32.22	(0.07)	60.99	(0.57)
26	A	2.61	(0.06)	0.58	(0.03)	7.44	(0.42)	1.92	(1)	13.69	(0.32)
26	B	5.14	(0.06)	1.88	(0.11)	36.28	(5.57)	324.06	(209)	74.15	(1.88)

26	C	1.18	(0)	0.03	(0)	2.16	(1.31)	1.02	(0.32)	1.93	(1.13)
26	Q	16.1	(0.8)	0.89	(0.02)	39.82	(0.24)	32.51	(0.33)	63.47	(1.38)
57	A	0.94	(0)	0.51	(0.02)	10.56	(0.35)	1.00	(0.37)	34.97	(1.46)
57	B	2.55	(0.08)	2.84	(0.17)	59.59	(0.81)	101.5	(0.69)	169.75	(4.42)
57	C	1.18	(0)	0.03	(0)	4.23	(0.98)	1.41	(1.03)	5.61	(1.82)
57	Q	6.08	(0.23)	1.07	(0.01)	39.36	(1.86)	36.18	(0.16)	84.57	(2.64)
59	A	0.94	(0)	0.41	(0.03)	9.73	(1.99)	1.59	(0.28)	17.07	(0.54)
59	B	2.48	(0.03)	1.49	(0.03)	38.69	(1.30)	97.30	(10.4)	83.53	(3.12)
59	C	1.18	(0)	0.03	(0)	4.02	(0.61)	0.59	(0.2)	4.06	(0.83)
59	Q	9.63	(0.72)	1.25	(0.02)	41.16	(1.54)	36.05	(1.02)	72.98	(1.12)
60	A	0.94	(0)	0.64	(0.03)	10.64	(1.22)	1.28	(0.58)	31.10	(1.18)
60	B	2.65	(0.14)	2.02	(0.04)	53.99	(1.20)	88.61	(1.94)	120.58	(4.86)
60	C	1.18	(0.00)	0.03	(0)	3.64	(0.61)	3.23	(1.75)	3.58	(0.36)
60	Q	7.48	(0.22)	0.89	(0.02)	37.74	(2.77)	29.60	(0.99)	69.35	(2.77)
61	A	0.94	(0.00)	0.36	(0.02)	10.97	(0.65)	1.52	(0.34)	14.68	(0.02)
61	B	2.83	(0.14)	1.87	(0.07)	46.58	(3.76)	92.56	(3.15)	87.89	(4.99)
61	C	1.18	(0)	0.03	(0)	2.63	(0.62)	1.26	(0.11)	3.58	(0.54)
61	Q	6.87	(0.74)	1.16	(0.11)	41.84	(2.16)	39.07	(3.91)	88.93	(7)
62	A	0.94	(0)	0.39	(0.02)	8.67	(1.06)	1.45	(0.11)	20.32	(0.39)
62	B	2.38	(0.08)	1.97	(0.09)	54.24	(0.11)	81.13	(2.93)	104.44	(0.45)
62	C	1.18	(0)	0.04	(0.01)	3.70	(0.06)	0.38	(0)	3.67	(0.37)
62	Q	6.68	(1.04)	1.03	(0.05)	38.79	(3.73)	35.28	(2.5)	75.62	(4.2)

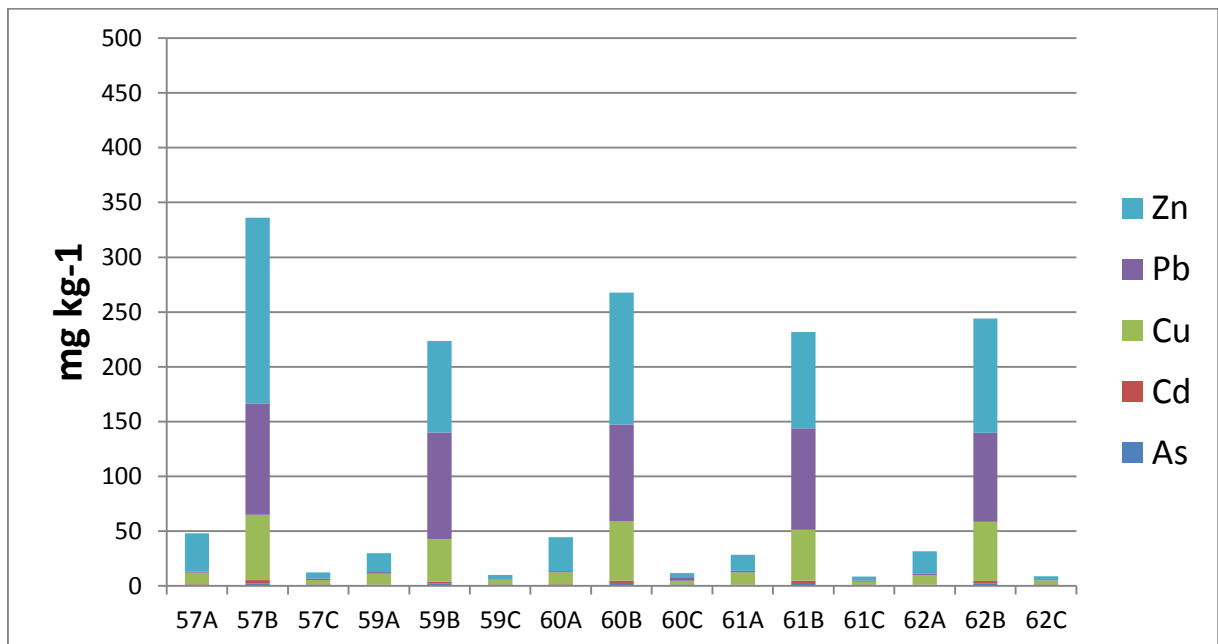
Graph 13 below shows us content of PTE in 5 samples with agricultural reclamation for each step of BCR analysis.

Graph 13. Content of PTE in samples with agricultural reclamation



Graph 14 below shows us content of PTE in 5 samples with forestry reclamation for each step of BCR analysis.

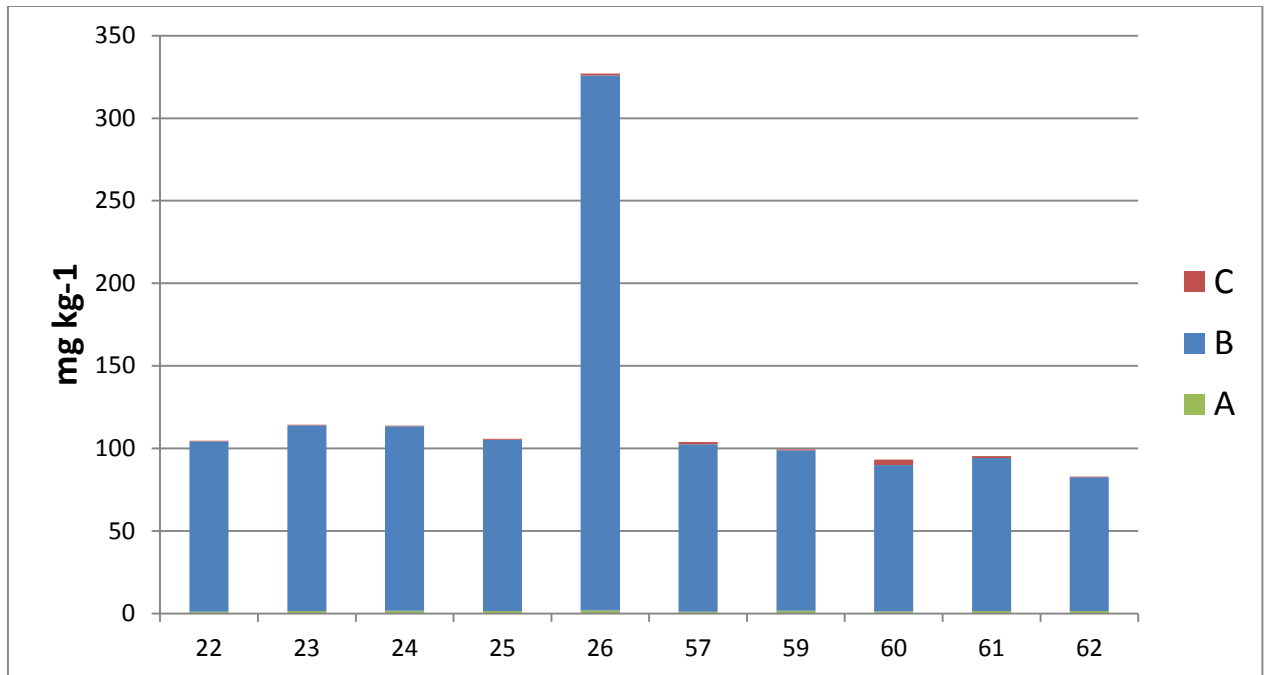
Graph 14. Content of PTE in samples with forestry reclamation



Graph 13 shows us that prevalence solution is solution B which consist the higher amount of PTE and the dominant element is Pb in the range from 100 to 300 mg/kg. Graph 14 has biggest meaning also in solution B but here is different prevalent element and it is Zn in the range from 100 to 200 mg/kg.

Graph 15 displays Pb composition for both types of reclamation (agricultural and forestry).

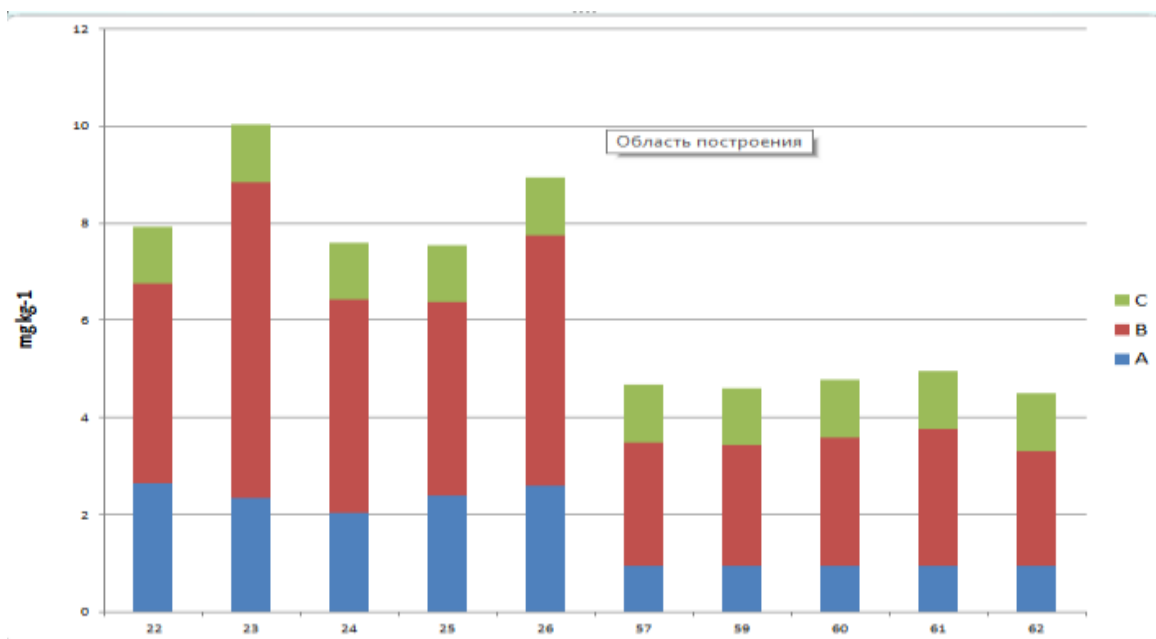
Graph 15. Lead (Pb) comparison of each sample and in each solution.



Graph 15 shows as that appearance of Pb higher for agricultural reclamation and lower for forestry reclamation measure. Determination limit for Pb is 0.06 mg/kg.

Graph 16 displays As composition for both types of reclamation (agricultural and forestry).

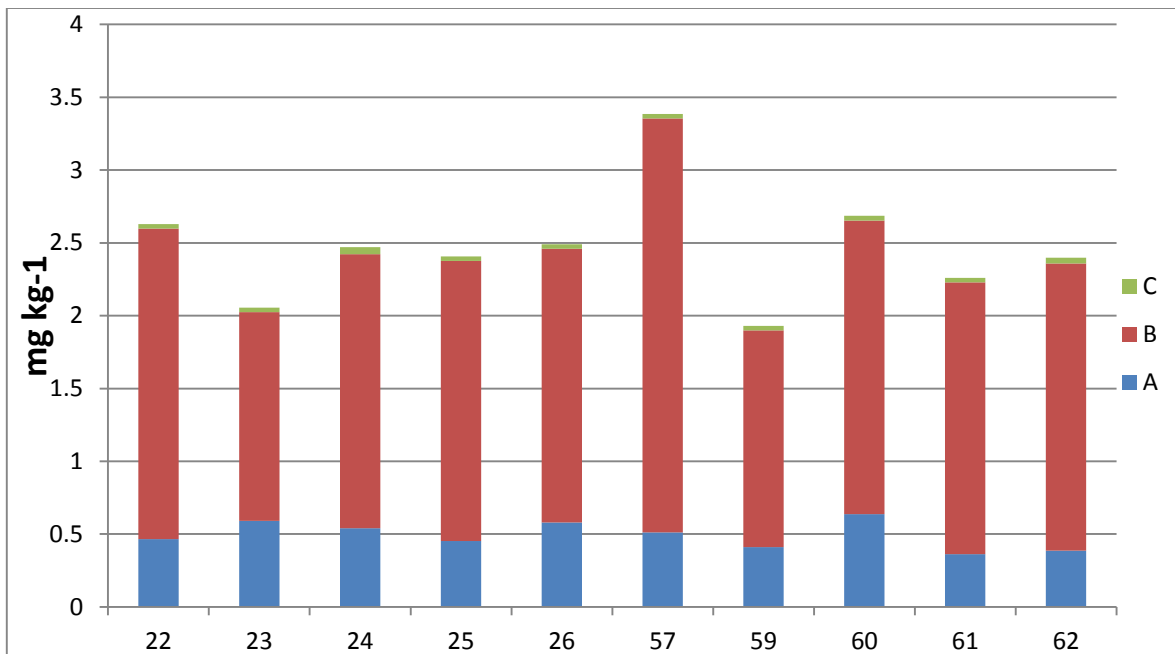
Graph 16. Arsenic (As) comparison of each sample and in each solution.



Graph 16 displays that amount of As also higher for samples with agricultural reclamation than for forestry reclamation. Determination limit for As is 0, 18 mg/kg.

Graph 17 shows Cd content for both types of reclamation (agricultural and forestry).

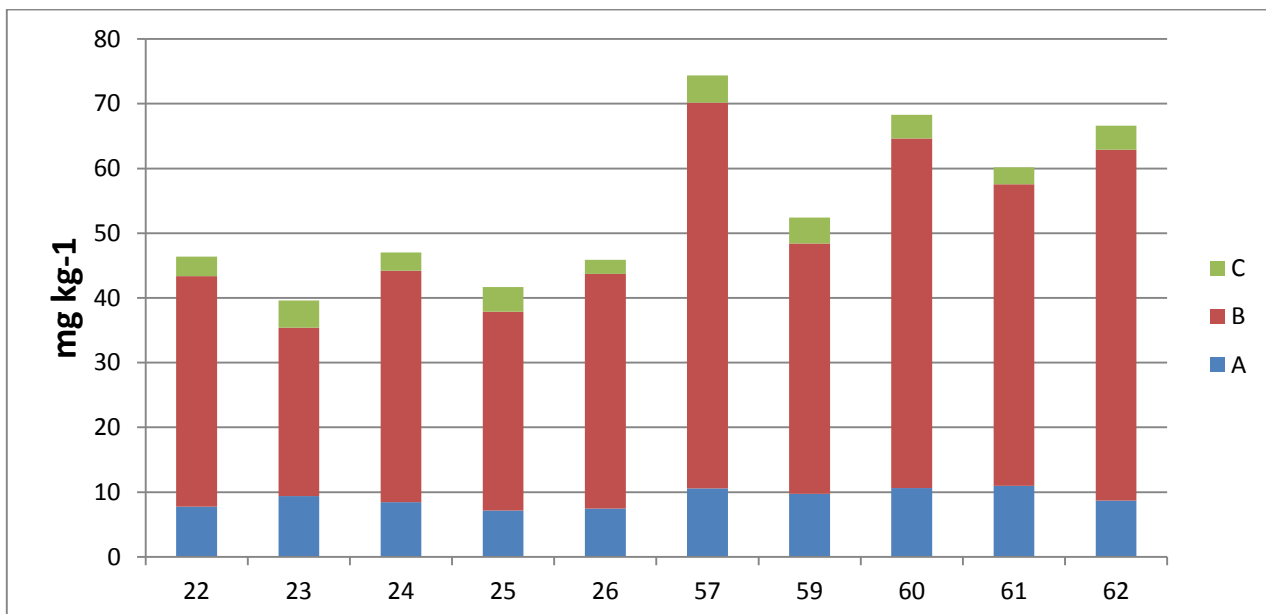
Graph 17. Cadmium (Cd) comparison of each sample and in each solution.



Comparison for Cd in Graph 9 reveals quiet large values for both types of reclamation in range to 1.3 to 3, 25 mg/kg. Determination limit for Cd is 0.005 mg/kg.

Graph 18 shows Cu content for both types of reclamation (agricultural and forestry).

Graph 18. Copper (Cu) comparison of each sample and in each solution.

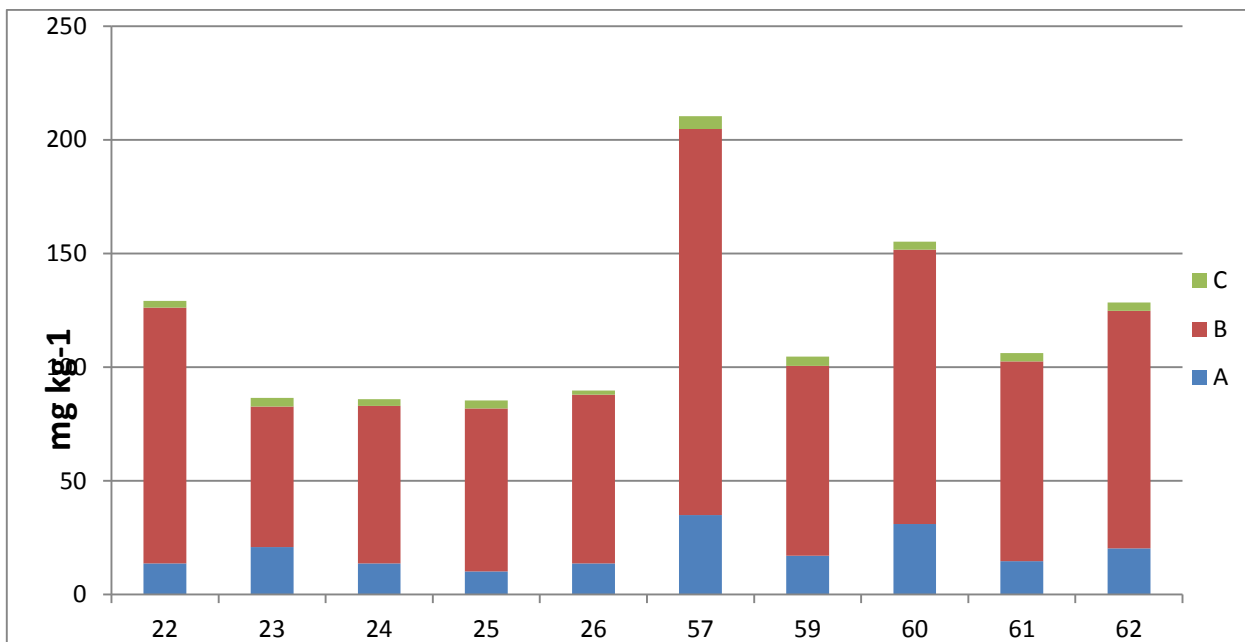


Graph 18 indicate higher rates for forestry, values from 35 to 60 mg/kg, than to agricultural one.

Determination limit for Cu is 0.13 mg/kg.

Graph 19 shows Cu content for both types of reclamation (agricultural and forestry).

Graph 19. Zinc (Zn) comparison of each sample and in each solution.



Zn comparison in Graph 19 shows us smaller values for agricultural type of reclamation except №22 which topsoiling method was used. Value for that sample is around 100 mg/kg. Samples from 57 to 62 is in the range from 75 to 215 mg/kg. Determination limit for Zn is 0.15 mg/kg.

6. Discussion

Contents and forms of potentially toxic elements in reclaimed dumpsite soils after brown-coal mining means that their determination depends on large-scale sampling and physical or conventional analysis techniques, which are time-consuming, inefficient, and expensive when applied on a large scale (Gholizadeh et al., 2015). Three main analysis were made: extraction of bioavailable elements due to dissolved solution of 1M NH_4NO_3 , BCR sequential analysis to determinate more exact content of potentially toxic elements and aqua regia extraction which determinate “pseudo” total metal content in a soil

This work is dedicated to study which can estimate the advantages and disadvantages of different reclamation measures, like forestry melioration, agricultural and topsoiling. Mine reclamation builds useful landscapes that will be appropriate for variety of aims ranging from the restoration of productive ecosystems to the creation of industrial and municipal resources. Nevertheless, determination of potentially toxic elements was the main research and in according to Gholizadeh et al. (2015) Elements (PTEs) in soils do not only impact the soil quality, but due to their persistent nature and long biological half-lives, can accumulate in the food chain and can eventually influence human health. Although the adverse effects of PTEs have long been known, and exposure to PTEs continues (and is even increasing in some areas), most of the former metallurgical tailing dumpsites are now abandoned. However, no particular safety measures are in place, and their environmental impact has received little attention.

Sample comparison for NH_4NO_3 extraction for Cu.

Cu (mg/kg)

Reclamation: agricultural and forestry.

Graph 20. Agricultural and forestry comparison for Cu.

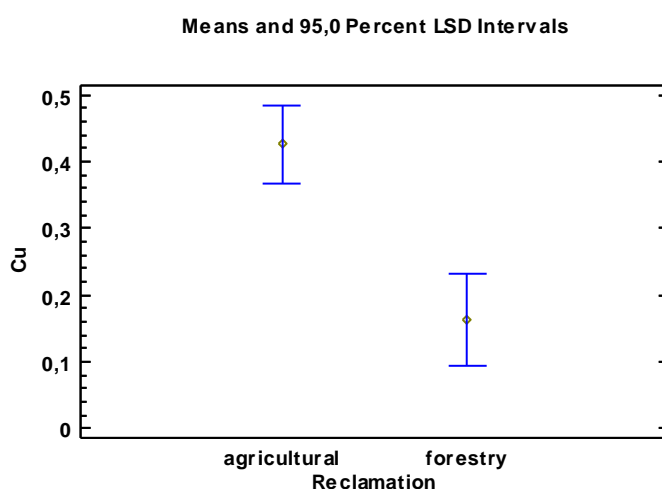


Table 6 demonstrates the variance of the data into two components: between-group component and within-group component. The F-ratio, which in this case equals 17.8452, is a ratio of the between-group estimate to the within-group estimate. Since the P-value of the F-test is less than 0.05, there is a statistically significant difference between the means of the 2 variables at the 95, 0% confidence level.

Table 6. Cu by Reclamation measure

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	0.570246	1	0.570246	17.85	0.0002
Within groups	1.02257	32	0.0319552		
Total (Corr.)	1.59281	33			

Table 7 displays the mean for each sample. It also shows the standard error of each mean, which is a measure of its sampling variability. The standard error is formed by dividing the pooled standard deviation by the square root of the number of observations at each level. The table also displays an interval around each mean. The intervals currently displayed are based on Fisher's least significant difference (LSD) procedure. They are constructed in such a way that if two means are the same, their intervals will overlap 95, 0% of the time.

Table 7. Means for Cu by forestry and agricultural reclamation with 95, 0 percent LSD intervals

Reclamation	Count	Mean	Std. error (pooled s)	Lower limit	Upper limit
agricultural	20	0,426	0,039972	0,368427	0,483573
forestry	14	0,162857	0,0477757	0,0940443	0,23167
Total	34	0,317647			

Cu (mg/kg)

Reclamation: topsoiling and without topsoiling.

Graph 21. With topsoil cover and without topsoil cover comparison for Cu.

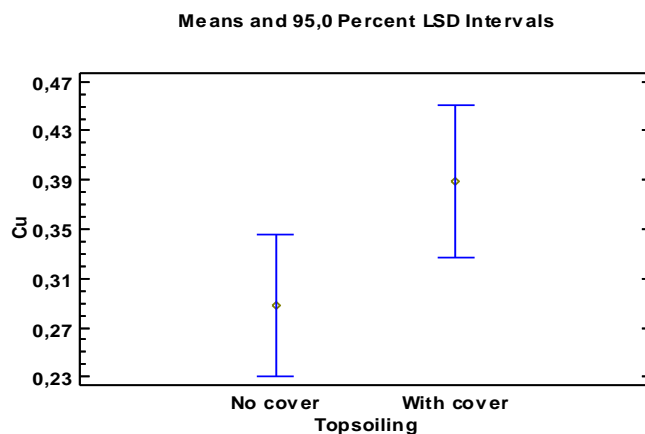


Table 8 decomposes the variance of the data into two components: a between-group component and a within-group component. The F-ratio, which in this case equals 2, 87163, is a ratio of the between-group estimate to the within-group estimate. Since the P-value of the F-test is greater than or equal to 0, 05, there is not a statistically significant difference between the means of the 2 variables at the 95, 0% confidence level.

Table 8. Cu by topsoiling reclamation measure

<i>Source</i>	<i>Sum of Squares</i>	<i>Df</i>	<i>Mean Square</i>	<i>F-Ratio</i>	<i>P-Value</i>
Between groups	0,131704	1	0,131704	2,87	0,0964
Within groups	2,29319	50	0,0458639		
Total (Corr.)	2,4249	51			

Table 9 shows the mean for each sample. It also shows the standard error of each mean, which is a measure of its sampling variability. The standard error is formed by dividing the pooled standard deviation by the square root of the number of observations at each level. The table also displays an interval around each mean. The intervals currently displayed are based on Fisher's least significant difference (LSD) procedure. They are constructed in such a way that if two means are the same, their intervals will overlap 95, 0% of the time.

Table 9. Means for Cu by Topsoiling with 95, 0 percent LSD intervals

			<i>Std. error</i>		
<i>Topsoiling</i>	<i>Count</i>	<i>Mean</i>	<i>(pooled s)</i>	<i>Lower limit</i>	<i>Upper limit</i>
No cover	28	0,288214	0,0404722	0,230733	0,345696
With cover	24	0,389167	0,0437149	0,32708	0,451254
Total	52	0,334808			

By study of Schulte et al. (2004) available Cu in soils is held mainly as a cation (Cu⁺⁺) on surfaces of clay minerals or in association with organic matter. Copper present as an impurity in silicate minerals or carbonates is largely unavailable. Organic matter and soil pH are the predominant factors influencing copper availability: decreases as organic matter increases.

Toxic levels of copper reduce seed germination, shoot vigor, and iron availability.

The possible reason that agricultural lands have more Cu (Graph 20) is because of the plants grow on them like beet, lettuce, onion, spinach, sunflower, and tomato which have relatively high copper requirements (Schulte et al., 2004). The same can be said about the lands with topsoil cover and without. Difference is existing because of the existing plants in the area of topsoiling.

Sample comparison for NH₄NO₃ extraction for Pb.

Pb (mg/kg)

Reclamation: agricultural and forestry.

Graph 22. Agricultural and forestry comparison for Pb.

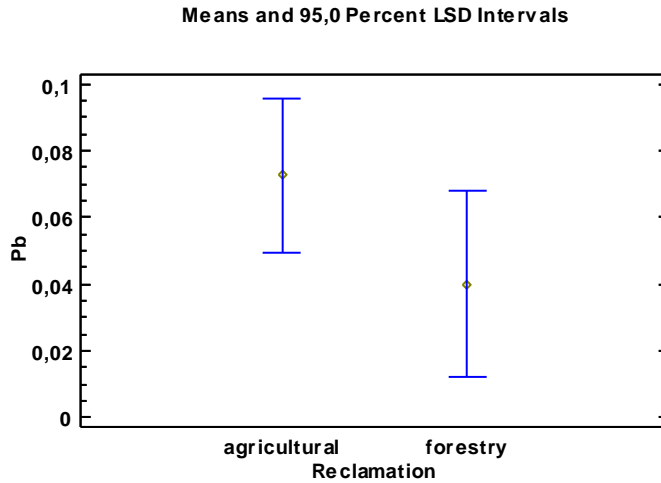


Table 10 table decomposes the variance of the data into two components: a between-group component and a within-group component. The F-ratio, which in this case equals 1, 66106, is a ratio of the between-group estimate to the within-group estimate. Since the P-value of the F-test is greater than or equal to 0, 05, there is not a statistically significant difference between the means of the 2 variables at the 95, 0% confidence level.

Table 10. Cu by Reclamation measure.

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	0,00869853	1	0,00869853	1,66	0,2067
Within groups	0,167575	32	0,00523672		
Total (Corr.)	0,176274	33			

Table 11 shows the mean for each sample. It also shows the standard error of each mean, which is a measure of its sampling variability. The standard error is formed by dividing the pooled standard deviation by the square root of the number of observations at each level. The table also displays an interval around each mean. The intervals currently displayed are based on Fisher's least significant difference (LSD) procedure. They are constructed in such a way that if two means are the same, their intervals will overlap 95, 0% of the time.

Table 11. Means for Pb by Reclamation with 95, 0 percent LSD intervals

Reclamation	Count	Mean	Std. error (pooled s)	Lower limit	Upper limit

agricultural	20	0,0725	0,0161813	0,0491935	0,0958065
forestry	14	0,04	0,0193404	0,0121434	0,0678566
Total	34	0,0591176			

Pb (mg/kg)

Reclamation: topsoiling and without topsoiling.

Graph 23. With topsoil cover and without topsoil cover comparison for Pb.

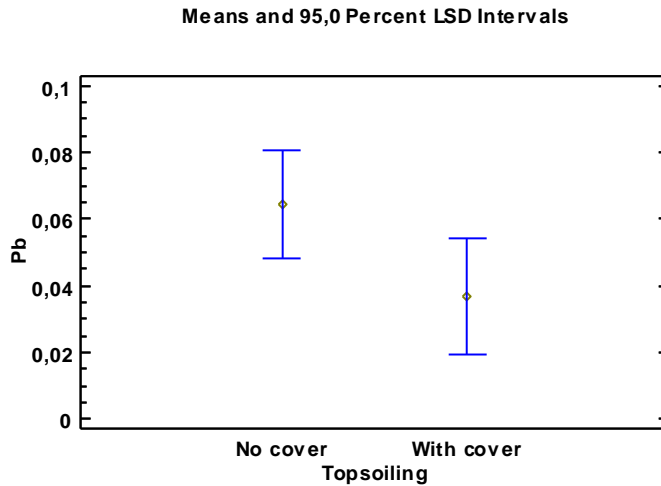


Table 12 decomposes the variance of the data into two components: a between-group component and a within-group component. The F-ratio, which in this case equals 2, 7259, is a ratio of the between-group estimate to the within-group estimate. Since the P-value of the F-test is greater than or equal to 0, 05, there is not a statistically significant difference between the means of the 2 variables at the 95, 0% confidence level.

Table 12. Pb by Topsoiling

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	0,00985788	1	0,00985788	2,73	0,1050
Within groups	0,180819	50	0,00361638		
Total (Corr.)	0,190677	51			

Table 13 shows the mean for each sample. It also shows the standard error of each mean, which is a measure of its sampling variability. The standard error is formed by dividing the pooled standard deviation by the square root of the number of observations at each level. The table also displays an interval around each mean. The intervals currently displayed are based on Fisher's least significant difference (LSD) procedure. They are constructed in such a way that if two means are the same, their intervals will overlap 95, 0% of the time.

Table 13. Means for Pb by Topsoiling with 95, 0 percent LSD intervals

			<i>Std. error</i>		
<i>Topsoiling</i>	<i>Count</i>	<i>Mean</i>	<i>(pooled s)</i>	<i>Lower limit</i>	<i>Upper limit</i>
No cover	28	0,064285 7	0,011364 7	0,0481448	0,0804266
With cover	24	0,036666 7	0,012275 3	0,0192325	0,0541009
Total	52	0,051538 5			

By study of US College of Agricultural Sciences (2015), soil lead is held tightly on the surfaces of very fine clay and organic matter particles. Therefore, when lead is added to the soil surface, it tends to accumulate in the upper 1 to 2 inches (2, 54-5, 08 cm) of soil unless the soil has been disturbed by activities such as excavation for building or tillage for landscaping and gardening. Some lead added to soil may combine with other soil elements to form lead-containing minerals. One such mineral that has extremely low solubility is lead phosphate (pyromorphite). Formation of this mineral is favored by high soil pH and high levels of lead and phosphate, conditions that would occur with the application of ground agricultural limestone and large amounts of phosphate fertilizer to a lead-contaminated soil. Airborne lead from industrial sources also may have contaminated some nearby residential soils.

The higher content of Pb in the soil without topsoiling obvious because it was brown-coal mining before, and the higher content of Pb in the forestry reclaimed can be because it was more techniques in there (to cut trees, than to excavate) which is the main source of Pb contamination.

Sample comparison for NH₄NO₃ extraction for Zn. Zn (mg/kg)

Reclamation: agricultural and forestry.

Graph 24. Agricultural and forestry comparison for Zn.

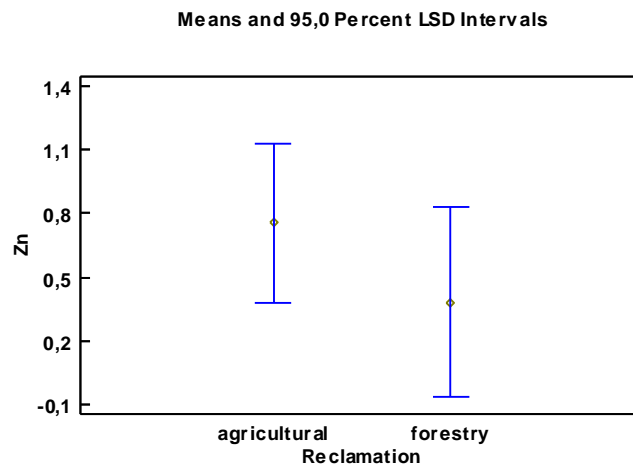


Table 14 decomposes the variance of the data into two components: a between-group component and a within-group component. The F-ratio, which in this case equals 0,857711, is a ratio of the between-group estimate to the within-group estimate. Since the P-value of the F-test is greater than or equal to 0, 05, there is not a statistically significant difference between the means of the 2 variables at the 95, 0% confidence level.

Table 14. Zn by Reclamation measure

<i>Source</i>	<i>Sum of Squares</i>	<i>Df</i>	<i>Mean Square</i>	<i>F-Ratio</i>	<i>P-Value</i>
Between groups	1,14796	1	1,14796	0,86	0,3613
Within groups	42,8289	32	1,3384		
Total (Corr.)	43,9769	33			

Table 15 shows the mean for each sample. It also shows the standard error of each mean, which is a measure of its sampling variability. The standard error is formed by dividing the pooled standard deviation by the square root of the number of observations at each level. The table also displays an interval around each mean. The intervals currently displayed are based on Fisher's least significant difference (LSD) procedure. They are constructed in such a way that if two means are the same, their intervals will overlap 95, 0% of the time.

Table 15. Means for Zn by Reclamation with 95, 0 percent LSD intervals

<i>Reclamation</i>	<i>Count</i>	<i>Mean</i>	<i>Std. error (pooled s)</i>	<i>Lower limit</i>	<i>Upper limit</i>
agricultural	20	0,7555	0,258689	0,382901	1,1281
forestry	14	0,382143	0,309193	-0,0631978	0,827483
Total	34	0,601765			

Reclamation: topsoiling and without topsoiling.

Graph 25. With topsoil cover and without topsoil cover comparison for Zn (mg/kg).

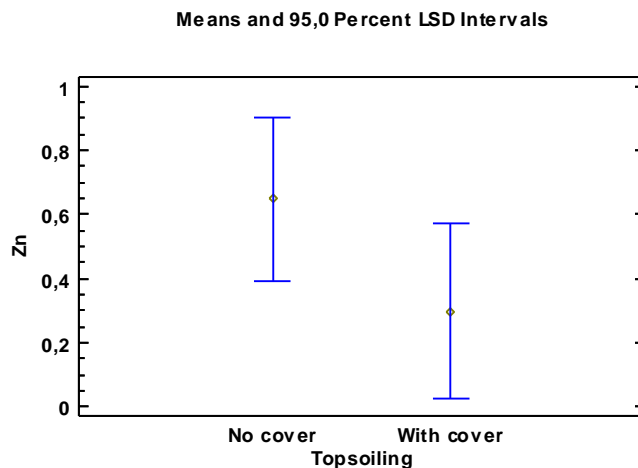


Table 16 decomposes the variance of the data into two components: a between-group component and a within-group component. The F-ratio, which in this case equals 1, 77258, is a ratio of the between-group estimate to the within-group estimate. Since the P-value of the F-test is greater than or equal to 0, 05, there is not a statistically significant difference between the means of the 2 variables at the 95, 0% confidence level.

Table 16. Zn by Topsoiling

<i>Source</i>	<i>Sum of Squares</i>	<i>Df</i>	<i>Mean Square</i>	<i>F-Ratio</i>	<i>P-Value</i>
Between groups	1,57608	1	1,57608	1,77	0,1891
Within groups	44,4574	50	0,889147		
Total (Corr.)	46,0335	51			

Table 17 table shows the mean for each sample. It also shows the standard error of each mean, which is a measure of its sampling variability. The standard error is formed by dividing the pooled standard deviation by the square root of the number of observations at each level. The table also displays an interval around each mean. The intervals currently displayed are based on Fisher's least significant difference (LSD) procedure. They are constructed in such a way that if two means are the same, their intervals will overlap 95, 0% of the time.

Table 17. Means for Zn by Topsoiling with 95, 0 percent LSD intervals

			<i>Std. error</i>		
<i>Topsoiling</i>	<i>Count</i>	<i>Mean</i>	<i>(pooled s)</i>	<i>Lower limit</i>	<i>Upper limit</i>
No cover	28	0,647143	0,1782	0,394051	0,900235
With cover	24	0,297917	0,192478	0,0245461	0,571287
Total	52	0,485962			

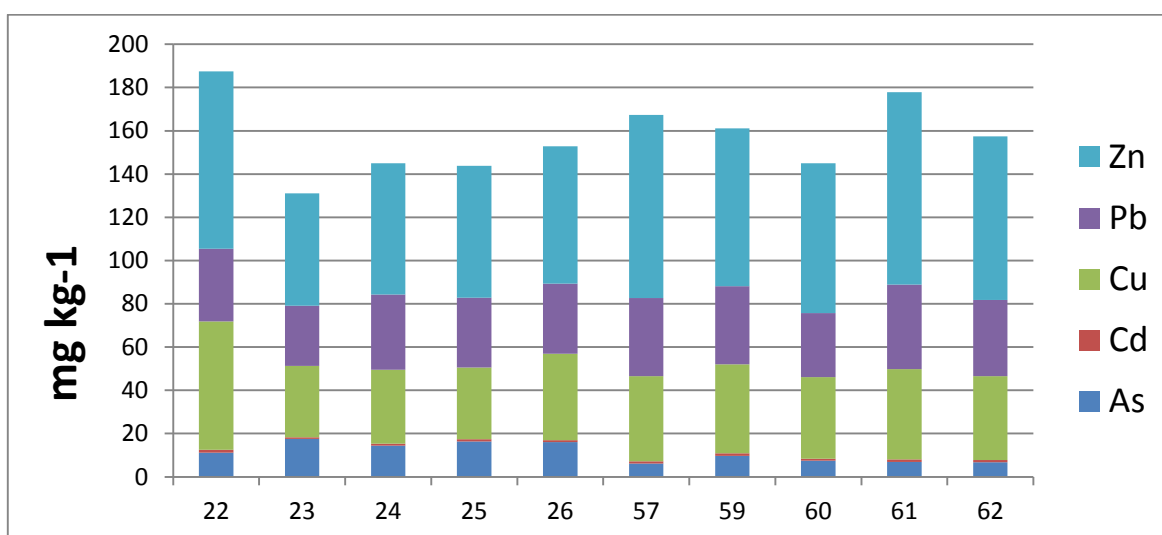
According to Alloway (2008) Zinc is a trace element found in varying concentrations in all soils, plants and animals and it is essential for the normal healthy growth of higher plants, animals and humans. Zinc is needed in small but critical concentrations and if the amount available is not adequate, plants and/or animals will suffer from physiological stress brought about by the dysfunction of several enzyme systems and other metabolic functions in which zinc plays a part. Due to Lenntech Water Treatment (2008), most zinc is added during industrial activities, such as mining, coal and waste combustion and steel processing. Some soils are heavily contaminated with zinc, and these are to be found in areas where zinc has to be mined or refined, or were sewage sludge from industrial areas has been used as fertilizer.

Higher content of Zn is in the soil with no cover obvious because it was brown-coal mining production. Agricultural and forestry reclaimed soils have not big differences of the values and also due to mining production.

The confirmation of low content of bioavailable potentially toxic elements was proved by NH_4NO_3 extraction (Table 4). Composition of main As, Cd, Cu, Pb, Zn are almost neglectable. As even under determination limit and cannot be recognized. If we will look at “pseudo” total content of ten samples that have been selected for agricultural and forestry reclamation we will see that the content of potentially toxic elements is also in the borders of the Czech law, so it cannot be dangerous both for vegetation and humans (Graph 26).

Graph 26 displays the contents of As, Cd, Cu, Pb, Zn from aqua regia extraction.

Graph 26. Content of PTE in aqua regia extraction.



Soil with topsoil cover has really low meanings of potentially toxic elements (Graph 1). That's mean that this soil can be productive for further using. According to Boruvka et al. (2012) Natural topsoil cover can generally improve the starting quality of the developing soil. It can facilitate further soil forming process, plant development, as well as the exploitation of the soils particularly for agricultural use. Spatial variation and distribution of soil properties on the dumpsites under study is very pronounced and can be only partly influenced by reclamation measures. From the point of view of reclamation practice, soil physical and chemical properties must be considered in complexity when planning the reclamation. Applied method of topsoil handling and spreading and its timing are also important, as they can cause soil compaction and unfavorable changes of soil physical properties.

7. Conclusion

The content of bioavailable elements in soil with topsoil cover and without topsoil cover is very small, so the hypothesis of influence of atmospheric deposition is not correct. The proportion of bioavailable forms of PTE in reclaimed soils is low, sometime even lower to detect them. Definitely, all bioavailable forms of PTE rates are below the Czech environmental standard for reclaimed soil.

Values, data and graphs for samples which were taken from soil with agricultural reclamation displayed different meanings for all PTE. Highest content of Pb was detected in one sample and it is more than 300 mg/kg, results for all the rest samples are lower. Pb is above the limit for one sample. Values of As in solution A for BCR sequential analysis – more than 2 mg/kg. Solution B has even larger amounts of As: mostly more than 4 mg/kg. All these meanings are below the Czech law. Biggest content of Cd contains in solution B in range of 1.5 to 3 mg/kg. Connotations for Cd in solution B are greater than in the Czech law. Greater amount of Cu is in solution B above 60 mg/kg, however, all the samples values below Czech law. The biggest Zn content about 150 mg/kg in solution B, other samples for solution B have numbers about 100 mg/kg. Solution C and A has really small meanings for all the samples. Zn is for all samples lower than Czech limit has for reclaimed (other) soils. Agricultural reclamation shows us that soil contaminated with Pb and Cd. Agricultural reclamation has only little higher values for Pb and Cd. Still all meanings are low, if it is higher than in law – greater values are not so much. Content of potentially toxic elements which was determined by BCR sequential analysis in the soils with agricultural reclamation is small.

Values in the data and graphs above show that samples which were taken from the forestry reclaimed soil have contrasting meanings for each PTE. Highest content of Pb in solution B and for all samples is about 100 mg/kg. Amounts of Pb in solutions A, C are minimal. All values for solution B below the Czech law. As for solutions A, B, C for all samples have more or less the same values and they are below the Czech law. Greatest amount of Cd for solution B is 3mg/kg, the smallest about 1.5mg/kg. All Cd values for solution B are above Czech law. Values for solution B have meaning for Cu all within the law. Samples have minimal connotations for solutions A and C. All values below the limit for other soils. Greatest amount of Zn is around 200 mg/kg for solution B– within the limit, other samples are less than 120 mg/kg. Forestry reclamation has one contaminant - Cd, sometimes meanings for that several times more than in the limit. All other elements are under Czech environmental law.

The toxicity of soil is low and not dangerous for agricultural application.

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