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Environmental Burden of Potentially Toxic Elements Originating from Silver Smelting Slag

Diploma Thesis

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Declaration

I certify that I prepared the MSc. Thesis on "Environmental Burden of Potentially Toxic Elements Originating from Silver Smelting Slag" by myself and I used only the literature sources which I quote and mention in the attached bibliography.

In Prague 13th April 2012

Signature ……………………………………..

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Keywords Contaminated Land, Risk Elements, Silver Smelting Slag, Leaching Experiment

Summary

Slag produced from the historical smelting of precious metals contain elevated levels of risk elements and remain a feature of the landscape for many centuries. This thesis focuses on the silver smelting slag of Kutná Hora. It identifies the "near total" and available contents of risk elements plus other nutrient elements, and the main factors which control their mobility. A leaching experiment is also included to determine the effect that rain water and a weak citric acid solution have on the dissolution of metals from the slag. The investigation of the slag and surrounding soils identified high 2M HNO_3 extractable contents of risk elements but comparatively low available contents (mean available % of "total" = Pb 0.9; Cd 18.9; Mn 12.8; Cu 1.8; Ag 0.8; Zn 1.6; As 0.6). There was an observed trend of overall decreasing risk element contents with increasing content of organic matter and decreasing pH (increase in organic matter correlates with decreasing pH R = 0.786). Solubility of risk elements also appears to be more dependent on pH than other factors as evident from correlation and Chi-Square statistics. The Vrchlice River sediments revealed high total concentrations of As (9.48 mg/kg), Mn (1,607. mg/kg) and Zn (1,556. mg/kg). The leaching experiment showed that Pd, Zn and Cd have low extractability by citric acid and the soluble concentrations of these elements decreased along with the decomposition of citrate. Other elements (Mn, Ca, Mg, K and Na) showed an overall increase after one month in citric acid solution. A rainwater simulation solution proved more effective in the dissolution of analysed elements whereby an overall increase was observed after one month in every case except for Pb. The content of Cd remained very low despite an overall increase (< 0.4 mg/kg). The rainwater simulation correlated significantly with a control solution of slightly higher pH for Cd, Zn, Mn, Ca and Mg indicating little difference in extracting power of water solvents over a pH range of at least 1.0. Growth of a vegetative cover on the Kutná Hora slag is most probably dependent on the availability of key macro and micro nutrients and a good substrate for rooting as availability of nutrients correlates with organic matter and pH. Toxicity of the slag is unlikely to be a reason for the absence of plants.

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1. Introduction

Slag deposits from mineral smelting operations are testament to typical historical industrial practices, whereby a lack of concern and understanding toward the fate of the pollutants and their effect on the environment, have left such areas in a state of contamination. Silver (Ag) mining was a thriving industry in the Czech town of Kutná Hora (KH) which emerged as a result of the exploitation of Ag bearing loads discovered, which some speculate to be as early as the 10th century. A large expansion and exploitation of the minerals in the region reigned from the second half of the 13th century and production continued to be strong up until the turn of the 17th century. At its peak, approximately 6 – 7 tonnes of Ag were produced from the KH mining industry in the latter half of the 14th century (Pauliš and Mikuš 1998). A common method of extraction was to process broken ores in smelters. Their operation required the use of pyritic sulphides and lead (Pb) which segregated Ag from the roasted ores. The by-product of the smelting process are the huge mounds of slag which intrude on the landscape, and remain barren and void of any significant vegetation up until the present day. The study area which is located along the Vrchlice River bank in the town of KH presents itself as a contaminated site both visually (given the absence of vegetation on the slag heap itself) and from the presence of risk elements (RE) contained in the slags which have been identified from prior study by colleagues at Czech University of Life Sciences (CULS). However, despite the initial study of the area, there are gaps in the information regarding RE composition, mobility and behaviour within the slags, particularly in the riverbank soils. This thesis serves to present an investigation into the RE distribution and composition along the Vrchlice River bank. It will study and consider the environmental character and parameters of the study area and determine whether or not there is a significant threat by the mobility of REs into the surrounding soils which have formed along the Vrchlice River bank and in the Vrchlice River sediments.

Through sampling and analysis of REs on the Vrchlice River bank, a significant contribution can be made to the modelling and understanding of the study area. This could provide information relevant for any clean up and remediation strategy that could be applied to such areas. Additionally, it will provide researchers with new data to assist in better understanding of these materials in the environment. Information obtained on the likely mobility of REs from slags into the surrounding soils could also be used to form new studies for other areas in the Kutná Hora region where slag has been deposited in significant quantities, and which may be affecting the health and quality of soils which are used for agricultural production.

2. Hypothesis, aims and objectives

2.1 Hypothesis

The concentration of risk elements will be considerably higher than soil guideline values in the soils which have formed in and around the Kutná Hora slag and the distribution of risk elements will be influenced by soil pH, organic matter and vegetation. In the leaching experiment, 1mM citric acid will be an effective solvent in the extraction of risk elements from slag and the rain simulation solution will be more effective in the dissolution of risk elements than a control solution.

2.2 Aims

To assess the environmental burden caused by potential REs leaching/weathering from the smelter slag placed on the Vrchlice River bank. To identify the main factors influencing the RE distribution in the surrounding soils and whether or not there is a significant risk of mobile elements entering soils on the Vrchlice River banks and within river sediments. Using the information obtained from the study, suggestions can be made on how to treat the slag.

2.3 Objectives

- Obtain background knowledge from writing of literature review
- Determine where to sample within the study area and develop a sampling and analysis plan
- Take samples and analyse for chosen risk elements and minerals in slag material and the soils from where they are taken. Use data interpreting techniques and relevant statistical analysis to determine which environmental parameters are responsible for the mobility, retention and biological availability of risk elements and minerals in the Vrchlice River bank soils.
- Use soil guideline values (SGV) to determine whether the site is classed as contaminated and to what extent.

- Perform a potential release assessment of risk elements from slag into solvents (rain simulation solution, low molecular mass organic acid and control solutions) by means of a leaching experiment

3 Literature review

3.1 Hazards and problems associated with risk elements

3.1.1 Risk element soil guideline values

Many historical and poorly managed industrial practices are responsible for high levels of exposure of hazardous REs to the environment. The dangers associated with such elements vary depending on many factors such as the element itself, concentrations and the species in which it occurs, pathways and targets, bioavailability, geomorphology and climate.

In response to these hazardous exposures, environmental authorities (typically in developed countries) often publish a set of general guidelines for risk assessment purposes of many REs. For the purpose of this study, reference will be made to soil guidelines published by the U.K Environment Agency, Table 3.1.1 (DEFRA 2011). The guideline values are derived using Contaminated Land Exposure Assessment (CLEA) model which has been developed for the delineation of guideline limits as criteria to help evaluate long term risks to human health (DEFRA 2011). Guidelines published for the Czech Republic which relate to agricultural land use (Reg. 13/1994) will also be referred to as they are appropriate to the area of study, see Table 3.1.2 (Podlešakova *et al.* 1990). It is interesting to note that the guideline values for Czech Republic are generally more conservative than those set in the U.K. Czech authorities have also given values for elements Be, Co, Cu, Mo, V and Zn where they are absent from the U.K guideline values. Although both authorities list guidelines for Hg, it is well documented in U.K guidelines with values for its varying species but only listed in elemental form in Czech guidelines. Neither country have published limits for Sb which is identified as a RE associated with smelter slag deposits (Table 3.3.1).

Guideline values for REs are obtained with consideration given typically to human health. These health implications are extensively described by toxicological studies. A concise table listing the basic health hazards associated with risk elements is listed in appendix A.

Table 3.1.1 U.K Soil Guideline Values as of 2011 (DEFRA 2011)

Contaminant	Soil Guideline Value (mg/kg)		
	Residential	Allotment	Commercial
As	20	20	500
Cd	30	8	1,400
Cr	200, (130 with plants)	130	5,000
Pb	450	450	750
Elemental Hg	1	26	26
Inorganic Hg^{2+}	170	80	3,600
Methyl H_3CHg^+	11	8	410
Ni	130	230	1,800
Se	350	120	13,000

Table 3.1.2 Soil Guideline Values for risk elements extractable with Aqua Regia (“total content”) and those extractable with 2M HNO_3 (simulating an extreme environmental scenario in which elements are mobilised in the environment) in Czech soils (Podlešakova *et al.* 1990)

Contaminant	Total content (mg/kg)		2M HNO_3 (mg/kg)	
	Sandy soils	Other soils	Sandy soils	Other soils
As	30	30	4.5	4.5
Be	7	7	2	2
Cd	0.4	1	0.4	1
Co	25	50	10	25
Cr	100	200	20	40
Cu	60	100	30	50
Hg	0.6	0.8	-	-
Mo	5	5	5	5
Ni	60	80	15	25
Pb	100	140	50	80
V	150	220	20	50
Zn	130	200	50	100

3.1.2 Varying toxicity of risk elements with speciation

The species in which a RE may occur in soil is governed by many properties, particularly pH, humus content and quality, and clay content (Borůvka and Vacha 2006). In addition to their concentrations, the toxicity of REs is dependent on their speciation. Chemical speciation of REs dictates its toxico-kinetic behaviour; influencing its adsorption, distribution, biotransformation and elimination (Evisa 2011). Therefore it is often necessary to perform analysis using both quantitative and qualitative methods. Due to the scale of this study, initial analyses will be limited to quantitative assessment through extractions of varying strength. However, the study remains open-ended, and where excessive bioavailable RE concentrations are observed within soils, there is the potential for a continuation of the study by deeper analysis of these selected elements.

3.1.3 Plants, risk elements and smelter slag

Metals are non-biodegradable and therefore persist for long periods in terrestrial environments. One of the pathways for the movement of metals in soils is uptake in plants. Some plants known as hyper-accumulators exhibit a tolerance to certain heavy metals and have the ability to accumulate high concentrations of metals in their tissues. Approximately 450 plants species have been classified as hyper-accumulators of heavy metals (Boularbah *et al.* 2006). *Thlaspi* species naturally adapted to metal rich soils in areas of Pb-Zn mineralization in Europe and are hyper-accumulators of Pb and Zn. *Thlaspi* species have been found to accumulate concentrations of over 3% Zn and 0.8% Pb (Alloway 1990). However, the majority of plant species are intolerant of heavy metals which exceed natural background levels in soil.

Table 3.3.1 shows Pb and Zn are among the most excessive REs associated with studied Ag smelter slags. Pb is readily absorbed by seedlings and adult plants, and an increase in Pb concentrations results in a decrease in the length and weight of roots and shoots of plants (Verma and Dubey 2003). Excessive Zn itself is toxic to plants and plant growth. Excess accumulation of Zn in plant tissues causes alterations in vital growth processes such as photosynthesis and chlorophyll biosynthesis (Stoyanova and Doncheva 2002). Plant establishment on Zn contaminated soils are further impaired because of Zn interference with P uptake (Shetty *et al.* 1994). In addition to Zn, the elements Cu and Mn which are described here as risk elements, are also micronutrients which are considered important in plant nutrition. However, in areas where anthropogenic activities have elevated their concentrations in soils to such excessive levels, the elements exhibit their toxicity. As also appears consistently in high concentrations where Ag smelting has been practiced and has a profound impact on plant establishment. Symptoms of As toxicity include poor seed germination and significantly reduced root structure, with effects influenced by the As-phosphates uptake relationship (Smith *et al.* 2010). Se is not classified as a metal but is highly phyto-toxic, and plants show symptoms of chlorosis at concentrations of around 4 mg/kg and total yellowing of younger leaves in higher concentrations; with complete inhibition of growth at levels beyond 20 mg/kg (Defra 2011). Vegetation tolerance to Ni toxicity is somewhat dependent on the plant species. Ni is also an essential micronutrient for many microorganisms. However, at millimolar concentrations, Ni inhibits the growth of most wild-type bacteria (Schmidt and Schlegel 1989). Cd is a well studied element in plants as it is known for its unfavourable effects on plant growth. Such negative effects include photosynthesis inhibition on a variety of fruiting and crop plants (Vassilev *et al.* 1995; Dong *et al.* 2005), and its interference with K uptake under certain circumstances (Ciecko *et al.* 2004).

In addition to the negative implications that risk elements in slags have on the vegetation with regards to phytotoxicity of elements, consideration must be given to the other physical and chemical conditions within the slag which may inhibit the successful growth and reproduction of plants. This includes, for example, pH, lack of organic matter and subsequent organic acids, lack of nutrients and nutrient holding capacity or availability of nutrients. As a consequence, a symptom which is consistent with slag deposits is an absence of any significant vegetation. With no vegetation, there will be little, if any, input of plant material for the creation of soil humus. Thus, there will be little mineralization and degradation of compounds which would otherwise serve as a source of nutrients for a microorganism community. Hardy pioneer plants can help establish a community of plants on these contaminated soils, but their development is slow and the diversity of species which occur there appears limited (photographs of vegetation at the study area can be viewed in appendix C).

3.1.4 Risk elements in the aquatic environment

Benedict *et al.* (2008) identified that even at low concentrations (mean 2.51 mg/L for 24 hour LC50), Pb in the aquatic environment correlates positively with the mortality of invertebrates which are important to the zooplankton community. These organisms are key components to the balance of the food chain and consequences of their elimination have potentially wide ranging effects. Hg is a very high risk element in the environment. The highly neurotoxic methylmercury is extremely persistent in the aquatic ecosystem and bioaccumulates in the food chain affecting a range of higher organisms (EPA 2011). Mn is well studied in the aquatic environment and its tendencies to attach to particles and settle in sediments have been described (ASTDR 2009). Mn in the form of manganese-oxides (MnO_2^{+4}, $Mn_3O_4^{+2/+3}$) form precipitates and therefore surface water Mn occurs mainly in suspension and accumulates in sediments, whereas groundwater which is under anaerobic conditions often contains elevated levels of dissolved Mn (EPA 2004). Cu is toxic in the inorganic form (Cu^{2+} most active and bioavailable), but is strongly bound in complexes and is harmless when unavailable. Therefore Cu toxicity in surface waters is correlated with DOC content (Kramer *et al.* 2004).

3.2 Behaviour of risk elements in soil

Behaviour of metals in the soil is very much dependent on the species in which they exist, which varies depending on the soil conditions. For example; soil pH and the presence of iron oxides, soil organic matter and levels of oxygen are parameters that can highly influence the species in which metals exist and consequently their mobility in soils (DEFRA 2011).

Where RE concentrations exceed background levels in any given terrestrial environment there is a risk of leaching of such REs to the groundwater. Navarro *et al.* (2008) analysed groundwater below a main slag dumping area. The results revealed elevated amounts of Cu (0.64 mg/L), Fe (40 mg/L), Mn (0.6 mg/L), Pb (5.1 mg/L), Zn (7.6 mg/L) and As (0.019 mg/L). This was attributed to the oxidation of sulphides from the slag dumps developing acid conditions which mobilise metal REs into the groundwater. These processes are particularly detrimental to the health of underlying, adjacent and downstream aquatic systems. High fish mortality for example, was documented in the Mokelumne River basin as a result of acid, metal rich surface runoff from Penn mine, California (Parsons *et al.* 2001). Surface-controlled dissolution of minerals and glass and sulphide oxidation will release metals to pore water solutions (Lottermoser 2002). These processes and the potential for solutes to reach water bodies will be dependent on many factors and parameters that will inevitably vary from one site to another; including weather and climate, mineralogy, geology etc. Ahmed *et al.* (2000) studied the dissolution behaviour of Co, Cu, Fe, Ni and Zn from smelter slag in aqueous sulphur dioxide. 81% Co, 60% Fe, 35% Ni and 68% Zn extraction were achieved within 3 hours, while the behaviour of Cu differed, with high initial dissolution but subsequent precipitation lowered its overall extractability. The same authors noted in a later publication that the addition of O_2 prevented the precipitation of Cu after dissolution (Ahmed *et al.* 2002). An interesting property of copper which is widely acknowledged, is that the concentrations of Cu in the soil solution are typically very low, due to the very strong binding behaviour of Cu with organic matter (OM). Behaviour of Pb and Zn in soil solutions is well studied and these elements are known to become increasingly mobile and dissolved in solution as ions with decreasing pH (Alloway 1990). Therefore a number of studies have focused on the immobilisation of these particular elements with the addition of various basic amendments (Cao *et al.* 2003; Hashimoto *et al.* 2008; Lin and Zhou 2009). Maskall *et al.* (1996) researched the mobility of Pb at various slag deposits in the U.K. At each deposit, surface concentrations were often high (>1%) yet relatively small amounts were found to be in mobile form. Much of the Pb fractions were found to be precipitated as insoluble compounds and being strongly bound to soil constituents. The insolubility of Pb was attributed partly to the weathering of Ca bearing minerals which raised pH of the slag, and the rate of migration varied depending upon the rock type (Maskall *et al.* 1996). Experiments on Pb smelter fly ash by Vitkova *et al.* (2009) demonstrate the importance of salt level in addition to pH on the leaching behaviour of the major contaminants.

Some elemental behaviours in soils can be generalised, for example Cd tends to be more mobile in soil than many other metals (mobility being highly dependent on pH), whereas Ni is described as having comparably low mobility in the soil environment (DEFRA 2011). However, the soil environment is highly complex and many physicochemical and biological factors influence RE mobility. The mineralogy of the slag/soil will be a considerable determining factor on the mobility of metals. Navarro *et al.* (2008) determine that the effects of secondary phase minerals formed during the weathering of mining slags are significant in the mobilisation of metals.

Bioavailability of metals is a key factor in their potential to cause harm. Metals which are bound as insoluble precipitates or are strongly sorbed to soil particulate matter such as clay colloids and OM are therefore less readily available for the uptake of plants. In response to this, many studies have focused on the use of amendments to ‘fix’ metals in contaminated soils, and to create a more favourable environment for the plant rhizosphere. Garden waste compost is a commonly studied amendment used in metal contaminated wastes and has proved successful in the reduction of various metals in solution (Bleeker *et al.* 2002; Lin and

Zhou 2009; Tandy *et al.* 2008). Other popular amendments for metal immobilisation and for improved soil composition include manure, sewage sludge and poultry waste.

To understand the mobility of various toxic metals and to model their availability for uptake by vegetation, the use of leaching tests, which seek to replicate natural field conditions, can provide useful data which aid in the knowledge of behaviour of REs of concern within the slag environment. An archetype of such tests would be those replicating regional precipitation or solutions surrounding the rhizosphere, (Piatak *et al.* 2004; Ettler *et al.* 2009c).

3.3 Anthropogenic sources of risk element

3.3.1 Silver smelting in the Czech Republic

According to Pauliš and Mikuš (1998), the earliest significant exploitation of Ag deposits in the Czech Republic date back to the second half of the 13th century and by the beginning of the 14th century KH had grown into one of the largest mining towns in Europe. The study area in this paper represents a significant site as the first areas of extraction occurred on natural silver exposures along the Vrchlice River bank. Several mines were operated within every load. In the first half of the 14th century annual Ag production stood at 5 – 6 tonnes (with 50 – 100 tonnes of Cu obtained), 90 % of which came from mining in KH. Mining activities had started to see a decline by the 15th century, and despite a revival in Ag mining in the 16th century, remaining lodes were of lower ore content with annual Ag production reduced to 2 – 4 tonnes, leading to an eventual decline of all mines in KH at the turn of the 17th century (Pauliš and Mikuš 1998).

Today there remains much evidence of the towns industrial and mining past. On a walk around tour of KH and its rural fringes, it is not uncommon to observe slag loaded with heavy metals mixed in with agricultural soils, used in construction, and lining the paths and roads of the villages. For this reason, the area is of interest to soil scientists for study and papers have been published on the area, such as the study by Králová *et al.* (2010). Their study focuses on As and other REs uptake into plants which occur on an area containing these slag materials.

3.3.2 Risk element composition of smelter slag

Various studies worldwide have focused on the analysis of smelter slag for their mineral, chemical and RE (typically metals) composition. Some of these studies are described here in order to identify patterns of RE occurrence at such sites. The composition of historical smelting slags depends on the composition of the ore and the fluxes used (Lottermoser 2002). However, practical studies on such sites generally identify a common group of RE metals in elevated concentrations. Research has been published for the determination of chemical composition of slag deposits at other sites in the Czech Republic. Ettler *et al.* (2009a) analysed slag from Ag-Pb smelting processes in the Bohutin region (approximately 60 km South West of Prague). Upon slag analysis, Ag was found to be relatively low (10.5 – 120.5 mg/kg). However, much higher Ag content values are reported from the same site; 375 mg/kg and 2950 mg/kg by Vurm (2001) and Huml and Studnicná (1984) respectively. A study of Pb –Ag smelting slags in Sierra Almagrera (Spain) identified maximum Ag concentrations of 180 mg/kg (Navarro *et al.* 2008). These widely varying values lead to the impression that given the large particulate structure of the slag, RE concentrations may vary widely between the heterogeneous slag samples. Other REs analysed at smelting slag deposits from Czech studies and others are shown in Table 3.3.1.

Table 3.3.1 Selected maximum RE values recorded at various smelter slag deposits (values given in mg/kg) ND = No Data. Those values highlighted in ***italic*** font represent average value where maximum was not available

Author (data type)	**Study area**	**Type of smelting**	**Ag**	**As**	**Cd**	**Co**	**Cu**	**Ni**	**Pb**	**Sb**	**Zn**
Ettler *et al.* 2009a	Pribram, CZ	Ag	120.5	465	ND	120.3	4119	205.1	319190	5490	49976
Navarro *et al.* 2008	Almeria, Spain (surface samples)	Pb-Ag	180	750	ND	83	ND	210	ND	620	8600
Navarro *et al.* 2008	(profile 1 – 3m)	“	42	36	0.5	16	183	44	2150	150	2280
Lima and Bernardez 2010	Bahia, Brazil	Pb	3.48	541	57.3	185	538	82.2	ND	201	ND
Manasse and Mellini 2002	Rocchette Pannocchieschi, Italy	Ag	ND	ND	ND	ND	3500	ND	9600	2500	7600
Lottermoser 2002	Chillagoe, Queensland, Australia	Cu–Pb–Ag-Au	***13***	***281***	***15***	ND	***5223***	***25***	***7605***	***85***	***23643***
Lottermoser 2002	Montalbion, Queensland, Australia	Ag	829	928	***13***	ND	***1410***	***<5***	***51620***	2660	***12266***
Ettler *et al.* 2009b	Tsumeb, Namibia	Pb - Cu	ND	28750	6939	26	106200	32	183000	ND	33125
Parsons *et al.* 2001	Penn mine, California	Zn - Cu	ND	59000	62000	ND	40000	ND	82000	8200	280000

In the Czech study by Ettler *et al.* (2009a), from 42 slag samples, the Pb rich glass was analysed and found to contain mean value of 23.05% Pb by weight in the form of PbO. Given the encapsulating effect of the glass, silicates and oxides, these structures have been traditionally considered relatively inert and resistant to weathering, therefore reducing the expected mobility of toxic REs bound within (Parsons *et al.* 2001). However, as a consequence of more recent studies, it is now the current understanding that these structures are considered to be reactive and are significant sources of metal contamination such as As, Pb and Zn (Ettler *et al.* 2003; 2009a). Piatak *et al.* (2004) also note that the reactivity of metal smelting slag deposits in nature is evident in the formation of secondary minerals. In non-glassy structures the highest content of Pb was found within the quenched feldspars with 15.35% (PbO) by weight (Ettler *et al.* 2009a). Rosado *et al.* (2008) found that Pb and As concentrations are greater in the smaller particle fractions, enriched in weathered material. It is now understood that the source of metal contamination from smelter slags can be related to any metal-bearing phase (Navarro *et al.* 2008). Pb is well studied and widely recognised to be a potentially mobile and toxic RE. Lima and Bernardez (2010) studied Pb smelter slag in Brazil containing 4.06% Pb by weight. The leaching study showed that the slag was stable at a pH greater than 2.8 under short term exposure. However, large amounts of Pb have been widely documented in the blood and hair of people living near the disposed Pb slag (Lima and Bernandez 2010). In the same study, Cd levels in the slag were investigated as elevated levels of Cd were also present in the hair and blood samples of the local populations, yet maximum concentrations at the site did not exceed 57.3 mg/kg (Lima and Bernandez 2010). This trend of non-excessive Cd concentrations is uniform for all the studied slag deposits of Ag smelting origin which are cited in this paper. However, slags which are derived primarily from smelting of Pb-Cu show much higher concentrations of Cd and As than those slags derived from the Ag smelters (Table 3.3.1). A trend that becomes evident is that the studied slag deposits originating from Ag smelting correspond with excessive concentrations of Cu and Zn (Table 3.3.1). The impact of these metals being in elevated concentrations may have more relevance on the vegetation than for human/animal implications. Therefore, remediation strategies targeting such pollutants must reflect the aims of the experiment and criteria for remediation. No official soil guideline values have been published for Cu and Zn by U.K authorities but limits are set by Czech guidelines as being given upper limits of 50 and 100 mg/kg respectively. As can be seen in Table 3.3.1, the maximum values in every example exceed these guideline limits for both Cu and Zn. Lottermoster (2002) attributed significant amounts of Zn in slag deposits to heavy metal bearing Fe-Ca phases, including glass, olivine and hedenbergite. Zn concentrations are notably high at all of the reviewed study locations (Table 3.3.1). This is a likely contributing factor to the lack of vegetation that is associated with smelter slag heaps. Soil guideline values set by the Environment Agency (Table 3.1.1) suggest that Ni is acceptable up to a value of 1,800 mg/kg (previously 5,000 mg/kg) with regards to human health, whereas a property with plants should not exceed soil Ni concentrations of 75 mg/kg (DEFRA 2002). Ni concentrations at Příbram in the Czech Republic exceed this value which delineates the limit of tolerance for most plants (Table

3.3.1). Soil guideline values for As are set low, particularly for residential properties and those growing vegetables for human consumption Table 3.1.1 (DEFRA 2011) and Czech authorities set the limits for As even lower at 4.5 mg/kg (Podlešakova *et al.* 1990). In each study cited within this thesis, the As concentrations far exceed the guideline value (Table 3.3.1). As is typically more toxic as trivalent compounds and inorganic As is generally more toxic than organic As (ATSDR 2009). Therefore speciation of elements is an important factor to consider. Soil guideline values for Sb have not been published, although the World Health Organisation (WHO) determines a guideline for drinking water Sb concentrations to be no more than 0.02 mg/L. Concentrations of Sb at smelter slag deposits appear to be significantly high, particularly at the Příbram site in the Czech Republic (Table 3.3.1).

In addition to the REs listed in Table 3.3.1, Rieuwerts and Farago (1996) studied the smelting and metal mining areas within Příbram, Czech Republic to assess local Hg levels. Results showed that along a transect Hg concentrations peaked at the point of the smelter area (2.32 mg/kg) and Hg topsoil concentrations were significantly correlated with distance from the smelter. A study on the site of an old Ag smelter in Potosi, Bolivia found soil Hg concentrations ranging from 0.105 – 155 mg/kg, 20 - 30,000 times greater than uncontaminated soils in the reference site (Hagan *et al.* 2010). The variation in values between those in Bolivia and the Czech Republic may be attributable to smelting practices.

The chemical degradation of the minerals which constitute smelter slag might be slowed down due to the lack of organic material input as a result of no vegetation being present where there are toxic levels of REs. Under the conditions present in a non-contaminated soil with a healthy microbial community, soil biological processes produce organic acids (oxalic, citric, tartaric) as well as larger humic and fulvic acid molecules. These acids not only provide H^+ ions which solubilise Al and Si, but also undergo complexation reactions with Al ions held within the structure of silicate minerals (Brady and Weil 2004). Ironically, the elevated presence of toxic elements in smelter slags which prevents establishment of vegetation and a significant microbial community may be a factor which prolongs the stability of minerals within slags and reduces the rate at which REs are mobilised.

Despite variations in mineral composition, dates of occurrence, smelter practices and RE abundance at differing slag deposits, smelter slags are well documented as sources of RE contamination (Ettler *et al.* 2009a; 2009b; Lima and Bernardez 2010; Lottermoser 2002; Navarro *et al.* 2008).

3.3.3 Other elements contained within smelter slag

In addition to the potentially hazardous elements which are associated with Ag smelter slags, there is also an elevated presence of potentially beneficial elements. This is evident from historical distributions of the material which suggests that the smelter slags of the Vrchlice River Valley were applied to agricultural land as a primitive fertilizer. Brady and Weil (2004) list one of the properties of basic slag as being its ‘slow availability’. Slag from the silver smelting process will undoubtedly share such properties and their use as a fertiliser would be long term. The smelter slags lining the Vrchlice River have been in place for centuries and so weathering of primary phase minerals will continually expose and release the elements bound within.

In a study by Manasse and Mellini (2002), an in depth analysis of smelter slag produced from base metal smelting (including Ag) identified that CaO is one of the major components (more than 10% on average), with MgO and K_2O also in significant occurrence. The elements Ca, Mg and K are important macronutrients and their presence runs contrary to any assumption that smelter slags are detrimental in all cases to vegetation and to the quality of surrounding soils.

3.4 Current knowledge available from previous work at the area of study

Prior to this investigation, the study area has been sampled and analysed to an extent by colleagues from CULS Department of Soil Protection and Conservation. Table 3.4.1 gives minimum and maximum readings obtained from the Southern side of the slag, away from the river bank. Figure 5.1.1 in chapter 5 shows the corresponding locations from which the samples were taken (black points).

Table 3.4.1 Maximum and minimum values of each risk element 'note' in parentheses are shown the probe number and the horizon where the value was measured

Element	min. (mg/kg)	max. (mg/kg)
Cu	18.3 (1O)	1027 (5 A-B)
Mn	68.4 (9O)	496 (5A-B)
Pb	153 (6O)	966 (2H)
Zn	30.0 (8Bv)	4907 (4B1)
Ag	0.23 (8O)	11.0 (4B2)
Cd	0.12 (8Bv)	6.07 (5A-B)

3.5 Leaching experiments

The release of inorganic contaminants from solid to liquid phase due to mineral dissolution, desorption and complexation processes is of paramount importance to this study. As is the effect of these processes on the slags which can be affected by a range of parameters, such as pH, redox reactions, DOM and microbial activities (Leaching.net 2011), that are expected to have a direct influence on the surrounding waters and soils.

In order to examine the activity of REs within solutions that occur in the natural environment, it is necessary to recreate those solutions in the laboratory, subject samples to their presence and analyse the effects. Low molecular mass organic acids (LMMOA) are such solutions that occur in nature and are likely to react with minerals and REs such as those found in the slag deposits at KH. LMMOAs typically occur in the rhizosphere soil and from decomposing plant litter and organic matter. Initial studies by Ettler *et al.* (2003) were conducted to simulate the presence of vegetation on metal contaminated slag and the effect that root exudates have on the mobility of present metals. Preliminary leaching tests were performed using citric solutions (20 and 8mM) in order to determine the kinetics of release of Pb, Cd, Zn and As (elements also associated with Ag smelter slag). These acidic concentrations are particularly high given that in common soil solutions, the concentration of low molecular weight organic acids (LMMOA) is up to 1mM, but were designed to demonstrate the maximum reactivity of slag in a soil environment (Ettler *et al.* 2004). In a later similar leaching study by the same author, other LMMOAs acetic and oxalic acids were included in addition to the citric acids.

Interestingly it was identified that the acetic and oxalic acids contained the higher amounts of metal, this time at much lower 500µM LMMOA concentrations (Ettler *et al.* 2009c). Reasons for which were attributed to complex formations being dependent on pH. However, it was concluded that at 500mM concentrations (those which represent a ‘higher range’ of acids in soil solution), all of the investigated LMMOAs were shown to strongly influence the mobility of metals released from fly ash into soil solutions (Ettler *et al.* 2009c). In addition to reacting with REs in soils, LMMOAs influence a range of soil properties and chemical behaviours. Chiang *et al.* (2006) analysed rhizosphere soil from three different forest tree species and results showed that exchangeable cations Ca, Mg, K and Na had in each case significantly higher concentrations than bulk soils.

Another way to simulate the natural processes that occur in the field is to conduct a leaching experiment which mimics precipitation. Piatak *et al.* (2004) proposed an effective precipitation experiment using a method based on a field leach test developed by Hagemann and Briggs (2000), whereby crushed and sieved samples were combined with deionised water or a solution that replicates Eastern United States precipitation (ESP) (mixture of H_2SO_4 and HNO_3 with deionised water to achieve pH 4.2). In spite of the ESP mixture being designed to mimic environmental precipitation, the results indicated a linear correlation between those concentrations (Zn, Ni, Cu and Co) extracted by ESP and those in deionised water. Whether it is a solution created to approximate regional precipitation or a simple deionised water extract, laboratory leaching tests indicate that metals can be released into these solutions from base and precious metal smelter slag (Piatak *et al.* 2004)

Tank leach tests are designed to evaluate leaching on a volume of product to leachate volume ratio. A monolith sample is placed inside a tank and subjected to exposure of the leaching liquid over prolonged periods, usually months (Leaching.net 2011). Results are given in mg/m^2 therefore giving an assessment of surface area related release.

The overall purpose of the leaching experiment in this study is to obtain an initial primitive assessment of the threat that the KH slags present to the surrounding soils. However, common purposes for leaching tests are to classify the leachability of materials to be in accordance with governments waste acceptance criteria, and to aid in the classification of materials for disposal into hazardous and non-hazardous wastes (Environment Agency 2010).

3.6 Remediation of contaminated soils

Risk assessment is a precursor to any remediation effort. Risk is a function of the hazard and vulnerability of a site and it considers many factors (geological, chemical and environmental analysis, sensitivity of receptors etc). Post risk assessment remediation may or may not be necessary and this is also determined by certain factors. One of the most important factors being the sites contamination status, usually defined by comparing the concentration of the elements/pollutants in concern with published national guideline values (Nathanail and Bardos 2007).

Many strategies have been adopted to deal with a range of contamination situations. The dig and dump approach is often the most practical and feasible in many situations, whereby contaminated materials are excavated and transferred to designated hazardous waste landfill sites, although such strategies are not likely to be a practical solution for mining wastes where such huge quantities of material occur.

Containment is an applied technique which acts by cutting the link between the source and the receptors. For example, using synthetic liners, geo-textiles, cement and clays to create underground barriers which stop lateral and vertical movement of leachates, divert or isolate groundwater, or can be used as a cover (Nathanail and Bardos 2007). Such techniques are the most practical when large volumes of waste are concerned, such as the smelter material in this study. However, alternative and more specific approaches target the individual contaminants, both organic, or like the pollutants in the KH slags, inorganic.

Treatment techniques can be in-situ or ex-situ, and include chemical, physical and biological amendments. However, when inorganic pollutants are concerned, chemical and physical techniques are the most suited approaches. Amendments to contaminated soils can be made to manipulate certain properties of inorganic pollutants, (such as mobility and toxicity).

Although biological techniques are normally reserved for organic pollutants, phyto-remediation techniques are becoming more commonly experimented with in the removal of inorganic pollutants (typically metals). One of the most effective processes is known as phyto-extraction, whereby metals are solubilised in the acidified area of the rhizosphere, then transported into the plants tissues above ground where they can be harvested, effectively removing certain concentrations of the targeted element from the site (EPA 2000).

4 Area of study

Kutná Hora is a traditional mining town ~ 60 km to the East of Prague in the Czech Republic. The locality of the study site is marked by a yellow ring in Fig 4.1.

4.1 Aerial description of study site

Figure 4.1 The study area is located approximately 1 km to the south of Kutná Hora parallel to the Vrchlice River

The upper image clearly illustrates the pile of slag materials with an almost complete absence of vegetation on the slag itself. The land surrounding the slag is densely vegetated with a significant forest canopy, and the slags extend through the soils down to the Vrchlice River. Pieces of slag can be found within the river bed and also on the opposite river bank.

4.2 Climate of Kutná Hora

Kutná Hora can potentially receive precipitation throughout the year with an average annual rainfall of 450 mm. However, most precipitation occurs in the summer months with July being the wettest month. The winter is comparatively drier with most precipitation coming in the form of snow. In the winter it is not uncommon for temperatures to remain in the minus for significantly sustained periods (Climate-zone 2011).

Understanding localised weather and climate, particularly precipitation, can contribute to the understanding of how and when dissolved particulate matter within the slag deposits is being mobilised.

4.3 Walk around site description

The first apparent observation when approaching the site is the sheer abundance of smelter slag material, placed not just on the main pile and in close proximity to the main pile but large quantities are scattered north of the adjacent river along the banks on the opposite side. The composition of the slag is visibly highly heterogeneous, with smelter slag rocks occurring in a large variety of sizes and shapes from up to 50 cm diameter boulders to gravel sized pieces. Mixed into the slag appears to be a variety of rocks and minerals. On close inspection of the rocks it is possible to identify a range of minerals and evidence of iron and copper by the orange and green powder like deposits on the rocks.

As can be seen in Figure 4.1, there is a clear boundary where the tree line ends and the bare slag is exposed. Whether this is due to a lack of organic matter and exposure to the sun and wind which prevents establishment of trees, or whether it is due to the toxic effects of the slag is difficult to determine by visual analysis. However, underneath the dense canopy of deciduous trees surrounding the river, the surface of the ground is heavily laden with slag material, yet vegetation persists in abundance and appears healthy, which suggests that plant establishment is probably impeded by a lack of substrate as opposed to the REs present in the slags. More visual evidence of plant colonisation is apparent in a succession like form, whereby lichens and mosses can be seen to grow on the inner fringes of the slag heap, followed by grasses. Once a sufficient organic horizon has developed on the surface, heathers can be seen to grow and also the establishment of trees predominantly of the species *Betula pendula*.

5 Sampling, methods and materials

5.1 Sampling

5.1.1 Objectives of the study reflected in the sampling

Source: The slag itself represents the source of contamination in the study area.

Pathway: Pathways include leaching through the slag, runoff of the slag surface, wind blown deposits and colluvial deposition. These pathways are possible due to precipitation and other weathering processes.

Target: Sensitive environmental receptors are the reason for concern regarding the slag deposit. These targets include the aquatic environment in the adjacent river, the quality of the soil environment surrounding the slag deposits and its ability to host healthy vegetation, and the slag itself which is currently void of any significant vegetation. Other targets may include birds and animals which graze or feed upon soil fauna and plants within the contaminated site.

In order to be able to model the area, it is necessary to consider these factors and to incorporate the overall objectives of the study. Figure 5.1.1 illustrates a transect approach to sampling the slag. The reason for this is to model the changes in element composition in a straight line, (theoretically the most logical likely path for leaching solutions), from one medium to another (slag – soil – river sediment). Samples from locations 1s and 3s are designed to give some degree of knowledge of how significant the change in RE concentrations are from the start of the slag pile to the end of the slag pile, with REs being transported by the flow of the river.

5.1.2 Sampling procedure

Samples of the slag were collected by hand from the surface. Samples from the layers beneath the main slag heap were also collected by digging a small pit (~0.5 m) which exposed the upper horizons (photographs of sample pits can be viewed in appendix D). From these horizons both soil and slag pieces were collected. Sample material was collected in plastic bags and labelled. The locations adjacent to the river were sampled in the same way as on the main slag heap. River sediments were collected by sifting the river bed surface with a trowel and bagging.

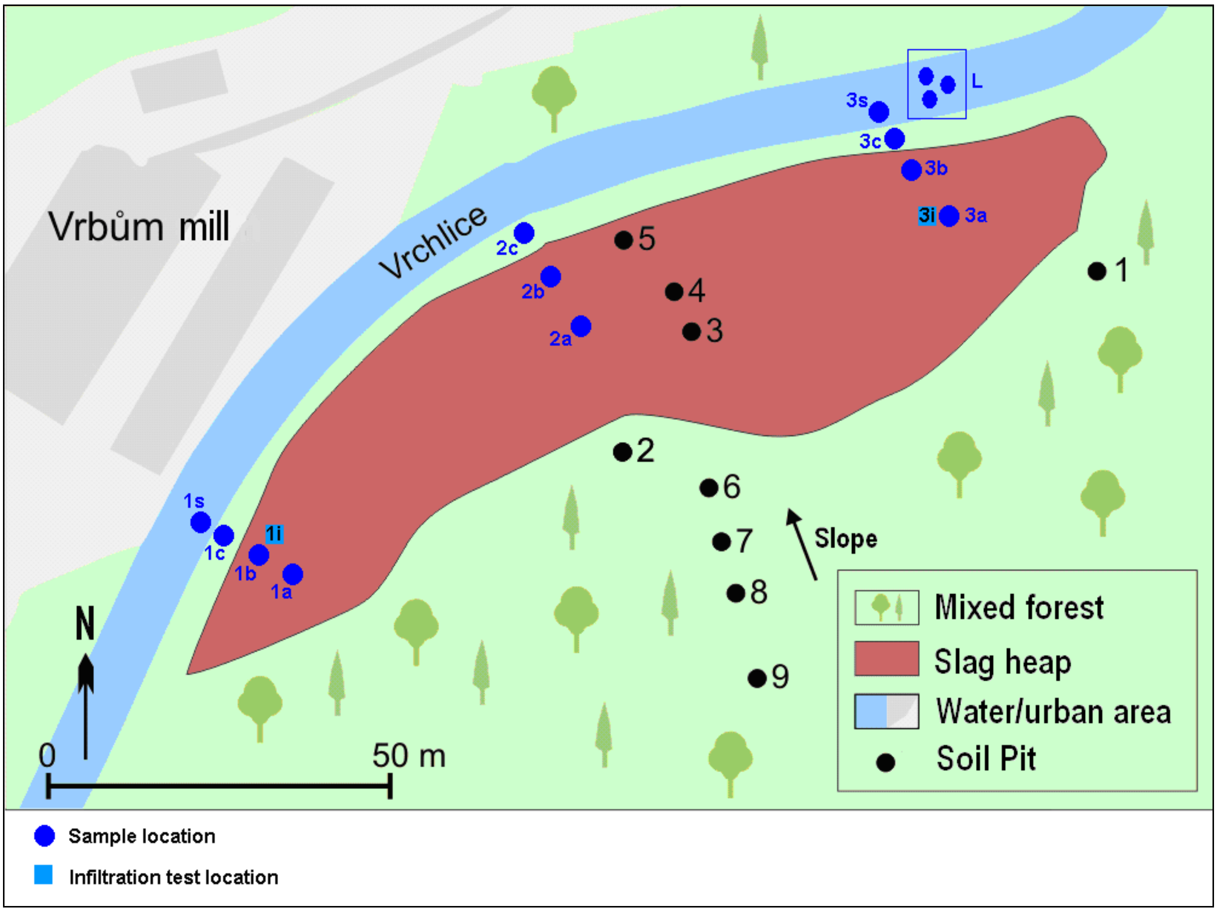


Figure 5.1.1 Sampling map: River flow is from West to East. Black points = previous study sample pits; Blue points = current sample pits. (L = lagoon samples)

5.1.3 Sample preparation

On return to the laboratory samples were air dried in the laboratory for several days. Slags were separated from the corresponding soil in each sample by grinding with a pestle and mortar and sieving soil to 2mm. Gravimetric weights were taken for soil, and slag samples were weighed after washing to remove dust and debris. Tables 5.3.1 and 5.3.2 show which samples and horizons were subjected to which particular analysis. After disturbing and sieving samples to produce separate soil and slag fractions, slags were ground in the mill to produce homogenised samples of approximately 1-2 mm diameter material which is suitable for analytical techniques (<2mm for extractions).

5.2 Sample treatment and analysis

5.2.1 Elements of interest for study and extraction solutions

The following REs were included in analyses based on the knowledge of general slag compositions obtained in the literature review and due to the suspected harmful elements that may be present, as evident in prior study of the site by colleagues at CZU:

Ag, As, Cd, Cu, Mn, Pb, Zn,

In addition to the 'Risk' Elements, analysis was conducted for the presence and concentrations of the following mineral elements:

Ca, Mg, K, Na

Slags are typically highly heterogeneous in structural material and mineral composition as well as chemically (Ettler *et al.* 2009a; Gee *et al.* 1997; Manasse and Mellini 2002). Therefore, in many similar studies, for bulk analysis, sampled slag materials are ground thoroughly to produce a homogeneous mixed sample, one which represents a mean composition of the slag from which it is obtained. For the analysis of soils within the smelter slag, it is necessary to sample from each individual soil horizon, as the distribution of REs is likely to differ significantly through the vertical profile. This is reflected in the sampling from pits to a depth of ~0.5 m.

Information on the total concentration of REs in contaminated soil alone is insufficient for the understanding of their mobility and availability for ecological processes (Brunzl *et al.* 1999). Fractionation is necessary in order to be able to analyse and understand a range of processes that will give a sufficient understanding of RE processes and mobility within the slag deposit.
Extractions for each sample were performed in duplicate to increase analytical precision. The following extractions were applied to samples:

- 2M HNO_3 extraction for 'total' contents approximation
- 1M NH_4NO_3 extraction for mobile fractions of REs (bioavailable)
- Water soluble extraction of slags (from leaching experiment control samples and pH amended reverse osmosis water; see Fig 5.4.1)
- 1mM Citric acid extraction of slags (from leaching experiment; see Fig 5.4.1)

5.2.2 Soil characteristics and parameters

In order to make any assessment on the likely behaviour of REs in the soils surrounding the smelter slag it is necessary to determine certain physical and chemical properties and basic soil characteristics. Soil samples were therefore analysed for the following properties:

- pH, organic carbon content (Corg), cation exchange capacity (CEC), soil salinity and texture.

Details of methodology for extractions and other tests mentioned above are given in chapter 5.4.

5.2.3 Water movement in soil

When studying contaminated soils, Nathanail and Bardos (2004) state that one of the most important features of a soil to understand is its permeability, and whether it will act as a pathway for contaminants to migrate. In response to this, simple infiltration tests can be conducted at selected locations on the slag. The chosen method is for unsaturated hydraulic conductivity which simulates to some extent the movement of rain water, and is performed using a mini-disk infiltrometer set to -2cm which covers a range of soils according to the manufacturer's guidelines.

Although not essential to this study, the aforesaid infiltration test can provide primitive information on how quickly the environmental solutions are being transported from their source through the smelter slag to potential targets, and may assist in building conclusions on the environmental fate of studied elements.

5.2.4 Risk element analysis in the Vrchlice River

In addition to the analysis of slag and soil samples, one way to characterise the RE distribution is to examine the elemental composition of the sediment of the adjacent river. Deposition of REs is most likely to occur in positions of the river where the water has decreased energy, for example on the convex points of a river bank or in pockets of dense vegetation.

Although one might expect the surface sediments to be laden with elevated concentrations of REs, the distribution of elements in a sediment profile are not uniform, but consist of a series of peaks and troughs in elemental compositions, corresponding with periods of industrial activity, abnormally high atmospheric depositions, and in certain cases, weapons testing (Ciszewski *et al.* 2008). In the case of this study, events which would create such elevated layers would have occurred many centuries ago (Pauliš and Mikuš 1998), with such elemental peaks being buried deep in the river bed. However, surface sediment analysis may prove that leaching, transport and deposition of REs into the river is still significant should the concentrations show to be significantly higher than soil guideline values.

5.2.5 Derived leaching experiment

Slag samples were ground to produce a structurally homogenous soil (~1-2mm). Although the slag sample material in the experiment is much finer than the majority of slag pieces which occur at the study site, the test represents a maximum case scenario, and yields results more quickly due to the larger surface area, given the time constraints in the laboratory.

Samples were subjected to a LMMOA (citric acid) and deionised water adjusted to obtain a pH value of approximately 4.6. This pH value is representative of rainwater collected from the Jizera Mountains in the Czech Republic over a period of 3 months and analysed for its composition as part of a study by Tejnecky *et al.* (2009). The pH value of 4.6 is an average of those values observed over the 3 months. The citric acid used is of 1mM concentration which is representative of those concentrations found in nature, particularly solutions in the rhizosphere and in soils which are rich in organic material.

For LMMOA tests, samples were treated in a citric acid solution in 10:1 liquid to solid ratio. (20 g of sample in 200 ml 1mM extract). A control solution was also included (reverse osmosis (RO) water with pH ~5.5), and each test was performed in duplicate. Samples were shaken for 5 minutes then left for the required times before analysis. At each time interval, samples were tested for pH, and analysed for metals using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP OES). Ion chromatography methods detect changes in the LMMOA concentrations itself as the leaching test time elapses. Leachate was sampled after 1, 24, 168 (week) and 720 (month) hours, influenced by the 2009 study by Ettler *et al.* (2009c) which yielded positive results up to 168 hours, with an additional analysis after 1 month included for the purpose of this study.

For rainwater simulation tests, the sample solution was less concentrated as rain usually occurs in large quantities under field conditions. Samples were treated in a 20:1 liquid to solid ratio (10g of sample in 200ml deionised water extract). Samples were shaken for 5 minutes and then analysed after 1, 24, 168 and 720 hours for pH and metals using ICP OES spectrometry and ion chromatography. Again, these samples were done in duplicate. The experimental plan can be seen in Figure 5.4.1.

5.3 Sample and analysis overview

Table 5.3.1 RE analysis of samples plan

Sample type			Extractions		
Location	Horizon	Fraction	Total	Plant available	Leaching experiment
1a	Surface	Slag	√		√
	A	Soil <2mm	√	√	
	B	Slag	√		
		Soil <2mm	√	√	
1b	A	Slag	√		
		Soil <2mm	√	√	
	B	Slag	√		
		Soil <2mm	√	√	
1c	A	Slag	√		
		Soil <2mm	√	√	
	B	Slag	√		
		Soil <2mm	√	√	
1s	Surface	Sediment <2mm	√		
2a	Surface	Slag	√		√
2b	A	Slag	√		
		Soil <2mm	√	√	
	B	Slag	√		
		Soil <2mm	√	√	
2c	A	Soil <2mm	√	√	
	B	Slag	√		
		Soil <2mm	√	√	
3a	Surface	Slag	√		√
	A	Slag	√		
		Soil <2mm	√	√	
	B	Slag	√		
		Soil <2mm	√	√	
3b	A	Slag	√		
		Soil <2mm	√	√	
	B	Slag	√		
		Soil <2mm	√	√	
3c	A	Slag	√		
		Soil <2mm	√	√	
	B	Slag	√		
		Soil <2mm	√	√	
	C	>2mm	√		
		Soil <2mm	√	√	
3s	Surface	Sediment <2mm	√		
Lagoon	Surface	Sediment <2mm	√		

Table 5.3.2 Selected physical/chemical analysis of samples

Sample type			Physical/chemical characteristics					Infiltration
Location	Horizon	Fraction	pH	Corg	CEC	Salinity	Texture	Unsaturated hydraulic
1a	Surface	Slag	√			√		
	A	Soil <2mm	√	√	√	√	√	
	B	Slag	√					
		Soil <2mm	√	√	√	√	√	
1b	A	Slag	√					√
		Soil <2mm	√	√	√	√	√	√
	B	Slag	√					√
		Soil <2mm	√	√	√	√	√	√
1c	A	Slag	√					
		Soil <2mm	√	√	√	√	√	
	B	Slag	√					
		Soil <2mm	√	√	√	√	√	
1s	Surface	Sediment <2mm	√	√	√		√	
2a	Surface	Slag	√			√		
2b	A	Slag	√					
		Soil <2mm	√	√	√	√	√	
	B	Slag	√					
		Soil <2mm	√	√	√	√	√	
2c	A	Soil <2mm	√	√	√	√	√	
	B	Slag	√					
		Soil <2mm	√	√	√	√	√	
3a	Surface	Slag	√			√		
	A	Slag	√					
		Soil <2mm	√	√	√	√	√	
	B	Slag	√					
		Soil <2mm	√	√	√	√	√	
3b	A	Slag	√					√
		Soil <2mm	√	√	√	√	√	√
	B	Slag	√					√
		Soil <2mm	√	√	√	√	√	√
3c	A	Slag	√					
		Soil <2mm	√	√	√	√	√	
	B	Slag	√					
		Soil <2mm	√	√	√	√	√	
	C	>2mm	√					
		Soil <2mm	√	√	√	√	√	
3s	Surface	Sediment <2mm	√	√	√		√	
Lagoon	Surface	Sediment <2mm	√	√	√		√	

5.4 Analysis methodology

5.4.1 Analysis of metal content

- 2M HNO_3 extraction: Shake 5 g of soil/ground slag samples with 50 ml 2M HNO_3 in a 100 ml PE bottle for 6 hours. Centrifuge at 11,000 RPM. Keep supernatant for AAS measurement (details of AAS in appendix).
- NH_4NO_3 extraction: Prepare a mixture of 80.04 g powdered NH_4NO_3 with 800 ml deionised water, then make up to the 1 L mark with deionised water. Shake 20 g of soil sample with 50 ml of prepared extractant. Shake for 2 hours then add a drop of 65% HNO_3.

5.4.2 Texture determination

Mix 40 – 60 g of soil samples (depending on density) with 20 ml Sodium Hexametaphosphate and approximately 50 ml water and bring to the boil. Decant the mixture into a cylinder and make up to 1 L mark with water. When cooled, mix thoroughly and take hydrometer and temperature readings at intervals 30 sec, 1, 2, 5, 15, 45 min, 2, 5 and 24 hours). Texture is determined by Stokes' Law. Texture curves for each sample are given in appendix F.

5.4.3 Soil pH in water suspension

Weigh 10g of dry sample (<2mm) into a beaker and add 50ml deionised water, stir for 5 min with a glass stick. Submerse the electrode; wait for equilibrium then record pH. Measurement was made by WTW inolab pH level 1, pH probe.

5.4.4 Salinity

Salinity of soil samples was determined by preparing samples in a 1:1 solution of Ethanol/deionised water and testing for conductivity using WTW inolab conductivity meter.

5.4.5 Organic carbon determination

Initial tests for Cox were performed by a modified Tyurin's method (oxidimetric titration). However, the method was too sensitive for the organic rich samples in this study and so Corg content was derived by the following method:

Crucible weight is determined, and then re-weighed with the sample inside. Sample is then placed inside the furnace for 90 minutes at ~520°c to combust all organic matter. The sample is then weighed again.

The following formula is applied:

$$\text{Corg} = \frac{\text{pre-furnace weight - post-furnace weight}}{\text{pre-furnce weight - crucible weight}} \times 100$$

5.4.6 Cation exchange capacity

CEC was determined by the Bower method as described by Hesse (1998): 2g of sample is shaken with 50 ml of saturating salt (1M sodium acetate) to saturate exchange sites. The soil is washed free of excess saturating salt by ethanol solution, and the sample is then shaken with 50 ml of 1M ammonium acetate to displace the adsorbed Na index cations. The solution is then analysed for Na by AAS.

5.4.7 Leaching experiment

Reaction vessels (200ml PE bottles) were prepared for a LMMOA solvent (1mM citric acid, pH 3.2) and rainwater simulation solution (deionised water with pH adjusted to 4.6) with the slag sample in a 10:1 and 20:1 ratio respectively (200ml 1mM citric acid : 20g slag, 200ml rainwater simulation solution : 10g slag). For each sample a replicate and a control (deionised water with pH ~ 5.5) were prepared. Each reaction vessel is independent for each time period (Figure 5.4.1). At each time interval, samples were filtered through a whatmann paper then tested for pH, and sent for analysis of metals at Charles University Prague by means of ICP OES. Ion chromatography was used to detect changes in the LMMOA concentrations. Analyses were performed at the intervals of 1, 24, 168 and 720 hours. Details of IC and ICP-OES can be viewed in Appendix E.

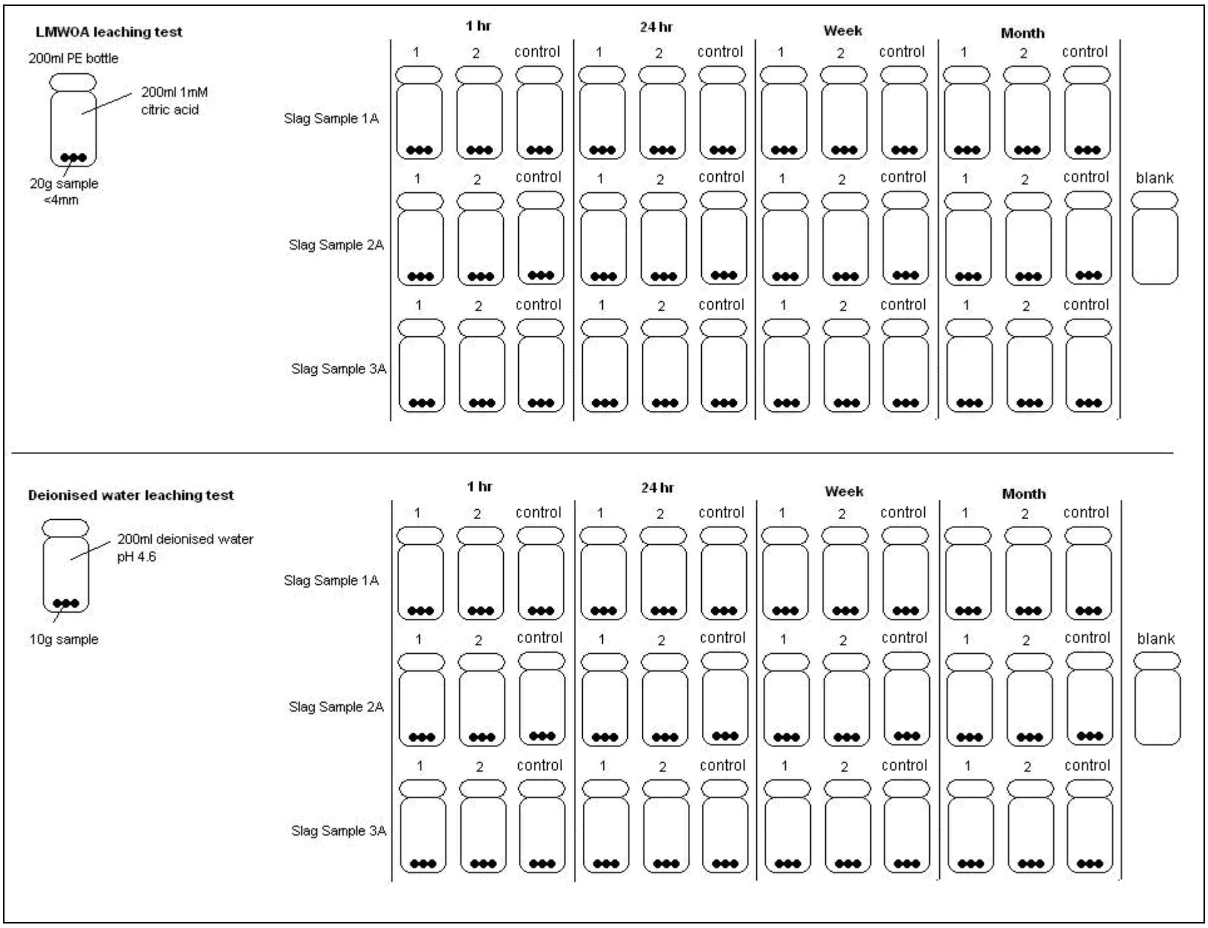


Figure 5.4.1 Treatment of surface slag samples in the leaching experiment

6. Results (data)

6.1 pH tests

Table 6.1.1 pH raw data

Location	Horizon	Fraction	pH
1a	A	Soil <2mm	3.92
	B	Soil <2mm	5.9
1b	A	Soil <2mm	5.08
	B	Soil <2mm	4.78
1c	A	Soil <2mm	4.92
	B	Soil <2mm	4.38
1s	Surface	Sediment <2mm	7.7
2b	A	Soil <2mm	5.5
	B	Soil <2mm	6.14
2c	A	Soil <2mm	3.98
	B	Soil <2mm	4.03
3a	A	Soil <2mm	5.4
	B	Soil <2mm	5.83
3b	A	Soil <2mm	4.93
	B	Soil <2mm	5.68
3c	A	Soil <2mm	5.56
	B	Soil <2mm	5.54
	C	Soil <2mm	5.15
3s	Surface	Sediment <2mm	7.56
Lagoon	Surface	Sediment <2mm	6.31

Table 6.1.2 Mean, standard deviation and variance of soil pH results from each sample line (a, b, c and sediments)

Sample location	Horizon	Mean pH	St.Dev	Variance
A line	A	4.66	1.047	1.095
	B	5.87	0.049	0.002
B line	A	5.17	0.295	0.087
	B	5.53	0.692	0.479
C line	A	4.82	0.795	0.632
	B	4.65	0.790	0.625
River side sediment	surface	7.63	0.099	0.010
Lagoon sediments	surface	6.31	-	-

6.2 Salinity (conductivity in ethanol/water extract)

Table 6.2.1 Conductivity of surface slag samples and sample pit soils

Sample	Conductivity (µS/cm)
1a Surface slag	33
1a B soil	25.2
1b B soil	28.8
1c B soil	144.4
2a Surface slag	27.1
2b A soil	27.9
2b B soil	21.7
2c A soil	166.7
2c B soil	159.1
3a Surface slag	32.5
3a A soil	29.9
3a B soil	21.8
3b A soil	141.2
3b B soil	34.3
3c A soil	69.3
3c B soil	29.5
3c C soil	28.9

6.3 Infiltration (Unsaturated hydraulic conductivity)

Table 6.3.1 Unsaturated hydraulic conductivity (K_h) of slag heap at selected locations

Sample location	**Tension**	**K_h (m/s)**	**Permeability**
1b 1st	-2	4.53^{-6}	Permeable
1b 2nd	-2	2.05^{-6}	Permeable
3a 1st	-2	5.86^{-6}	Permeable
3a 2nd	-2	5.07^{-6}	Permeable
3a 3rd	-2	4.78^{-6}	Permeable

The resulting permeability for all the above samples correspond to sand and gravel soil types containing fine grained fraction (5 – 15%). Due to error during the field analysis the 3rd replicate at location 1b has been discarded.

6.4 2M HNO_3 extraction

Table 6.4.1 2M HNO_3 extraction mean results for risk elements in ground slags

Sample location	Horizon/ soil layer	Fraction	mg/kg **Pb**	mg/kg **Cd**	mg/kg **Mn**	mg/kg **Cu**	mg/kg **Ag**	mg/kg **As**	mg/kg **Zn**
1a	surface	slag	684.4	10.9	742.2	1156.2	3.26	40.15	21135.3
	B	slag	683.2	14.12	297.2	1821.4	4.05	56.30	13580.0
1b	A	slag	656.4	2.57	423.4	1249.4	3.66	27.55	8420.4
	B	slag	1129.8	7.85	387.1	1776.5	6.41	22.88	11271.1
1c	A	slag	402.6	4.56	322.0	774.9	3.2	25.58	10950.9
	B	slag	301.7	3.99	371.1	703.3	4.26	22.53	10611.1
2a	surface	slag	848.4	10.66	554.1	1820.1	5.47	22.87	19540.5
2b	A	slag	339.3	5.58	712.3	2140.6	4.05	20.84	14716.2
	B	slag	357.6	4.19	941.0	2714.0	5.08	18.08	19177.9
2c	B	slag	216.8	3.6	440.7	1106.8	5.44	25.36	12315.4
3a	surface	slag	320.2	8.97	897.4	1129.1	2.61	ND	24389.5
	A	slag	568.1	6.2	941.5	2914.8	5.13	17.18	12830.5
	B	slag	501.6	7.17	858.2	1770.0	5.33	7.64	16701.4
3b	A	slag	357.1	2.94	678.9	1076.0	5.07	27.68	9422.3
	B	slag	510.9	7.04	771.4	1835.1	4.59	17.07	12963.9
3c	A	slag	451.8	7.63	701.1	1876.9	4.5	8.96	15066.2
	B	slag	470.9	6.13	715.0	1580.6	3.8	20.92	14146.1
	C	>2mm	187.7	2.69	601.4	307	2.29	19.71	4397.0

Table 6.4.2 2M HNO_3 extraction mean results for Ca, Mg, K, Na in ground slags

Sample location	Horizon/soil layer	Fraction	mg/kg **Ca**	mg/kg **Mg**	mg/kg **K**	mg/kg **Na**
1a	surface	slag	2335.1	1313.1	677.8	357.3
	B	slag	3219.4	463.5	771.2	266.5
1b	A	slag	3900.6	998.7	1206.1	357.3
	B	slag	3024.5	634.6	618.3	241.9
1c	A	slag	3341.1	645.2	612.9	228.6
	B	slag	2169.5	670.1	582.1	219.6
2a	surface	slag	3124.9	1026.3	1067.4	342.8
2b	A	slag	2357.9	1141.9	1099.4	316.0
	B	slag	1096.4	1532.9	458.5	203.6
2c	B	slag	1292.8	1199.8	515.1	204.2
3a	surface	slag	3850.1	1476.2	769.5	304.1
	A	slag	2274.0	938.7	732.7	255.0
	B	slag	2507.8	1263.5	771.5	272.7
3b	A	slag	2653.3	1033.4	965.9	257.8
	B	slag	2730.5	929.8	801.5	252.5
3c	A	slag	2712.4	1198.9	800.5	227.6
	B	slag	2243.2	1241.0	952.4	251.0
	C	>2mm	1800.8	3311.2	3023.3	169.1

Table 6.4.3 2M HNO_3 extraction mean results for risk elements in soils

Sample location	Horizon/ soil layer	Fraction	mg/kg **Pb**	mg/kg **Cd**	mg/kg **Mn**	mg/kg **Cu**	mg/kg **Ag**	mg/kg **As**	mg/kg **Zn**
1a	A	soil	381.5	0.6	107.3	227.6	2.97	80.3	638.8
	B	soil	1486.0	12.35	519.8	2121.7	3.63	173.8	9949.5
1b	A	soil	861.3	3.33	581.8	1038.5	3.66	85.6	2824.0
	B	soil	1727.4	4.66	631.0	2005.1	4.16	48.8	5695.4
1c	A	soil	288.9	1.46	731.6	304.0	4.77	57.0	1918.0
	B	soil	357.9	2.31	1494.5	415.2	5.19	49.2	2453.3
2b	A	soil	758.9	9.03	1161.3	3527.6	3.95	71.7	10621.2
	B	soil	1055.7	9.7	1173.7	3411.4	4.04	155.8	11359.0
2c	A	soil	99.4	1.18	190.9	248.8	1.75	ND	1194.8
	B	soil	123.9	1.04	186.5	374.9	2.74	ND	1311.0
3a	A	soil	1425.3	13.57	815.9	3943.4	4.21	114.2	8185.6
	B	soil	1269.7	17.35	809.4	3363.2	4.6	51.0	12135.2
3b	A	soil	609.4	5.23	994.4	1320.3	4.23	96.7	2826.5
	B	soil	2381.1	86.7	846.6	5160.0	5.04	35.9	7735.1
3c	A	soil	783.1	6.68	730.9	2077.5	3.75	73.6	5367.1
	B	soil	1161.8	9.28	779.6	3116.8	4.22	87.1	6591.8
	C	soil	248.2	2.23	525.8	220.9	1.98	48.0	1324.6

Table 6.4.4 HNO_3 extraction mean results for Ca, Mg, K, Na in soils

Sample location	Horizon/soil layer	Fraction	mg/kg **Ca**	mg/kg **Mg**	mg/kg **K**	mg/kg **Na**
1a	A	soil	980.7	1080.9	842.4	155.7
	B	soil	2049.3	1152.7	1244.1	236.2
1b	A	soil	3432.5	1222.8	932.2	174.5
	B	soil	1782.7	1429.4	1001.2	171.6
1c	A	soil	11019.6	1215.0	688.5	157.2
	B	soil	5823.7	1384.1	899.7	131.4
2b	A	soil	1743.8	1980.9	1498.2	210.3
	B	soil	1331.7	1904.3	1237.7	203.3
2c	A	soil	7120.0	728.0	703.4	132.4
	B	soil	5974.7	837.2	859.4	130.1
3a	A	soil	1691.3	1238.2	1047.0	186.8
	B	soil	2065.0	1367.2	1121.6	215.8
3b	A	soil	6223.1	1312.1	832.4	137.0
	B	soil	2360.4	1157.7	1111.4	200.4
3c	A	soil	3611.3	1711.5	1280.1	163.9
	B	soil	2369.5	1815.4	1487.1	182.0
	C	soil	831.7	3460.0	2411.7	111.0

Table 6.4.5 2M HNO_3 extraction mean results for risk elements in river sediments

Sample location	Horizon/ soil layer	Fraction	mg/kg **Pb**	mg/kg **Cd**	mg/kg **Mn**	mg/kg **Cu**	mg/kg **Ag**	mg/kg **As**	mg/kg **Zn**
1s	surface	sediment	114.2	0.71	1607.4	89.8	2.19	9.48	1308.0
3s	surface	sediment	85.6	0.48	841.6	85.4	2.28	6.67	1181.7
lagoon	surface	sediment	90.1	1.13	1118.2	61.2	2.17	8.76	1556.4

Table 6.4.6 2M HNO_3 extraction mean results for Ca, Mg, K, Na in river sediments

Sample location	Horizon/soil layer	Fraction	mg/kg **Ca**	mg/kg **Mg**	mg/kg **K**	mg/kg **Na**
1s	surface	sediment	5232.3	10571.8	1418.9	205.2
3s	surface	sediment	2658.8	6042.5	1043.6	173.9
lagoon	surface	sediment	4452.1	10588.1	1209.2	156.3

6.5 1M NH_4NO_3 extraction

Table 6.5.1 NH_4NO_3 extraction mean results for risk elements in soil samples

Sample	mg/kg **Pb**	mg/kg **Cd**	mg/kg **Mn**	mg/kg **Cu**	mg/kg **Ag**	mg/kg **As**	mg/kg **Zn**
blank	0.10	0.02	0.1	0.07	0.03	0.27	ND
1a A	15.93	0.26	22.2	5.0	0.05	0.49	27.9
1a B	0.46	1.34	12.9	7.4	0.05	ND	100.5
1b A	1.67	0.45	92.6	3.8	0.01	0.34	42.7
1b B	18.75	1.28	50.1	100.0	0.02	0.02	78.6
1c A	0.36	0.11	143.8	1.2	0.04	0.59	16.5
1c B	0.89	0.36	403.7	1.9	0.04	0.70	54.3
2b A	1.33	1.21	23.1	45.1	0.05	0.40	93.9
2b B	0.49	1.31	17.2	34.7	0.07	0.10	91.5
2c A	0.56	0.22	84.1	1.3	0.01	0.25	37.5
2c B	0.74	0.29	87.4	2.4	0.01	0.33	45.2
3a A	2.60	2.80	14.5	123.8	0.07	0.08	70.0
3a B	1.79	2.74	12.7	48.4	0.05	0.29	85.7
3b A	2.06	0.29	102.9	6.3	ND	0.81	26.4
3b B	2.21	2.31	17.0	67.7	0.01	0.17	33.2
3c A	0.61	0.41	54.0	6.9	0.03	0.81	20.4
3c B	0.79	0.73	22.2	21.5	0.01	ND	26.9
3c C	17.79	1.15	16.5	25.0	0.004	ND	42.7

For Cu and Cd there appears to be a very strong binding in the soils that are richer in OM, rendering them relatively insoluble in the NH_4NO_3 supernatant. However, in a study by Schoning and Brummer (2008), a regression analysis was made between the two extractants NH_4NO_3 and NH_4Cl. In the cases of Pb and Cd in particular it was observed that these heavy metals have a strong tendency to form chloro-complexes with NH_4Cl. The authors then continue to conclude that the Cd- NH_4Cl complexation offers a better imitation of the mobilisation effect of the rhizosphere than by a NH_4NO_3 extraction. For the heavy metal Mn, the reverse is true; whereby results show that it was in the OM rich soils that the higher Mn concentrations extractable by NH_4NO_3 were observed.

Table 6.5.2 NH_4NO_3 extraction mean results for Ca, Mg, K, Na in soil samples

Sample	mg/kg **Ca**	mg/kg **Mg**	mg/kg **K**	mg/kg **Na**
blank	25.1	3.3	9.2	35.1
1a A	620.4	89.6	389.3	313.4
1a B	682.5	42.8	126.9	77.8
1b A	2486.6	325.7	508.1	87.7
1b B	685.0	72.8	150.8	47.2
1c A	5424.0	662.1	650.0	66.4
1c B	4061.6	329.7	292.5	48.8
2b A	694.1	75.3	125.9	36.4
2b B	651.2	52.3	130.7	35.6
2c A	3989.9	367.3	536.4	59.1
2c B	3689.4	348.7	518.6	65.7
3a A	511.2	25.6	96.2	34.8
3a B	522.3	25.1	89.9	36.7
3b A	3658.0	466.4	341.5	60.3
3b B	806.4	74.4	166.6	37.0
3c A	3005.4	363.9	374.4	41.8
3c B	1082.3	123.3	229.3	32.1
3c C	631.6	97.0	290.9	40.2

6.6 Organic carbon content (Corg)

Table 6.6.1 Soil organic carbon results by means of gravimetric method

Soil sample	C org (%)
1a A	44
1a B	6.57
1b A	41.6
1b B	11.8
1c A	67.2
1c B	49
2b A	11.4
2b B	6
2c A	68.6
2c B	63.8
3a A	6.8
3a B	5.8
3b A	52.4
3b B	7.8
3c A	25.8
3c B	9.4
3c C	3.6

6.7 Texture classification of soil

Table 6.7.1 Sand, silt and clay fractions contained in soil samples (%)

Sample	Sand (0,05 - 2 mm)	Silt (0,002 - 0,05mm)	Clay (< 0,002mm)	Soil texture type
1a_hor.A	ND	ND	ND	ND
1a_hor.B	72.57	22.64	4.79	Sandy loam
1b_hor.A	ND	ND	ND	ND
1b_hor.B	60.08	39.54	0.38	Sandy loam
1c_hor.A	ND	ND	ND	ND
1c_hor.B	79.42	17.32	3.26	Loamy sand
2b_hor.A	60.58	37.17	2.25	Sandy loam
2b_hor.B	54.63	37.77	7.6	Loam
2c_hor.A	60.82	36.77	2.41	Sandy loam
2c_hor.B	60.79	35.71	3.5	Sandy loam
3a_hor.A	61.71	35.99	2.3	Sandy loam
3a_hor.B	74.06	23.06	2.88	Loamy sand
3b_hor.A	72.82	23.13	4.05	Sandy loam
3b_hor.B	70.2	25.77	4.03	Sandy loam
3c_hor.A	72.69	23.5	3.81	Sandy loam
3c_hor.B	66.64	28.6	4.76	Sandy loam
3c_hor.C	34.49	46.94	18.57	Silt loam

6.8 Cation exchange capacity (CEC)

Table 6.8.1 CEC mmol(+)/100g for samples

Sample	CEC mmol(+)/100g
1a A	95
1a B	23
1b A	88
1b B	32
1c A	148
1c B	108
2b A	29.25
2b B	18.75
2c A	191.25
2c B	167.75
3a A	19.25
3a B	21.25
3b A	38.5
3b B	22
3c A	50.5
3c B	27.75
3c C	19

6.9 Leaching experiment

Table 6.9.1 Results from LMMOA (1mM citric acid) leaching experiment, (bdl) = below determination limit

test	sample	time		Pb mg/kg	Zn mg/kg	Cd mg/kg	Mn mg/kg	Ca mg/kg	Mg mg/kg	K mg/kg	Na mg/kg
CA	1a	1 hour	1	0.692	37.60	0.016	2.78	65.5	5.13	10.78	6.45
CA	1a	1 hour	2	1.003	61.88	0.034	4.92	118.1	9.39	14.95	11.57
control ca	1a	1 hour		bdl	11.88	0.002	1.15	685.8	5.86	13.00	13.36
CA	1a	24 hours	1	0.192	74.72	0.056	7.15	166.6	12.89	18.10	11.71
CA	1a	24 hours	2	0.309	71.92	0.053	6.60	150.1	12.23	19.54	16.15
control ca	1a	24 hours		bdl	23.16	0.000	2.75	115.0	7.27	18.27	17.95
CA	1a	week	1	0.163	36.18	0.022	4.43	101.7	7.77	12.18	9.38
CA	1a	week	2	0.215	52.74	0.040	6.90	162.2	12.42	21.38	18.92
control ca	1a	week		bdl	35.59	0.005	3.56	1240.0	6.78	16.01	12.93
CA	1a	month	1	bdl	17.80	0.003	5.26	106.8	9.26	18.85	13.92
CA	1a	month	2	bdl	17.66	0.000	6.75	124.1	12.74	28.86	25.20
control ca	1a	month		0.015	121.00	0.051	6.81	1701.0	11.50	20.15	14.29
CA	2a	1 hour	1	1.225	249.30	0.134	4.79	92.0	5.77	22.26	9.41
CA	2a	1 hour	2	1.598	241.60	0.144	4.51	90.5	5.66	21.54	14.30
control ca	2a	1 hour		0.017	61.39	0.054	0.96	338.0	2.05	14.36	11.05
CA	2a	24 hours	1	0.231	259.80	0.153	7.14	106.4	7.20	26.92	18.04
CA	2a	24 hours	2	0.277	253.20	0.170	6.71	98.8	7.09	26.86	18.65
control ca	2a	24 hours		0.038	59.94	0.039	1.08	284.2	1.86	12.58	9.83
CA	2a	week	1	0.153	262.60	0.184	7.18	117.6	8.04	33.77	23.54
CA	2a	week	2	0.130	236.20	0.134	6.66	117.6	7.70	27.88	16.31
control ca	2a	week		0.057	170.30	0.115	3.29	618.7	3.60	22.47	14.88
CA	2a	month	1	0.359	277.60	0.180	7.06	115.9	7.40	36.15	31.87
CA	2a	month	2	0.561	232.60	0.137	5.55	109.8	7.10	27.36	16.22
control ca	2a	month		0.145	385.10	0.335	5.75	950.9	5.29	26.33	15.22
CA	3a	1 hour	1	0.291	264.00	0.053	4.91	114.6	8.09	22.73	16.15
CA	3a	1 hour	2	0.245	273.30	0.050	4.99	113.0	6.88	19.96	11.59
control ca	3a	1 hour		bdl	50.740	0.014	0.82	348.6	2.25	11.15	10.64
CA	3a	24 hours	1	0.061	234.50	0.057	5.85	116.9	8.20	19.37	16.61
CA	3a	24 hours	2	0.053	225.50	0.056	5.75	114.8	8.00	20.60	17.68
control ca	3a	24 hours		bdl	81.39	0.010	2.11	804.7	3.41	14.14	12.28
CA	3a	week	1	0.316	264.40	0.062	7.37	163.1	8.46	25.08	20.78
CA	3a	week	2	0.284	256.70	0.072	6.60	148.6	8.26	24.71	21.28
control ca	3a	week		bdl	141.10	0.041	2.80	1010.0	3.53	15.54	15.00
CA	3a	month	1	0.486	259.70	0.060	6.29	188.6	8.00	18.95	15.10
CA	3a	month	2	0.598	250.30	0.071	6.73	194.0	8.16	22.76	21.73
control ca	3a	month		0.002	308.10	0.118	4.68	1944.0	5.38	16.07	14.62

Table 6.9.2 Results from rain simulation leaching experiment (bdl) = below determination limit

test	sample	time		Pb mg/kg	Zn mg/kg	Cd mg/kg	Mn mg/kg	Ca mg/kg	Mg mg/kg	K mg/kg	Na mg/kg
RS	1a	1 hour	1	bdl	8.12	bdl	0.58	36.7	3.11	11.58	12.67
RS	1a	1 hour	2	0.056	8.89	bdl	0.73	43.3	4.00	12.71	12.95
control rs	1a	1 hour		bdl	13.51	bdl	1.05	1428.0	4.48	17.41	21.82
RS	1a	24 hours	1	bdl	20.18	bdl	2.52	103.6	6.54	22.74	24.30
RS	1a	24 hours	2	bdl	20.48	bdl	2.16	98.9	5.85	17.58	18.68
control rs	1a	24 hours		bdl	19.69	0.002	1.77	1793.2	5.09	14.53	17.19
RS	1a	week	1	0.002	60.68	0.016	4.09	134.7	7.72	33.24	30.52
RS	1a	week	2	bdl	45.90	0.008	2.95	114.1	5.78	21.48	19.16
control rs	1a	week		bdl	46.92	0.010	3.79	2702.0	7.30	18.02	16.31
RS	1a	month	1	bdl	158.96	0.090	5.55	156.4	9.05	43.26	28.62
RS	1a	month	2	0.024	159.54	0.100	5.76	161.0	9.30	47.18	20.72
control rs	1a	month		bdl	216.20	0.104	8.55	4072.0	14.73	30.78	29.06
RS	2a	1 hour	1	bdl	58.26	0.044	0.77	28.1	2.34	20.88	13.59
RS	2a	1 hour	2	0.150	33.08	0.024	0.50	18.6	2.12	16.20	14.32
control rs	2a	1 hour		bdl	33.62	0.022	0.52	462.4	2.21	16.85	21.36
RS	2a	24 hours	1	bdl	90.12	0.048	1.52	39.8	2.93	30.96	28.94
RS	2a	24 hours	2	bdl	82.34	0.052	1.26	37.7	2.73	22.64	19.63
control rs	2a	24 hours		bdl	82.78	0.060	1.26	807.2	3.15	26.20	26.08
RS	2a	week	1	0.024	196.90	0.172	2.96	64.5	3.74	25.70	16.19
RS	2a	week	2	0.016	152.88	0.132	2.12	51.5	3.39	47.88	47.10
control rs	2a	week		bdl	160.24	0.150	2.25	1215.2	4.75	36.58	31.22
RS	2a	month	1	0.096	277.40	0.280	2.91	71.5	3.76	27.26	23.14
RS	2a	month	2	0.074	417.40	0.350	5.72	111.5	6.08	39.92	30.56
control rs	2a	month		0.200	346.20	0.328	3.78	1908.8	5.05	30.14	22.16
RS	3a	1 hour	1	0.050	43.08	0.008	0.73	32.0	2.84	16.24	13.34
RS	3a	1 hour	2	bdl	52.28	0.010	0.91	41.8	4.14	15.82	15.45
control rs	3a	1 hour		0.070	44.54	0.006	0.78	742.4	2.91	17.88	19.03
RS	3a	24 hours	1	0.028	92.40	0.024	1.58	65.4	3.11	19.33	19.12
RS	3a	24 hours	2	bdl	89.62	0.024	1.60	62.9	3.04	20.30	21.70
control rs	3a	24 hours		0.048	82.12	0.020	1.48	1239.6	3.15	16.04	20.98
RS	3a	week	1	0.000	175.40	0.040	2.89	138.7	4.60	26.32	27.58
RS	3a	week	2	bdl	192.18	0.074	3.38	115.3	4.18	21.60	19.90
control rs	3a	week		bdl	161.44	0.048	3.08	2199.2	4.61	19.51	17.85
RS	3a	month	1	bdl	446.00	0.182	4.98	188.5	5.83	35.10	31.74
RS	3a	month	2	0.008	406.80	0.192	4.78	147.6	5.67	28.10	30.12
control rs	3a	month		bdl	299.80	0.106	3.14	2949.6	3.80	16.76	16.89

7. Results interpretation and discussion

7.1 General soil characteristics

7.1.1 pH

When the pH values are averaged out for each sample type (A line = mineral type soils on the slag heap, B line = plateau on the slag pile with some influence from vegetation inputs, C line = riverside bank heavily influenced by dense canopy of vegetation) as can be seen in table 6.1.2, there is an overall trend of pH increasing with depth on the mineral soils on the slags, and a general decrease of pH with depth in the riverbank soils.

Decreasing pH with depth in the Corg rich soils, (mainly samples from localities C), are most likely attributable to the leaching of organic acids and decomposing OM out of the upper horizons and into the lower horizons, carrying with them nutrients and REs which are soluble under the acidic conditions.

Conditions on the slag differ however. As results from the leaching experiment show (see chapter 7.4), without any continuous acidifying inputs from vegetation for example, dissolution of the slag material is actually resulting in the increasing of soils pH.

The hypothesis that an increase in OM results in a decrease in pH and thus more acidic conditions is shown to be valid as Figure 7.1.1 illustrates.

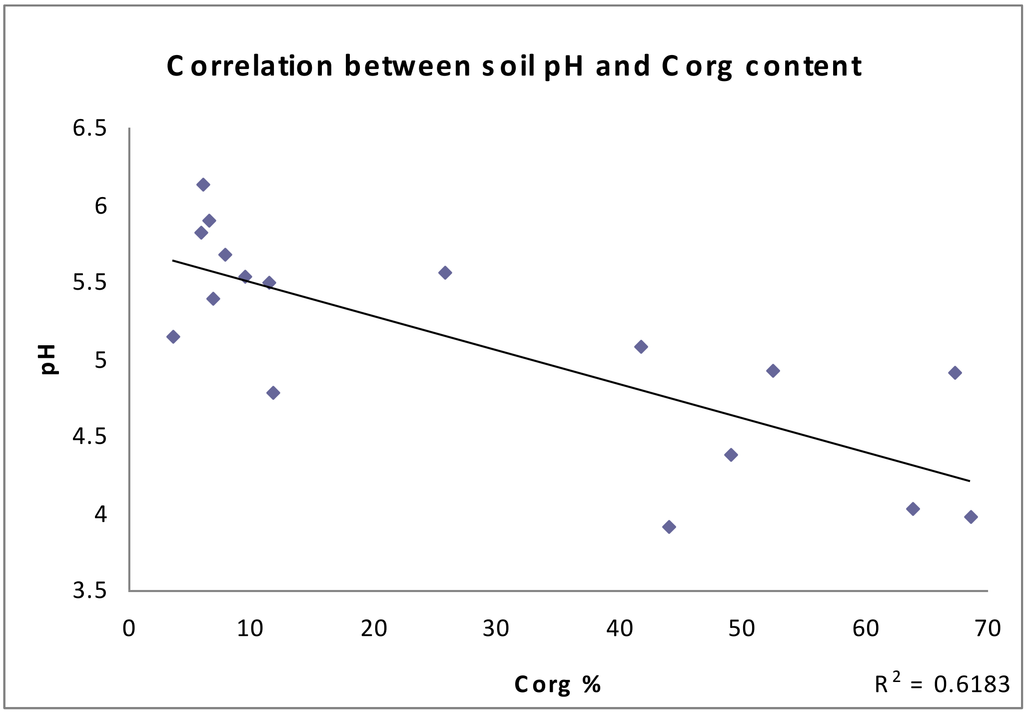


Figure 7.1.1 Correlation between soil organic carbon content and soil pH in soil samples (R = 0.786, critical P-value (CV) = 0.482 at 5% significance)

As Figure 7.1.1 shows, the pH drops within the range of 2 values as organic carbon contents increases over a range from less than 5% up to almost 70%. The trend is significant due to R value exceeding the critical P-value, (CV) when α significance = 5% taken from Taylor (2007) for correlation and regression analysis. .

pH will prove to be a highly significant factor for the mobilisation and retention of REs within the slags as the following data presented in this thesis will identify. Its relationship to Corg as a result of organic matter inputs is equally as significant.

The pH – OM relationship is likely to be the most influential factor in successful colonisation of plants on the slags at Kutná Hora. The correlation between Corg and pH and bioavailability of essential macronutrients (particularly Mg and K) is highly significant as will be demonstrated further in this chapter.

7.1.2 Soil organic carbon content

Corg in the soil samples was determined by means of the gravimetric/combustion method (results Table 6.6.1). It was anticipated that this would be a significant factor in the contents of cationic REs and nutrient elements that would be present in a given horizon. The bio-available concentrations in particular were expected to fluctuate with increases/decreases in Corg content (as a result of OM in soils) due to their sorption potential and CEC. Fig 7.1.2 confirms this to some degree with a very tight and highly significant correlation (R = 0.991) between organic carbon content and conductivity.

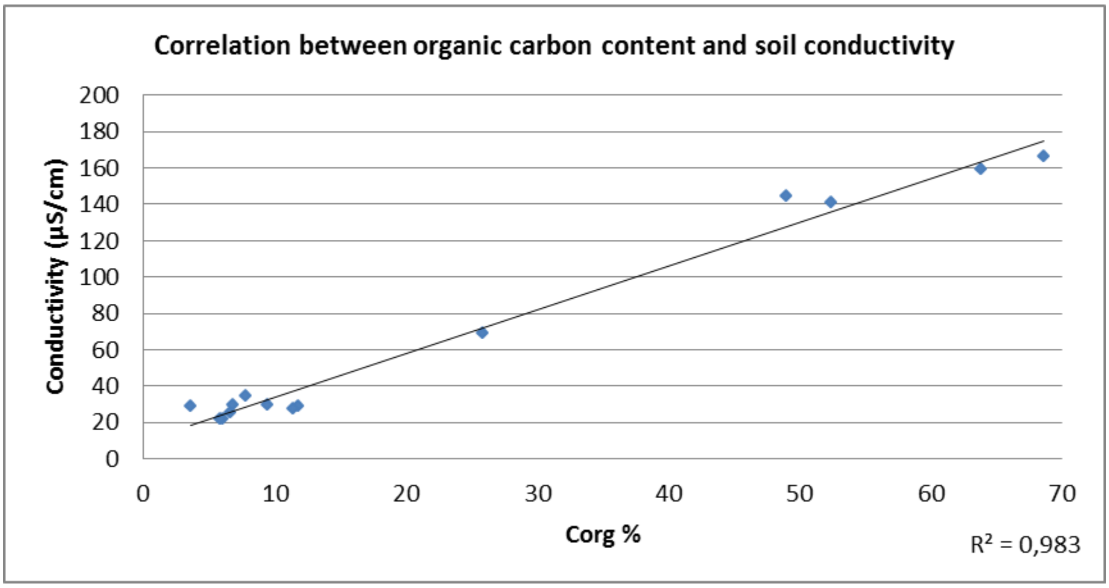


Figure 7.1.2 Soil conductivity dependence on soil organic carbon (5% CV = 0.532)

As it is widely understood in the general field of soil science, the ability of organic matter to bind cations is typically increasing with increasing pH (see Figure 7.1.5) and vice versa (Alloway 1990). This effect that pH has on the sorption of risk elements has been demonstrated on mine wastes by the author of this thesis in a previous study (Ash 2009), (Figure 7.1.3 and Figure 7.1.4). It is an example of the complexity of the processes that we understand in soils creating a somewhat hypocritical set of rules (By increasing OM in mining wastes, then the CEC and binding sites are increasing for the sorption of metals/minerals, but on the other hand, as Figure 7.1.1 highlights, an increase of OM in soils also correlates with increased acidity and therefore minerals are mobilised as opposed to being bound to the CEC). Hence, the pH and type of OM in soils cannot be overlooked.

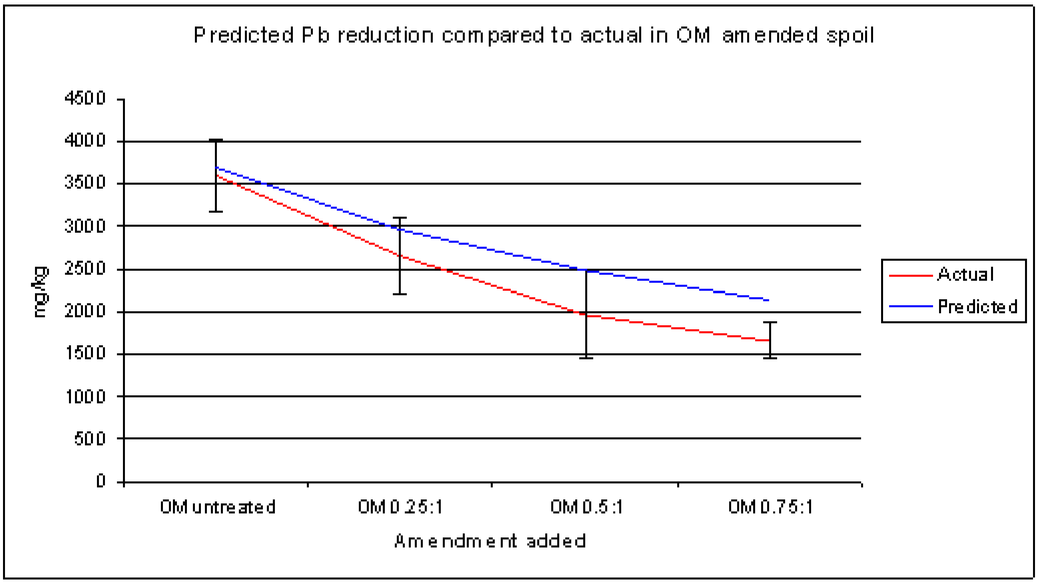


Figure 7.1.3 Effect of an organic matter amendment with high pH (7.2) on bioavailable Pb in mine wastes from South West England (Ash 2009)

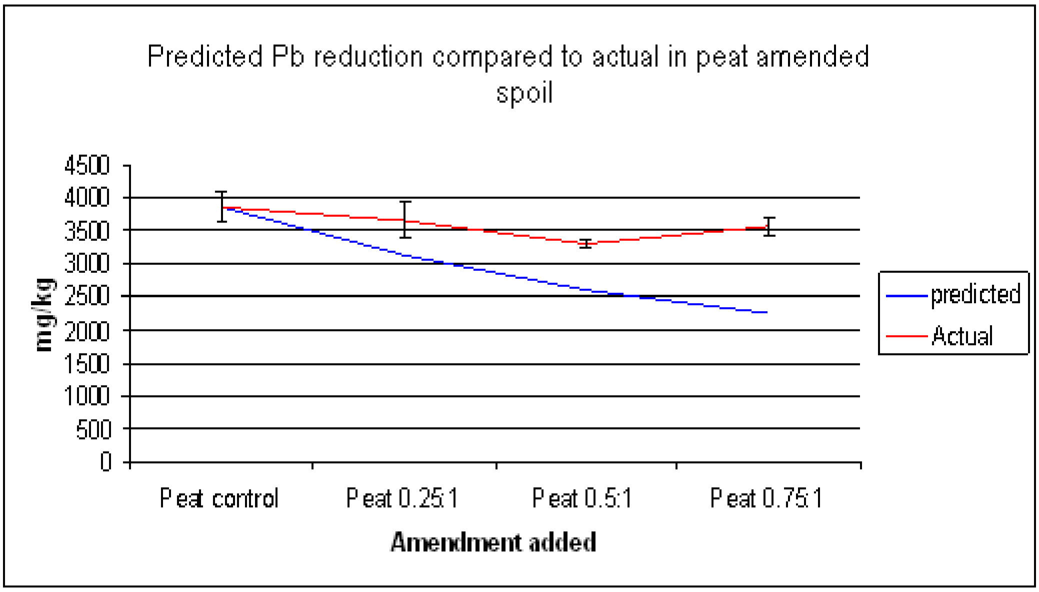


Figure 7.1.4 Effect of an organic matter amendment with low pH (3.6) on bioavailable Pb in mine wastes from South West England (Ash 2009)

7.1.3 Soil texture

Soil samples were categorised into the three basic fractions, sand, silt and clay (Table 6.7.1) for simplicity and to enable drawing on more concise conclusions within a relatively large amount of data. As expected there is a wide variety of soil types according to where samples were collected on the sampling area. There is a general trend of increasing clay fraction with increasing soil depth. This would be expected as weathering of primary minerals which were formed from parent material or from the slags themselves results in downward migration of smaller particles through the highly permeable structure of the slags. What is the most striking feature is that a C horizon was exposed during sampling in the river bank soils which is in stark contrast to the overlying soils. Within a very sharp gradient and a matter of centimetres, the organic rich sandy B horizon of sample 3C makes an abrupt transition to the clay rich mineral C horizon. Subject to investigation, it is suspected that the C horizon may be the underlying soil of the surrounding area including the dumpsite of the slags.

As previously described, the CEC phenomenon has a profound effect on REs behaviour including its mobility and availability to biological organisms (Alloway 1990). Of course, one of the most recognised features of clays is its binding affinity for cations (in some cases anions via hydrogen bridging) and their potentially very high CEC (Brady and Weil 2004).

Common knowledge about the characteristics and behaviours of soils will dictate that with an increase in negatively charged surfaces comes an increase in CEC. Typical sources of these negative surfaces come from clays, clay colloids, organic matter and destabilised organic acids. Therefore if the Corg and clay content in samples were to be correlated with CEC then one would expect to see a positive linear trend. Figure 7.1.5 illustrates the situation for clay contents and organic matter. The results are somewhat inconsistent with what would be expected. Clay exhibits an insignificant correlation (R = 0.204, compared to CV = 0.532) and there is even a negative trend. However, the range of values for clay is small (0 – 18 %). The organic matter however, fits very well with the data for CEC and displays a highly significant positive trend. This may raise questions regarding the validity of the textural analysis (texture curves can be viewed in Appendix F), or the inclusion of organic rich samples in the data is distorting results (where OM is high and clay is low, CEC is high because of the presence of the OM). Where clays are present they are most likely to be low activity clays of poor quality.

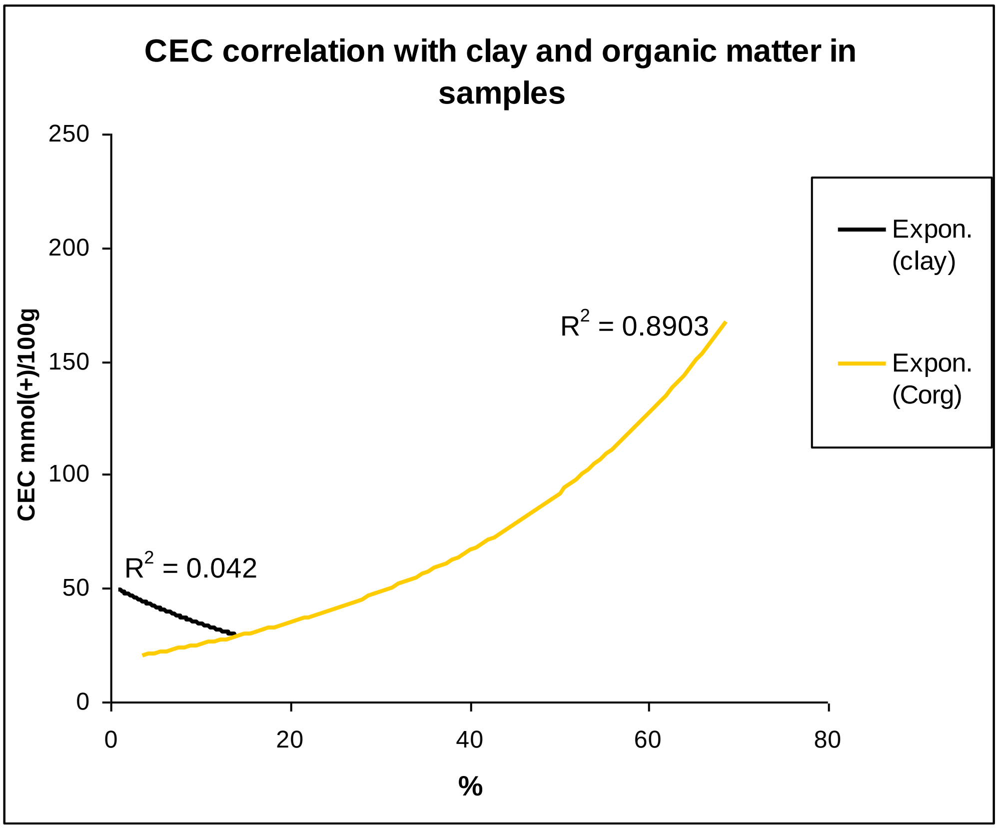


Figure 7.1.5 correlation of CEC with clay and Corg in samples (5% CV = 0.532)

7.2 Plant nutrient elements

In addition to surveying the study area for risk elements, it is important to consider the nutrients within the soils, particularly if one of the aims is to understand why the site is largely devoid of any significant vegetation.

The following table lists analytes which were included in the analysis of soils from the study area:

Table 7.2.1 Nutrient elements analysed in the study, table from Brady and Weil (2004)

Macronutrient	*Primary*	K
	Secondary	Ca, Mg
Micronutrient		Cu, Mn, Zn,
Trace elements		Na

Of course, Cu, Mn and Zn are listed as risk elements in excessive concentrations, however, a complete unavailability results in symptoms of deficiency.

The following set of graphs show the correlation between the bioavailability of nutrients listed (Table 7.2.1) and corresponding pH and Corg values. These graphs are included to illustrate the likelihood that, without a significant organic horizon (as is the case on the slag heap), there is a highly reduced availability of nutrients for the establishment of vegetation. In the case of the riverbank soils where organic matter is prevalent, the opposite is true and a high availability of these nutrients are observed.

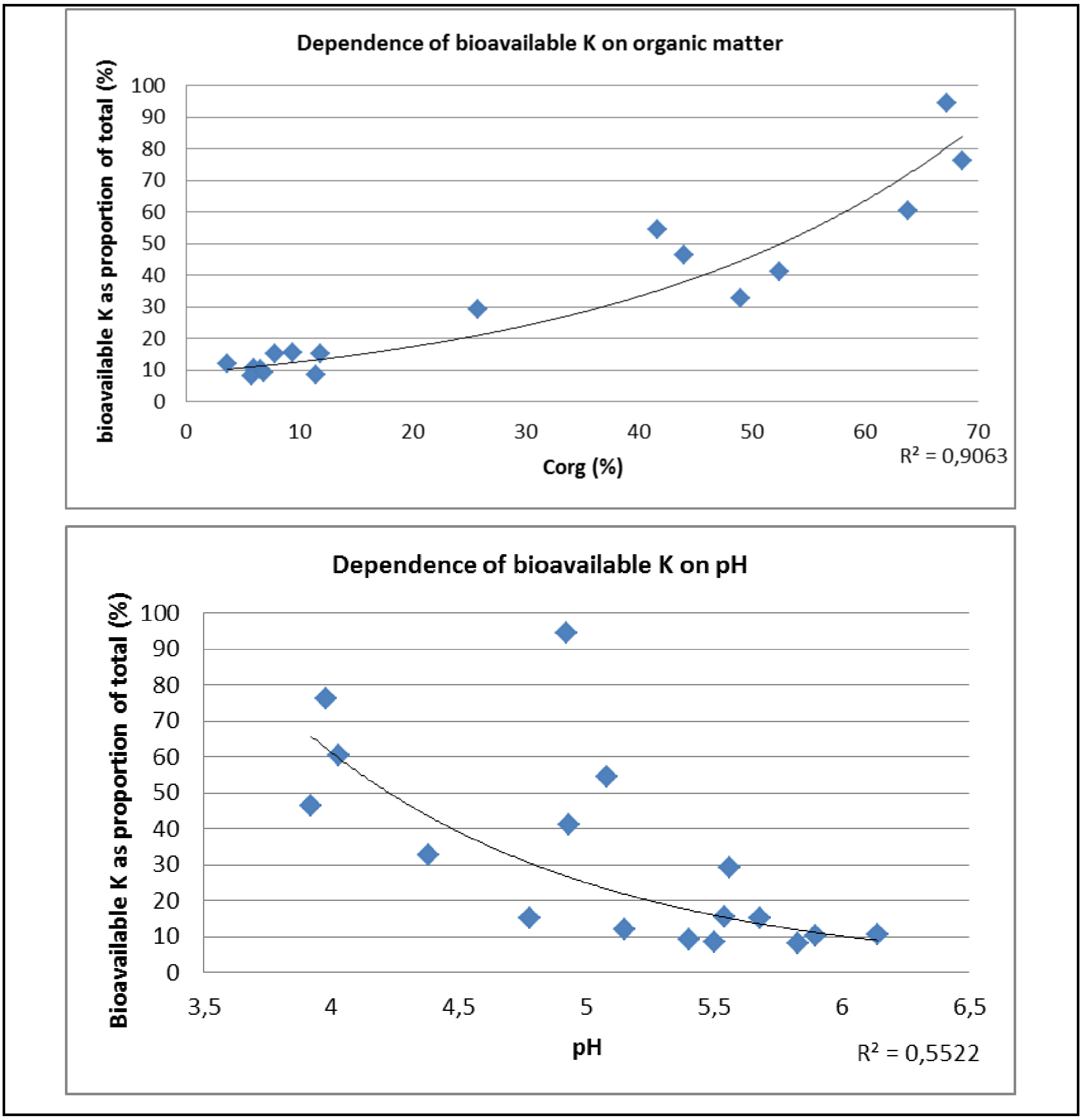


Figure 7.2.1 Dependence of bioavailable K on organic matter (top) and pH (bottom), (5% CV = 0.482)

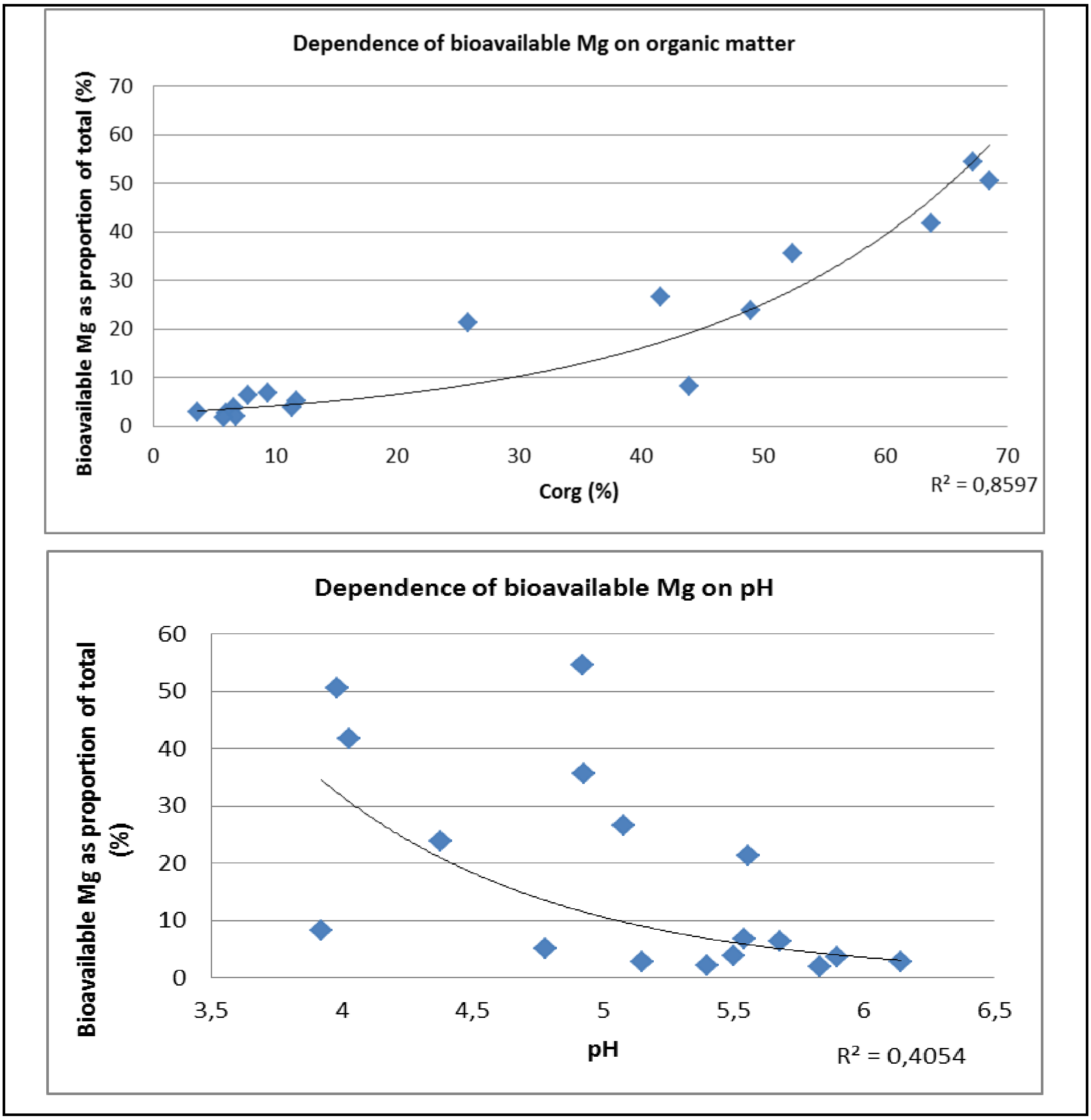


Figure 7.2.2 Dependence of bioavailable Mg on organic matter (top) and pH (bottom), (5% CV = 0.482)

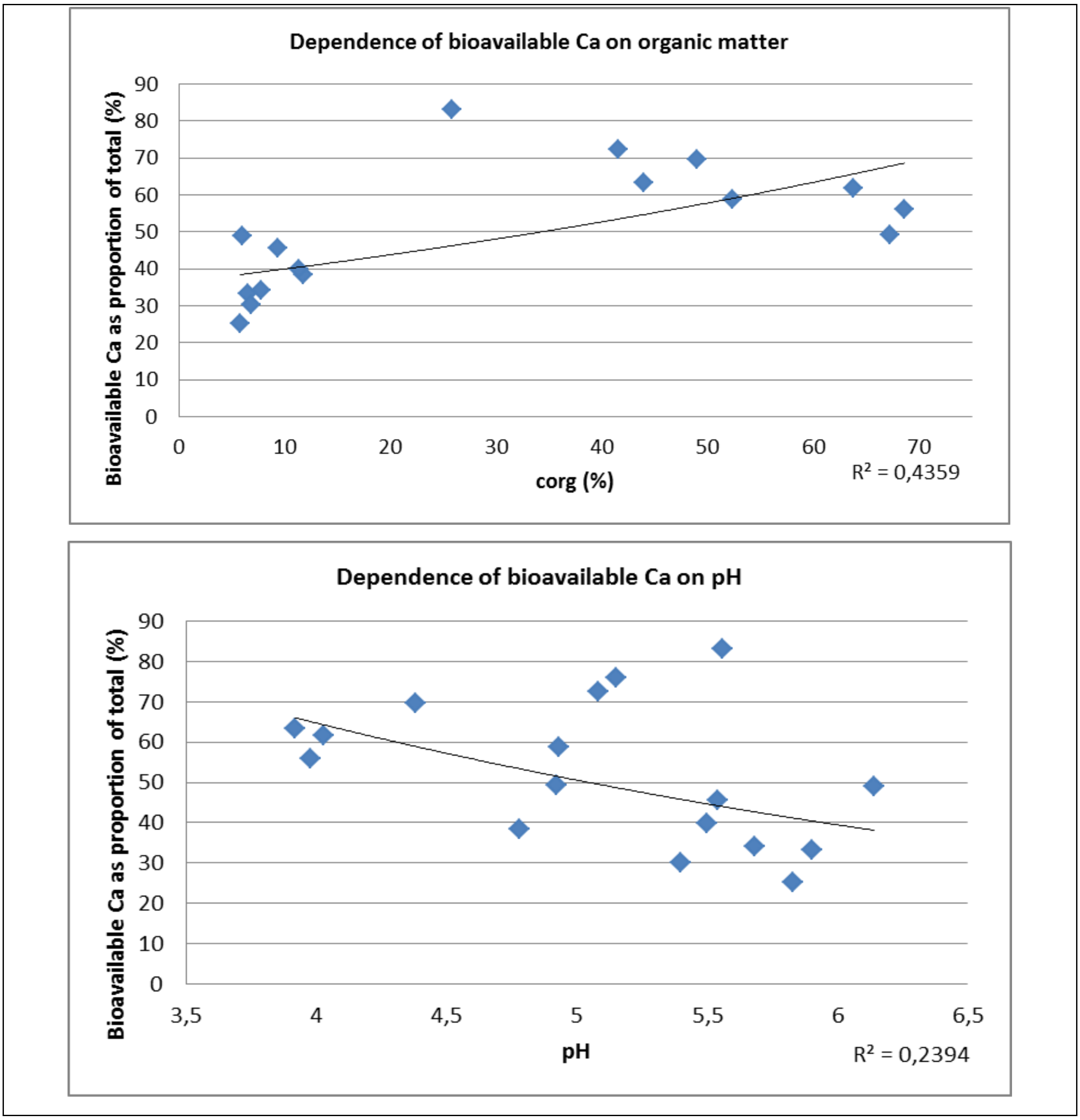


Figure 7.2.3 Dependence of bioavailable Ca on organic matter (top) and pH (bottom), (5% CV = 0.482)

Note that for Ca the data points are more scattered and according to the 5% of significance critical value the correlation is not highly significant (Corg R = 0.66, pH R = 0.489). However, the trend is still in the same direction as the other nutrient minerals for both Corg and pH correlation. A pattern that was identified is the relationship between Ca and available Pb (Figure 7.2.4). It appears that Ca inhibits the mobility of Pb, probably by causing Pb to form precipitates as described by Maskall *et al.* (1996). As the graph illustrates, bioavailable

Pb only occurs at concentrations above 3 mg/kg when Ca is present in the lower concentrations (<2000 mg/kg).

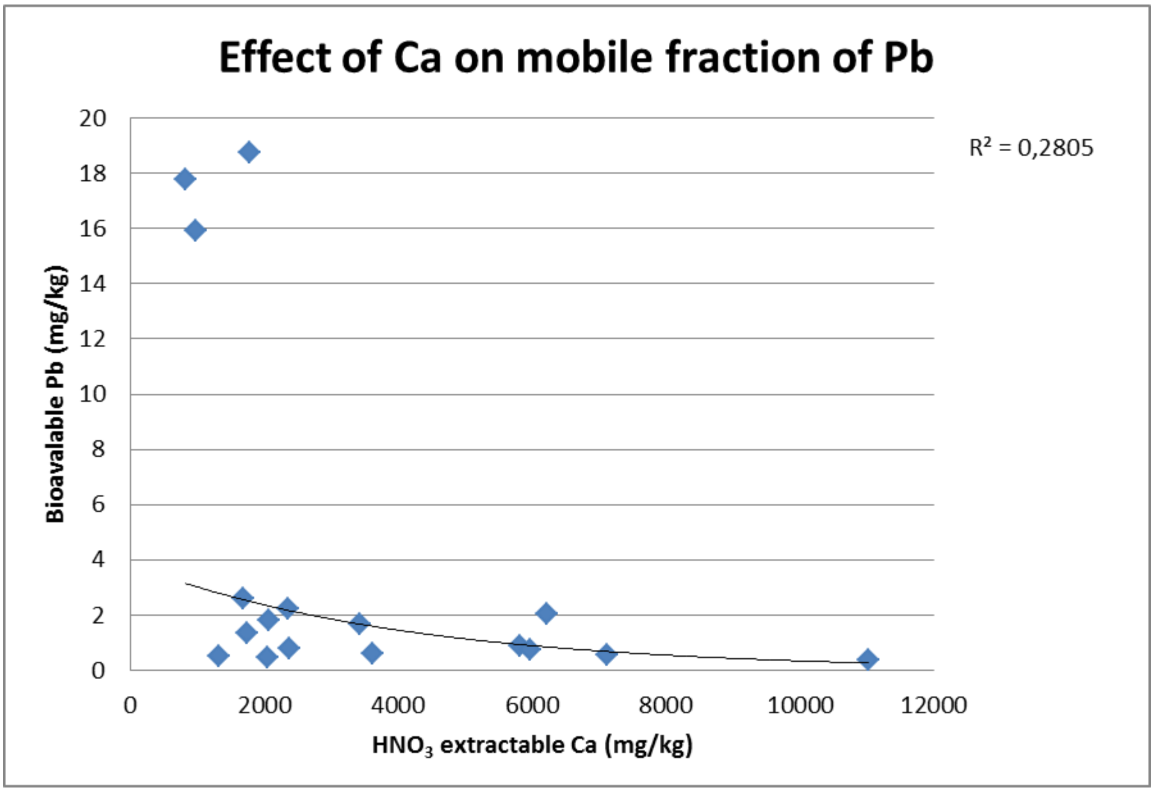
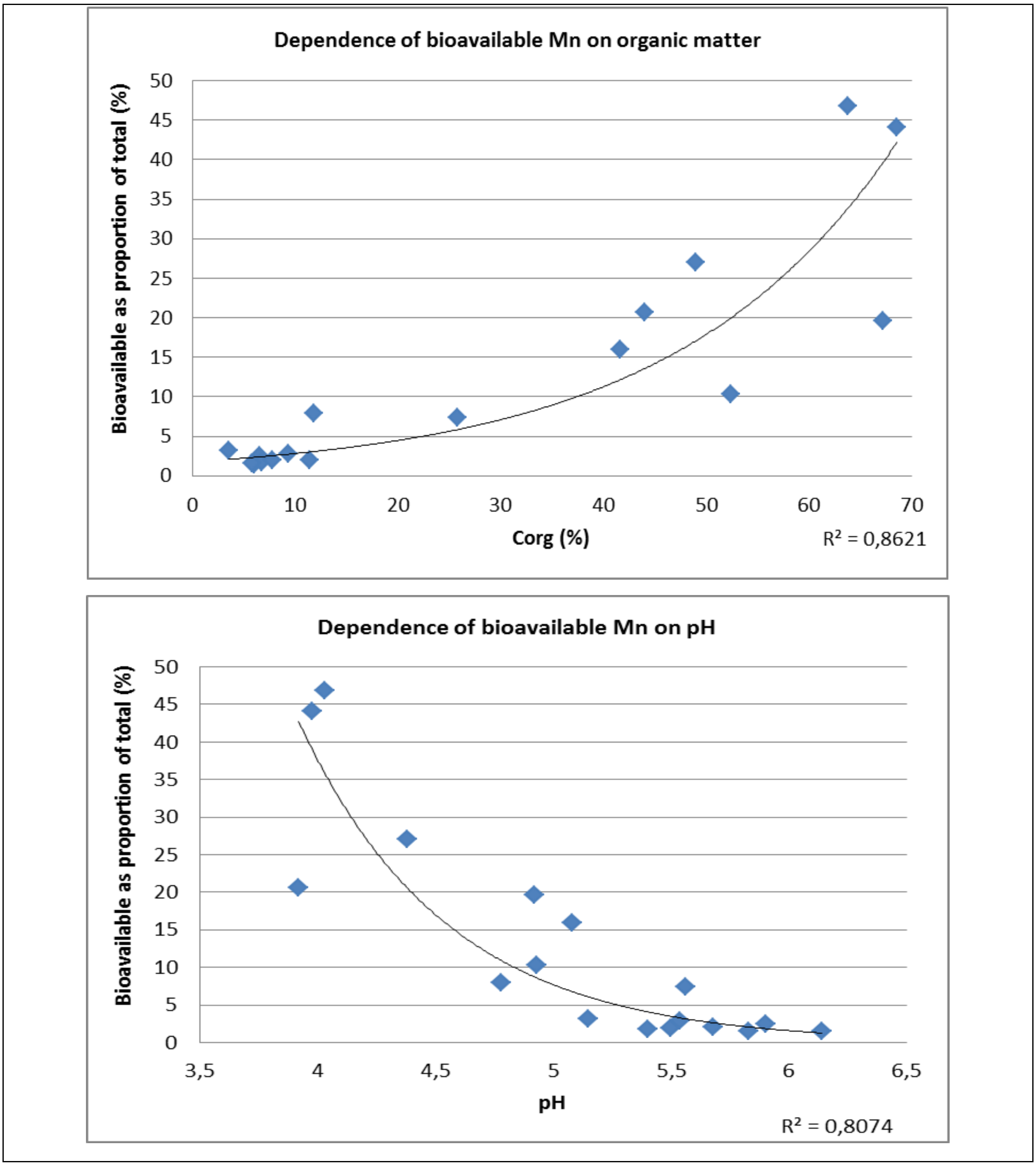


Figure 7.2.4 Relationship between Ca and the mobile/bioavailable fraction of Pb in samples

For Cu the data points are widely scattered and no correlation could be identified for pH. The relationship of bioavailable Cu to Corg and clay contents is discussed in section 7.3.



Dependence of bioavailable Mn on organic matter

Dependence of bioavailable Mn on pH

Figure 7.2.5 Dependence of bioavailable Mn on organic matter and pH (5% CV = 0.482)

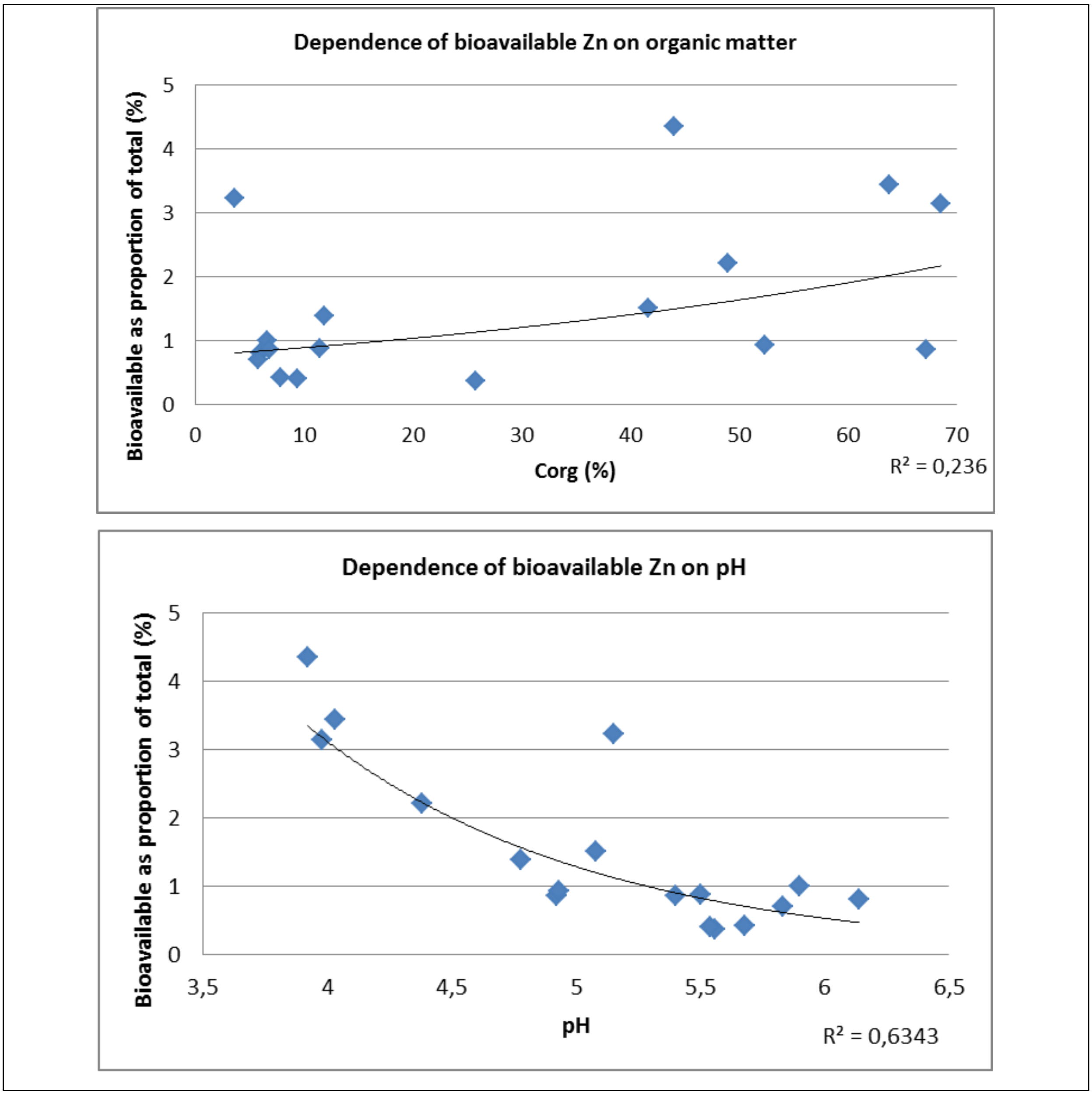


Figure 7.2.6 Dependence of bioavailable Zn on organic matter and pH (5% CV = 0.482)

Although bioavailable Zn shows less strong dependence on Corg there is a highly significant trend with pH (R = 0.796 compared to CV = 0.482).

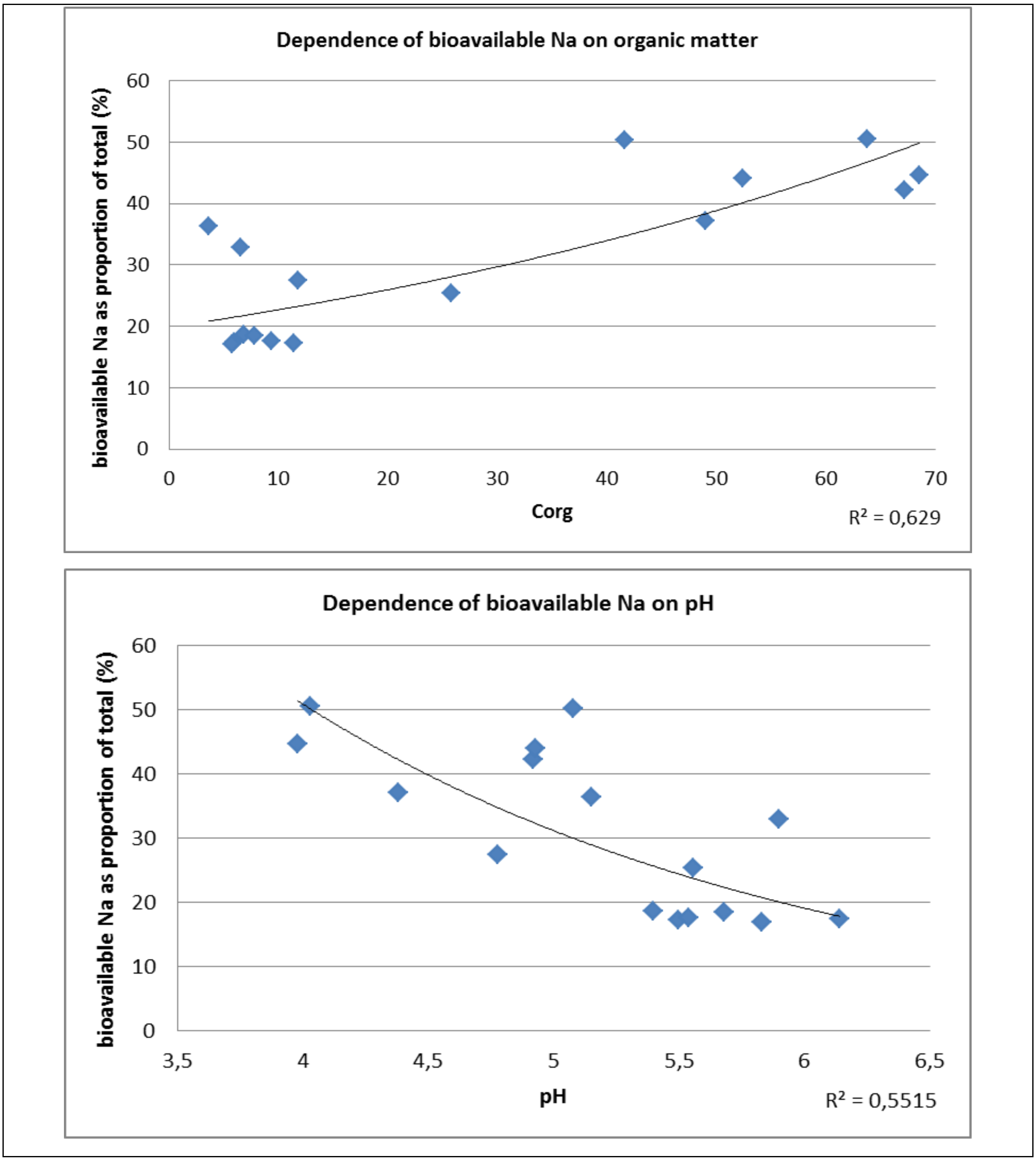


Figure 7.2.7 Dependence of bioavailable Na on organic matter and pH (5% CV = 0.482)

What the graphs consistently show is that with increasing contents of organic matter comes an increased bioavailability of nutrients from the total amounts bound in the soil. As for pH, the lower range of pH values observed across the scale results in increased bioavailable nutrients. Lower pH also correlates with additional Corg values in samples.

A consequence of this observation may favour a new hypothesis; that rather than the reason for an absence of vegetation on the slags being due to toxicity from elevated concentrations of risk elements, it may be the situation that plants cannot become established here due to the deficiency of essential nutrient elements (K and Mg in particular).

This could explain why there is a dense canopy of vegetation over the river banks. It may be conceivable that after the slags were originally dumped, there was no vegetation, but due to periodic flooding of the riverbank over the years, receding floods will have left behind deposits of sediment and organic matter sufficient enough to support pioneer plants, which over many decades will continue to add more organic material to the soil. Once there is a well-developed O-horizon, the chemistry of the soils have evolved into a more acidic, reducing environment which will release and solubilise essential nutrient minerals from the slags into the soil matrix enabling their uptake by plants. Once deciduous trees are established, the annual fall of leaf litter will create the deep organic rich horizons that are observable today.

It is to our understanding due to visual evidence that the slags from historic smelting in KH are widespread in the region and that these materials have been used for a number of purposes including for fertilisation of the surrounding agricultural soils.

7.3 Risk elements

7.3.1 Bioavailability of risk elements in the riverbank soils

Following on from the discussion of the transition between horizons in the sample 3C, an observation was made which relates the clays ability to adsorb REs (rendering them non-bioavailable) to the changes in pH that accompany the changing soil horizons (Figure 7.3.1) Bioavailability of REs was calculated for each sample from NH_4NO_3 extract as a proportion of the total (HNO_3 extract) within the same sample. These bioavailable concentrations and soil pH were plotted to see how they change with soil depth.

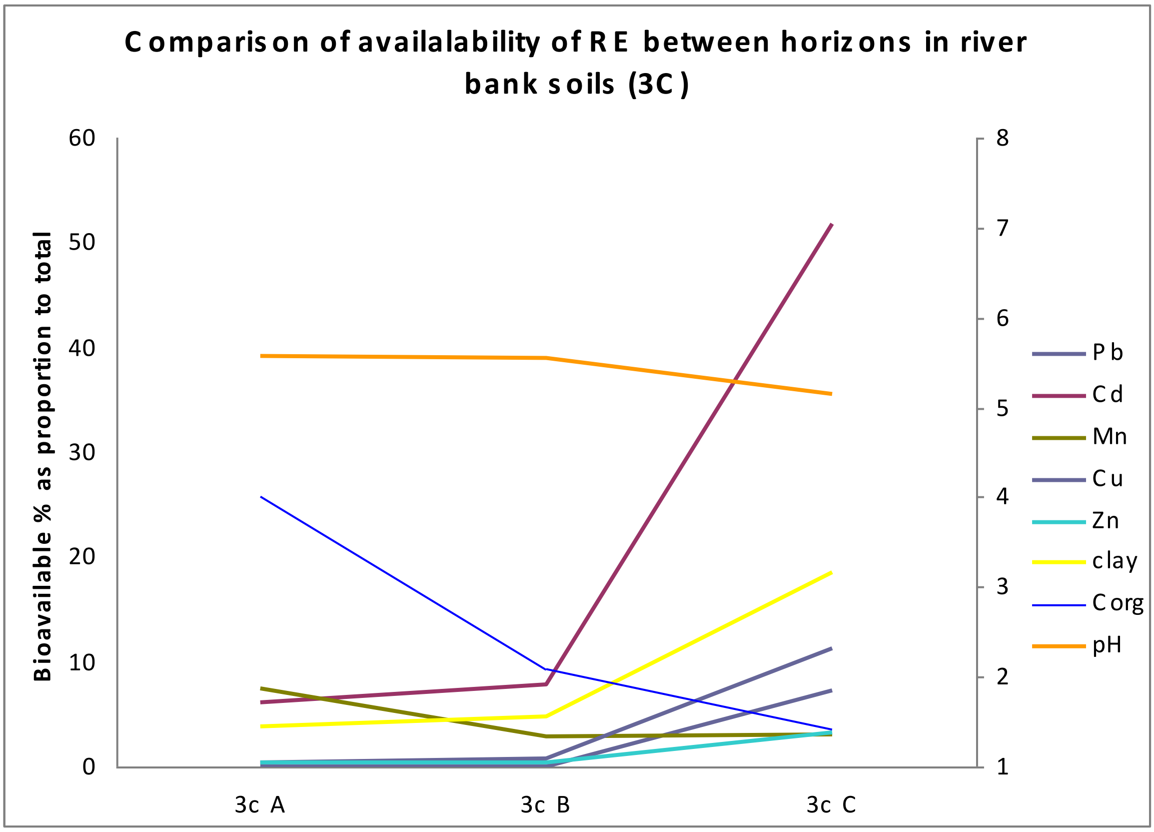
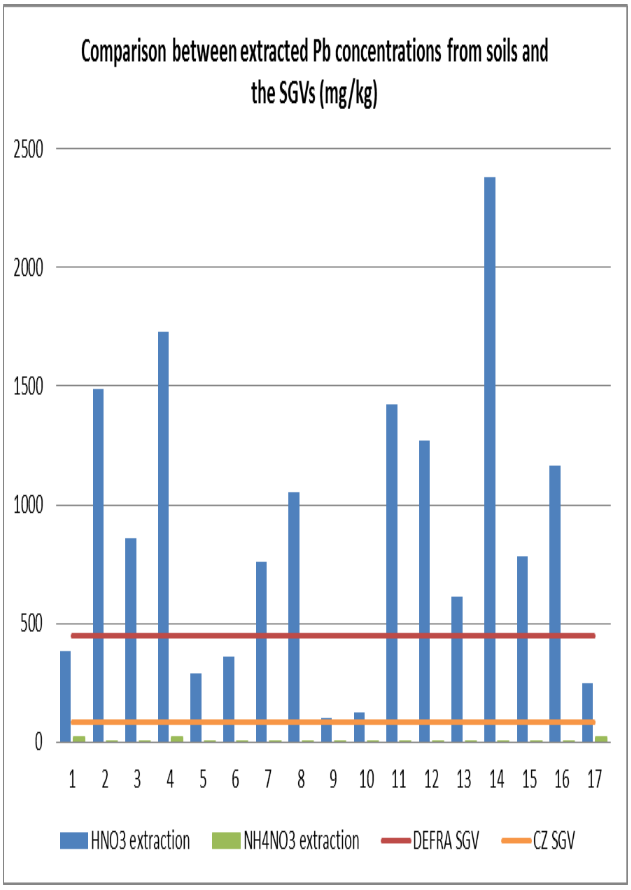


Figure 7.3.1 Changes in bioavailable RE concentrations, Corg % (left scale) and pH (right scale) with differing horizons in the sample locality 3C

As Figure 7.3.1 clearly shows, pH is decreasing with decreasing soil depth, particularly with the transition from the B to the C horizon. Clay content is increasing with depth, again, most notably with the transition from the B to the C horizon. REs bioavailability is in each case (with the exception of Mn) significantly increasing. Despite the increase in clay with depth (and consequent increase in CEC), REs are becoming increasingly mobile (more bioavailable) and not strongly adsorbed to the surface of clay as would be expected. It is evident on inspection of Figure 7.3.1 that the binding affinity of REs to clay is strongly dependent on pH, and without raising pH, any attempt to immobilise REs by addition of clays is most likely to be unsuccessful. It should also be noted that organic matter is also decreasing but does not correlate with pH in this example as discussed previously (Figure 7.1.1). The author of this thesis had similar experiences with clay amendments whereby the addition of montmorillonite clay to mining wastes with no pH adjustment had no effect on bioavailable Pb and Zn, whereas a $CaCO_3$ amendment which raised pH from ~ 4.6 up to ~ 8.6 proved to be very effective in immobilizing Pb and Zn, reducing availability many fold from the unamended sample (Ash 2009).

The evidence mounts throughout this paper that the bioavailability of REs is determined not so strongly by soil texture, but is primarily influenced by pH.

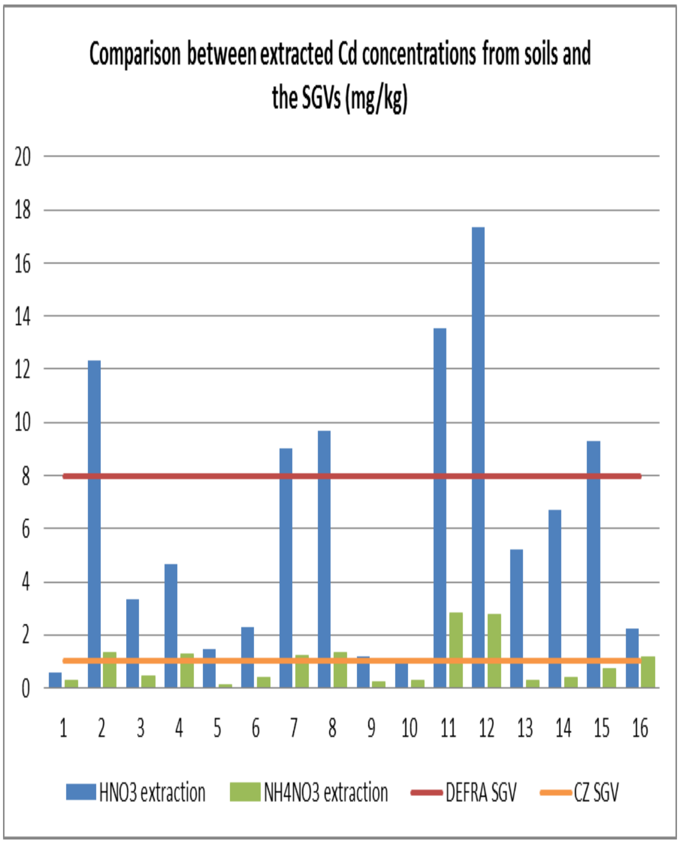
7.3.2 Comparison of risk element concentrations to soil guideline values



Sample		HNO_3 extraction	NH_4NO_3 extraction	Pb (%) bioavailable proportion to HNO_3
1a A	1	381.45	15.93	4.18
1a B	2	1485.90	0.46	0.03
1b A	3	861.25	1.67	0.19
1b B	4	1727.35	18.75	1.09
1c A	5	288.85	0.36	0.12
1c B	6	357.90	0.89	0.25
2b A	7	758.85	1.33	0.17
2b B	8	1055.65	0.49	0.05
2c A	9	99.40	0.56	0.56
2c B	10	123.90	0.74	0.60
3a A	11	1425.25	2.6	0.18
3a B	12	1269.65	1.79	0.14
3b A	13	609.35	2.06	0.34
3b B	14	2381.05	2.21	0.09
3c A	15	783.05	0.61	0.08
3c B	16	1161.75	0.79	0.07
3c C	17	248.15	17.79	7.17

Figure 7.3.2 Difference between total (HNO_3) and plant-available (NH_4NO_3) Pb in soils

It is evident that despite high HNO_3 extractable values for Pb which is contained in soils (above both Czech and U.K SGVs in most cases), the amount which is actually available for plant uptake is very low. These findings are consistent with the reports by Maskall *et al.* (1996) who also experienced large deposits of Pb on mining wastes but very little in the mobile form. The highest bioavailable Pb occurs in sample 1a A horizon (a partially vegetated island within the main slag heap) and in sample 3c horizon C (the clay rich acidic layer which presumably underlies the study area).



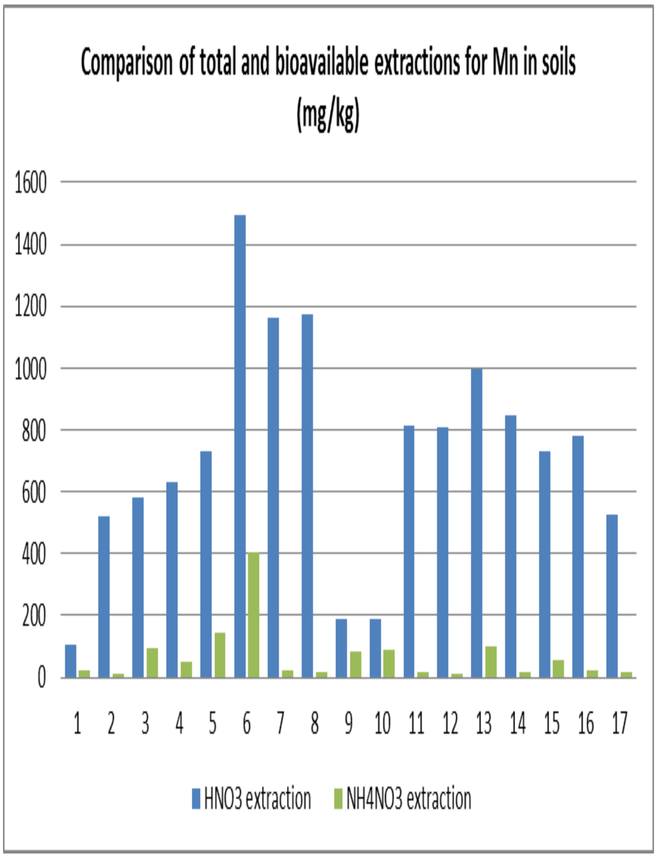
Sample		HNO_3 extraction	NH_4NO_3 extraction	Cd (%) bioavailable proportion to HNO_3
1a A	1	0.60	0.26	43.1
1a B	2	12.35	1.34	10.9
1b A	3	3.33	0.45	13.4
1b B	4	4.66	1.28	27.5
1c A	5	1.46	0.11	7.7
1c B	6	2.31	0.36	15.8
2b A	7	9.03	1.21	13.4
2b B	8	9.70	1.31	13.5
2c A	9	1.18	0.22	18.7
2c B	10	1.04	0.29	27.7
3a A	11	13.57	2.80	20.6
3a B	12	17.35	2.74	15.8
3b A	13	5.23	0.29	5.6
3b B	-	86.70	2.31	2.7
3c A	14	6.68	0.41	6.2
3c B	15	9.28	0.73	7.9
3c C	16	2.23	1.15	51.9

Figure 7.3.3 Difference between total (HNO_3) and plant-available (NH_4NO_3) Cd in soils

The bioavailable proportions from the total are notably higher for Cd than for Pb, which is also described by Rosseli *et al.* (2003). However, the total concentrations are not particularly high (the highest total value only a little of twice that of the DEFRA SGV). The concentrations of Cd that are available for uptake are therefore also small. One sample has not been included in the chart. Sample 3b B appears as an anomalous value in the data and has been removed from the bar chart to keep the scale in perspective for viewing purposes. The presumption that this result is an anomaly due to analytical error can be disproved due to the replication in the analysis (Table 7.3.1). The reality of the situation is that although so far the data has shown that the slags at Kutná Hora are not as toxic as initially suspected, they are heterogeneous materials and therefore it is likely that "hotspots" of contamination will occur. The soil from horizon 3b B also contains the highest HNO_3 extractable concentrations of Pb and Cu.

Table 7.3.1 HNO_3 extraction showing duplicate results of Cd for sample 3b B

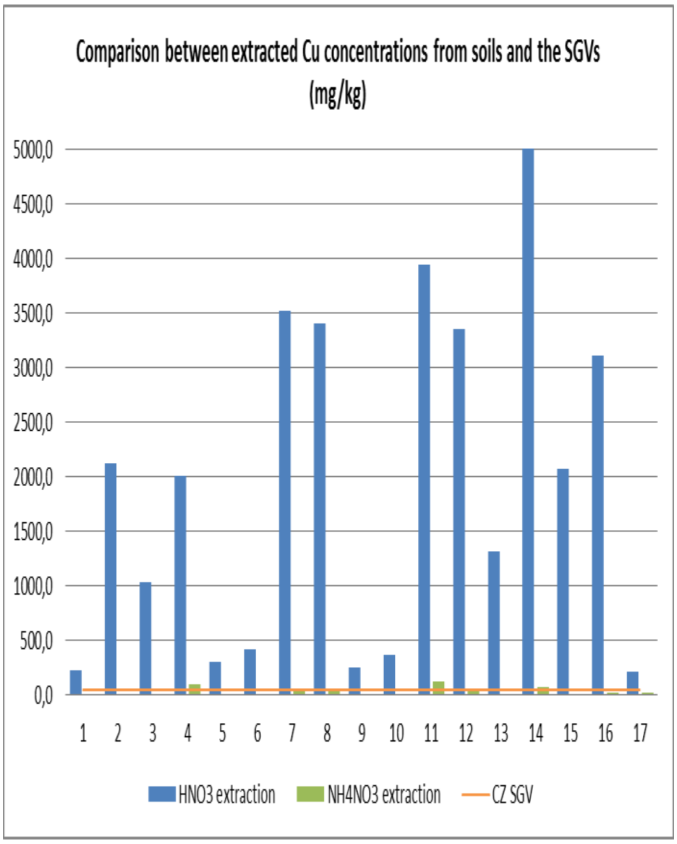
Sample	Horizon	Replicate	mg/kg
3b	B	1	71.1
		2	102.3
		mean	86.7
		St.dev	22.06



Sample		HNO_3 extraction	NH_4NO_3 extraction	Mn (%) bioavailable proportion to HNO_3
1a A	1	107.3	22.18	20.66
1a B	2	519.8	12.87	2.48
1b A	3	581.7	92.60	15.92
1b B	4	631.0	50.12	7.94
1c A	5	731.6	143.76	19.65
1c B	6	1494.5	403.69	27.01
2b A	7	1161.3	23.09	1.99
2b B	8	1173.7	17.23	1.47
2c A	9	190.9	84.08	44.04
2c B	10	186.5	87.36	46.83
3a A	11	815.9	14.50	1.78
3a B	12	809.4	12.65	1.56
3b A	13	994.4	102.93	10.35
3b B	14	846.6	17.04	2.01
3c A	15	730.9	53.95	7.38
3c B	16	779.6	22.15	2.84
3c C	17	525.8	16.53	3.14

Figure 7.3.4 Difference between total (HNO_3) and plant-available (NH_4NO_3) Mn in soils

No guideline value is published by either U.K or Czech authorities for contents of Mn in soils. However, Mn contents in soils can occur naturally as high as 1200 mg/kg (Brady and Weil 2004), more than twice the highest observed bioavailable value from the KH slags. The majority of samples contained very low bioavailable concentrations of Mn, (typically < 100mg/kg). At these levels, the Mn is likely to exhibit a favourable response by plants rather than negative symptoms. The higher bioavailable concentrations are shown to be in the organic rich and acidic soils, as Figure 7.2.5 illustrates by correlation.



Sample		HNO_3 extraction	NH_4NO_3 extraction	Cu (%) bioavailable proportion to HNO_3
1a A	1	227.6	5.0	2.20
1a B	2	2121.6	7.4	0.35
1b A	3	1038.5	3.8	0.37
1b B	4	2005.0	99.9	4.98
1c A	5	304.0	1.2	0.39
1c B	6	415.2	1.9	0.46
2b A	7	3527.6	45.1	1.28
2b B	8	3411.4	34.7	1.02
2c A	9	248.8	1.3	0.51
2c B	10	374.9	2.4	0.65
3a A	11	3943.4	123.8	3.14
3a B	12	3363.2	48.4	1.44
3b A	13	1320.3	6.3	0.47
3b B	14	5160.0	67.7	1.31
3c A	15	2077.5	6.9	0.33
3c B	16	3116.8	21.5	0.69
3c C	17	220.9	25.0	11.32

Figure 7.3.5 Difference between total (HNO_3) and plant-available (NH_4NO_3) Cu in soils

Figure 7.3.5 highlights that Cu is massively concentrated above the SGV in some of the soils which occur on the site of the Kutná Hora slags. Although the 2M HNO_3 extractable “total” contents suggest extreme contamination at many points, the bioavailable Cu is miniscule in comparison. These results are agreeable with the findings by Ahmed *et al.* (2000), who describe the initial dissolution of Cu from smelter slag which is quickly followed by its subsequent precipitation which renders the Cu unavailable. The higher concentrations for both the HNO_3 and NH_4NO_3 extractions occur in the mineral soils, counter to results that have been observed for other elements. This is confirmed in Figure 7.3.6 which shows that the bioavailable (as a proportion to “total”) is actually lower in the organic rich soils. The literature on the subject of metals retention in soils agrees that Cu (and Pb) are metals that are strongly fixed in the soil mainly due to intensive sorption on to OM (Zhou and Wong 2001). However, this does not explain then why the “total” contents are so low in the organic matter rich samples (5, 6, 9, 10) in Figure 7.3.5. It may be the case that Cu is so strongly bound to the OM that the 2M HNO_3 extraction is not strong enough to solubilise the Cu. Alternatively it is possible that because the organic matter rich horizons correlate to those with more acidic conditions, the Cu is mostly leached out of these soils, and that the Cu which is adsorbed onto the OM is too strongly bound for detection by a weak extracting agent.

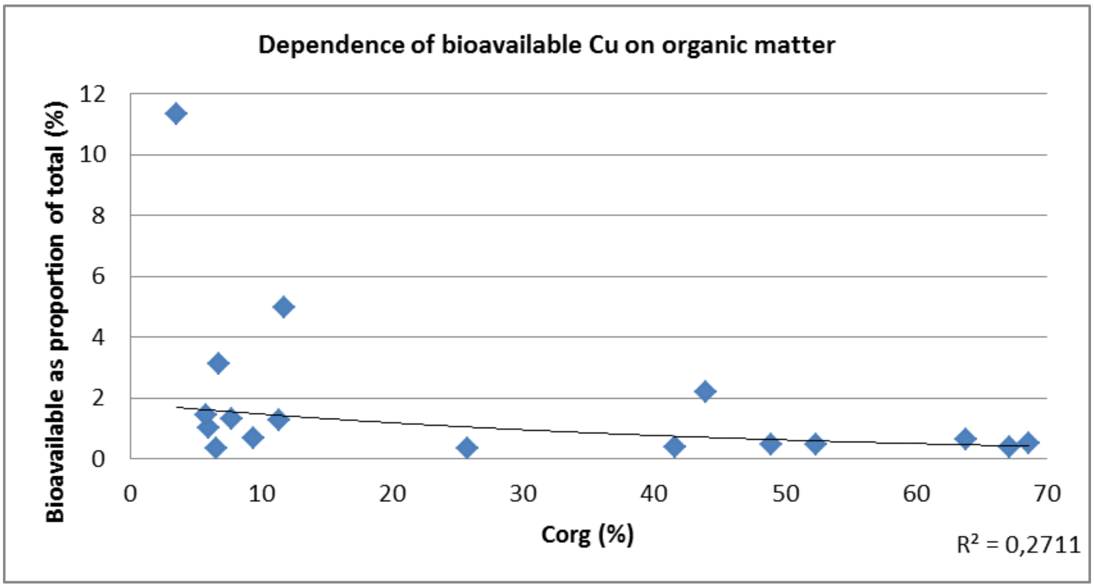
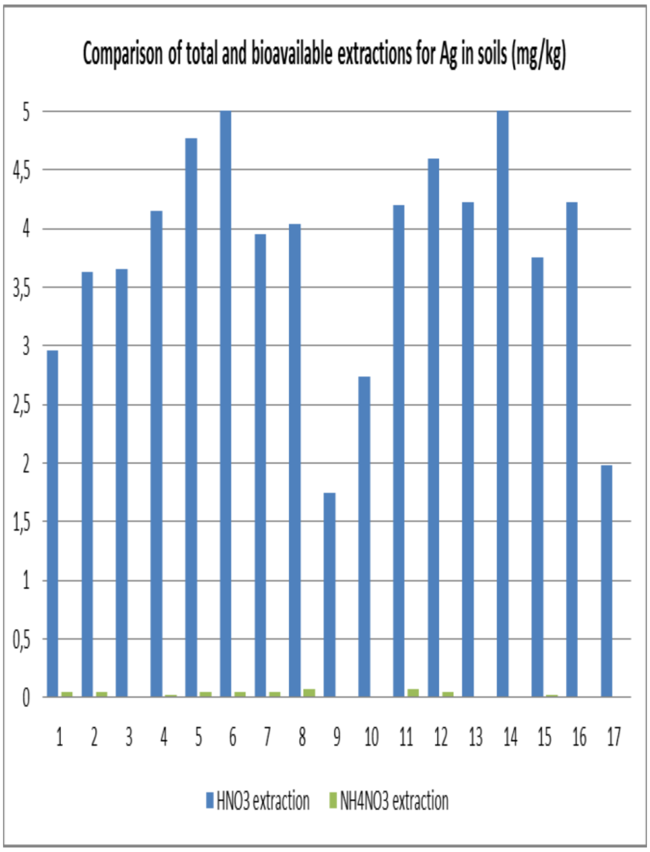


Figure 7.3.6 Relationship between Cu and organic matter (an opposite trend to those observed for other elements) (5% cv = 0.482)

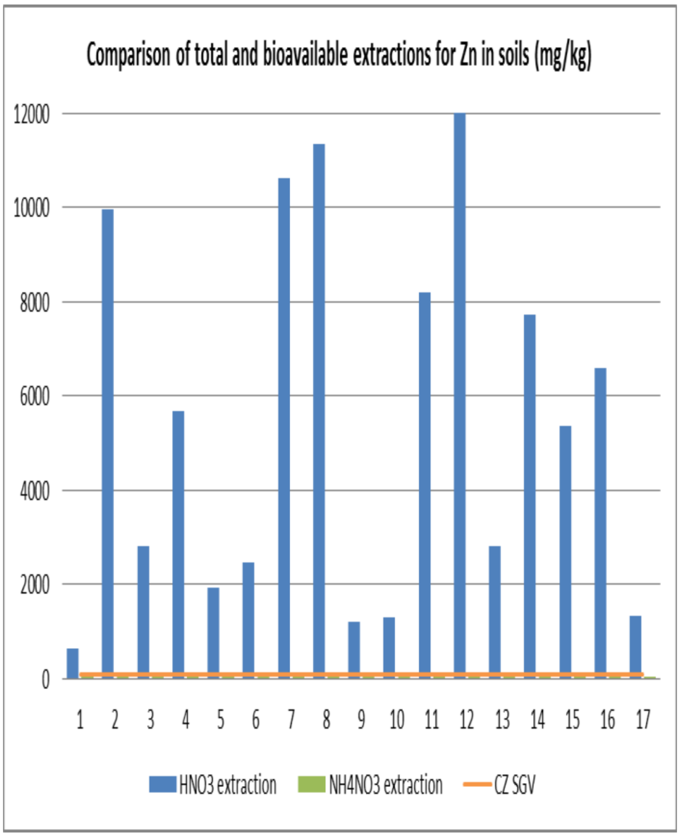
As the graph shows, there is a trend of higher availability of Cu where Corg is lower, although the trend is very weak. The highest value for bioavailable Cu as a proportion to "total" occurs at 3c C horizon (also the case for Pb and Cd). This is one of the more acidic soils observed on the study area (pH 5.15) and is heavily influenced by its proximity to the river. At the time of sampling the soil was wet, and it is likely to be saturated at periods throughout the year due to periodic rising of the water table during times of high river discharge. If sample 3c C were to be removed from the graph then it would appear that Cu is mostly unavailable at the presence of even small amounts of organic material.



Sample		HNO_3 extraction	NH_4NO_3 extraction	Ag (%) bioavailable proportion to HNO_3
1a A	1	2.97	0.05	1.67
1a B	2	3.63	0.046	1.27
1b A	3	3.66	0.014	0.37
1b B	4	4.16	0.024	0.57
1c A	5	4.77	0.041	0.85
1c B	6	5.19	0.042	0.81
2b A	7	3.95	0.049	1.23
2b B	8	4.04	0.065	1.61
2c A	9	1.75	0.012	0.69
2c B	10	2.74	0.008	0.27
3a A	11	4.21	0.07	1.66
3a B	12	4.6	0.045	0.98
3b A	13	4.23	ND	ND
3b B	14	5.04	0.011	0.22
3c A	15	3.75	0.025	0.66
3c B	16	4.22	0.01	0.24
3c C	17	1.98	0.004	0.19

Figure 7.3.7 Difference between total (HNO_3) and plant-available (NH_4NO_3) Ag in soils

The same pattern continues for Ag whereby the bioavailable proportion accounts for no more than 1.7% of the total in any sample.

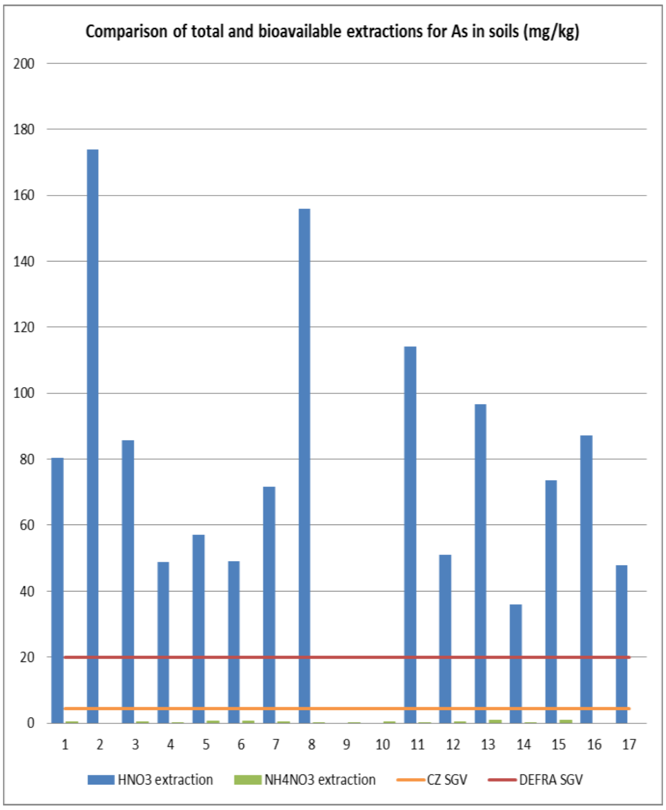


Sample		HNO_3 extraction	NH_4NO_3 extraction	Zn (%) bioavailable proportion to HNO_3
1a A	1	638.8	27.86	4.36
1a B	2	9949.5	100.50	1.01
1b A	3	2824.0	42.66	1.51
1b B	4	5695.4	78.60	1.38
1c A	5	1918.0	16.47	0.86
1c B	6	2453.3	54.28	2.21
2b A	7	10621.2	93.94	0.88
2b B	8	11359.0	91.51	0.81
2c A	9	1194.8	37.48	3.14
2c B	10	1311.0	45.22	3.45
3a A	11	8185.6	70.00	0.86
3a B	12	12135.2	85.74	0.71
3b A	13	2826.5	26.42	0.93
3b B	14	7735.1	33.20	0.43
3c A	15	5367.1	20.36	0.38
3c B	16	6591.8	26.88	0.41
3c C	17	1324.6	42.73	3.23

Figure 7.3.8 Difference between total (HNO_3) and plant-available (NH_4NO_3) Zn in soils

Available Zn is very low compared to HNO_3 extractable “total” contents, (< 2% on average). So small that Czech SGV limits virtually obscure the bioavailable values on the graph. This appears to be in disagreement with the literature that characterizes Zn as being highly bioavailable and mobile (Rosseli *et al.* 2003).

A consistent trend which is evident with all of the analyses is that the total contents can be very high and being characteristic of extremely contaminated soils, and yet the bioavailable fraction (represented by a NH_4NO_3 extract) remains very low (lower than SGVs in most cases). This is also true of the findings by Králová *et al.* (2010) where areas of vegetated land which are ‘contaminated’ by the KH slags were investigated for their impact on individual plant species.



Sample		HNO_3 extraction	NH_4NO_3 extraction	As (%) bioavailable proportion to HNO_3
1a A	1	80.31	0.49	0.61
1a B	2	173.83	ND	ND
1b A	3	85.63	0.34	0.40
1b B	4	48.80	0.02	0.05
1c A	5	56.97	0.59	1.04
1c B	6	49.16	0.70	1.42
2b A	7	71.68	0.40	0.55
2b B	8	155.81	0.10	0.06
2c A	9	ND	0.25	ND
2c B	10	ND	0.33	ND
3a A	11	114.17	0.08	0.07
3a B	12	51.02	0.29	0.56
3b A	13	96.66	0.81	0.84
3b B	14	35.92	0.17	0.47
3c A	15	73.61	0.81	1.11
3c B	16	87.09	ND	ND
3c C	17	47.95	ND	ND

Figure 7.3.9 Difference between total (HNO_3) and plant-available (NH_4NO_3) As in soils

Maximum HNO_3 extractable “total” values for As reach no more than 175 mg/kg. Compared to observations at different mining sites by other authors (see Table 3.3.1), the total observed As at KH slags is relatively low, although it is several fold higher than the delineated guideline values for residential and agricultural soils as set by DEFRA, and is 38 x higher than the Czech SGV. Bioavailable fractions are particularly small for As, (only 0.6% of the total on average and 1.42% the total as a maximum value which occurs in the organic rich riverbank soil horizon).

7.3.3 "Total" contents of risk elements in soils

This section examines the total contents in soils from the KH slags and the relationship that they exhibit between the soil parameters pH, organic matter content and clay content. Note that in the Figures (7.3.10, 7.3.11, 7.3.12), the scale has been fitted for Cd and Ag on the left and other analytes on the right axis. Note that there is no inclusion for As, this is because there was no correlation at all and due to the scale the data would have to be shown on a separate meaningless graph.

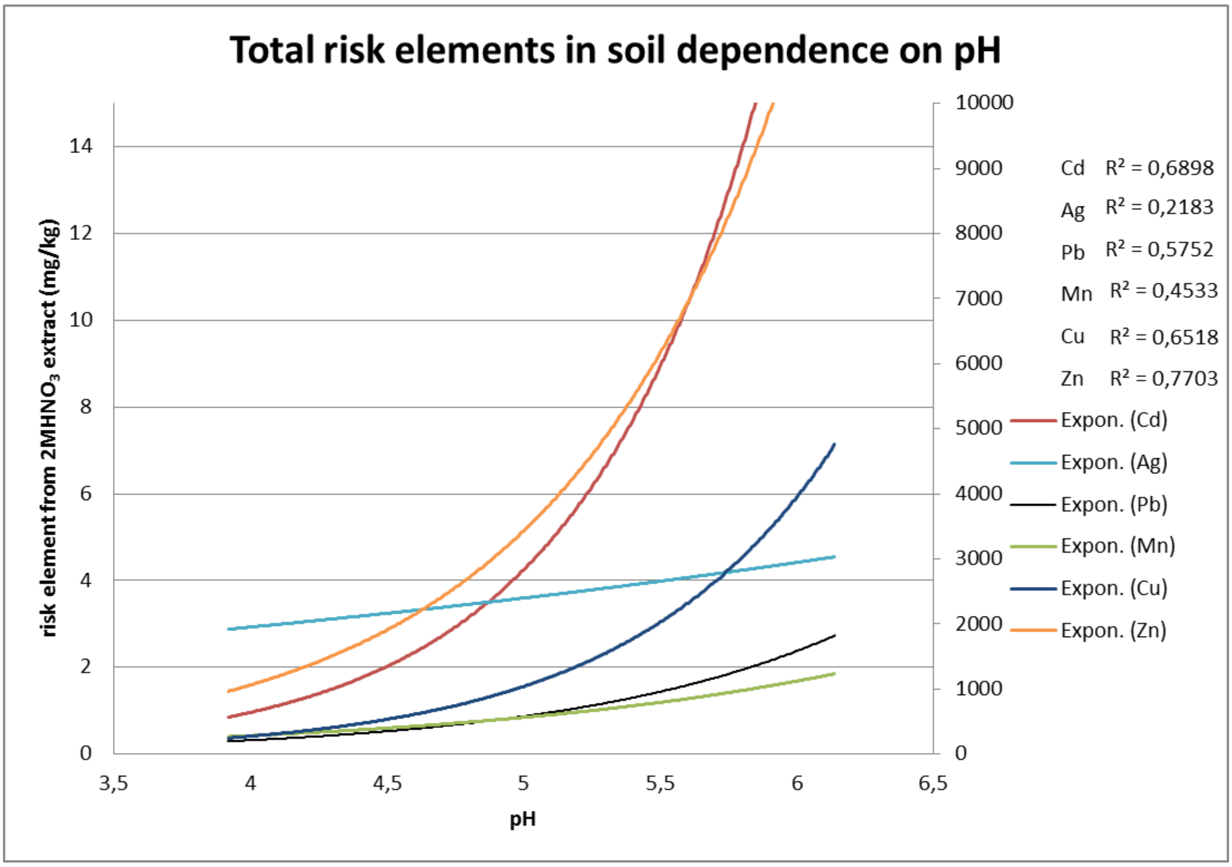


Figure 7.3.10 Correlation between total (2M HNO_3 extraction) risk elements in soil and soil pH (5% CV = 0.482), (Cd, Ag = left axis)

As Figure 7.3.10 clearly demonstrates, there is a significant trend (for all elements except for Ag, R = 0.467 compared to CV = 0.482) whereby an increase in soil pH results in greater retention of elements in soils, either by precipitation or by increased adsorbing of metals to soil negatively charged particle surfaces.

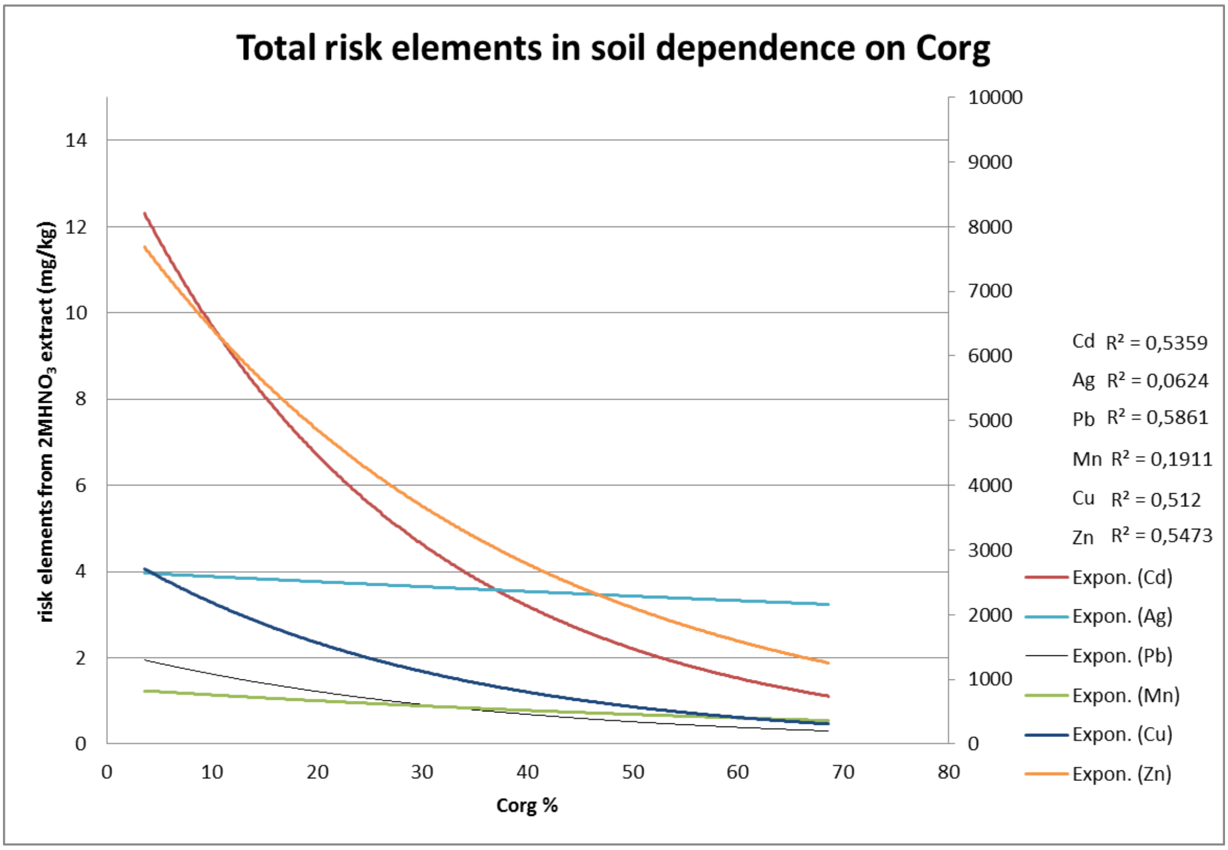


Figure 7.3.11 Correlation between total (2M HNO_3 extraction) risk elements in soil and soil Corg (5% CV = 0.482), (Cd, Ag = left axis)

With the exception of Mn and Ag, Figure 7.3.11 shows a significant uniform trend whereby an increased concentration of organic carbon in the soils results in a lower concentration of metals which are extractable by 2M HNO_3 (which is likely to be close to overall total contents).

The significance from this trend between Corg and metal contents is not determined by the presence of exchangeable surfaces (as this would show an opposite trend) but by the correlation between pH and soil organic matter. As it was shown by Figure 7.1.1 at the start of this chapter, an increase in Corg correlates very significantly to a decrease in pH or an increase in acidity. Therefore where Corg contents in soils increase, the pH is consequently lowered, and then metals are more readily solubilised in the soil solution and can be leached out of these organic rich horizons. The soils which have the high organic matter contents also occur at the areas of dense vegetation. It may be a consequence of root exudates from plants and trees which also cause the loss of metals from these soils. Another factor that should not be overlooked is the fact that the soil samples that contained the larger percentages of organic matter came from the river bank soils which are subjected to constant wetting from their proximity to the river. This will be a likely contributing factor to the trend that is shown in Figure 7.3.11 whereby those soils which are high in OM are also having the metals which they contain leached out by constant wetting and periodic flooding.

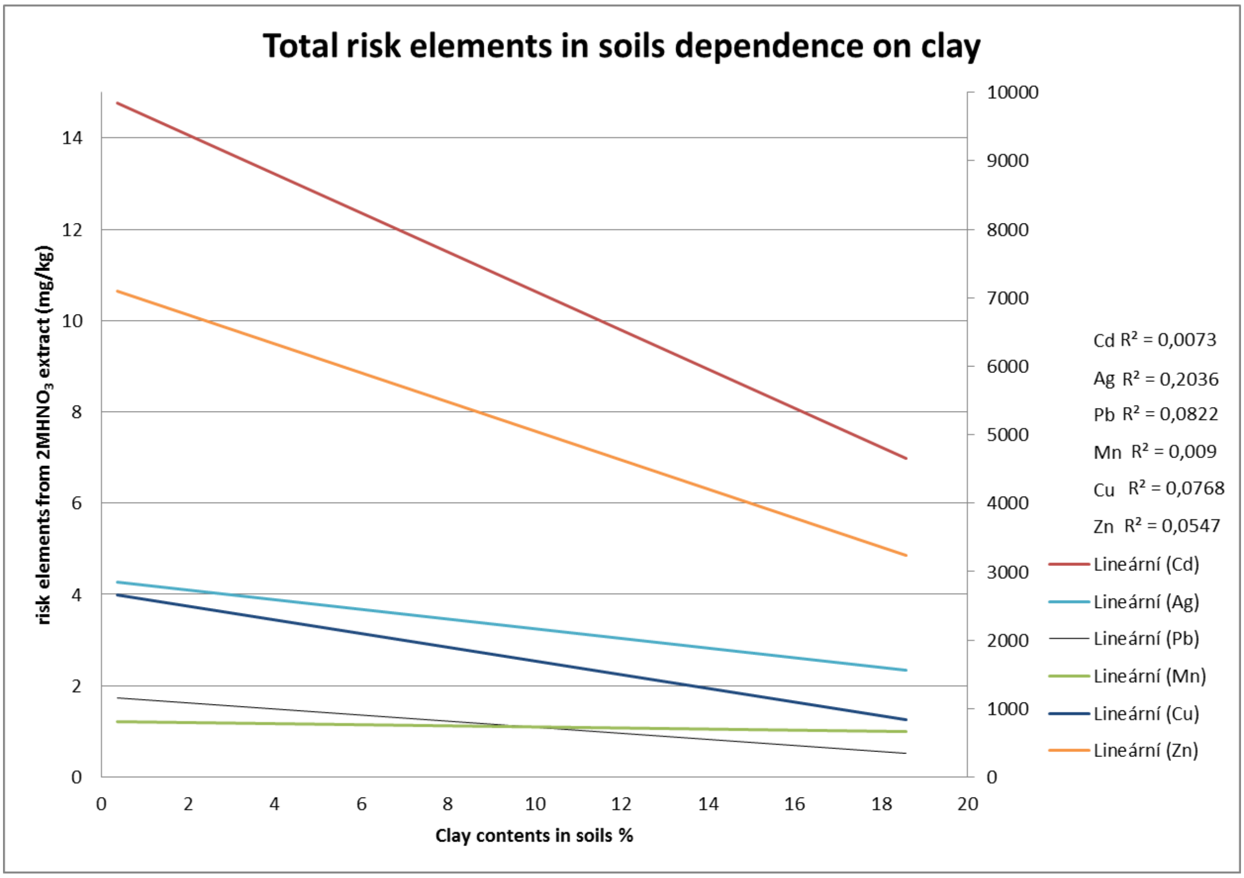


Figure 7.3.12 Correlation between total (2M HNO_3 extraction) risk elements in soil and soil clay (5% CV = 0.532), (Cd, Ag = left axis)

When analysing the correlation in Figure 7.3.12 the first detail to consider is the significance level for each trend line. The data are widely scattered without a good fit, and none of the R values exceed the critical P-value. A probable cause for the negative trend in the graph is due to the fact that the data point which contains the abnormally high clay percentage (20%) came from the sample which is situated underneath the river bank soils. As a consequence, the clay rich sample is also very acidic due to leaching from the organic rich horizons situated above. The range of values for clay is particularly small (range = < 5% for all soils except for 3c C) which makes it difficult to identify a significant trend.

It is very apparent that the 2M HNO_3 extractable REs at the KH slag deposit are not so directly dependent upon the cation exchange provided by the organic matter or clays alone, but REs extractability is dictated predominantly by pH.

Another way to present the retention of REs in the soils is to compare their concentrations to the concentrations of REs that are in the slags from which REs are weathered. This can be done by looking at the soil concentrations as a proportion of the slags concentrations and making them a percentage (RE in soils/RE in slags x 100). It then stands to reason, that if the value is greater than 100%, then the concentration of REs in the soil is higher than the concentration of REs in the slags from which they were weathered. If the value is greater than 100% then the soils must be retaining the REs to some extent. Table 7.3.1 illustrates clearly which soils are accumulating metals and which are leaching them by means of showing the ratio between metals concentration in soils and concentration in slags.

Table 7.3.1 Ratio between RE concentrations in soil and RE concentrations in slags from samples (green indicates an accumulating soil, red indicates a losing soil)

	Pb			Cd			Mn			Cu		
	Soil	Slag	%	Soil	Slag	%	Soil	Slag	%	Soil	Slag	%
1a B	2,2	1	217,5	1	1,1	87,5	1,7	1	174,9	1,2	1	116,5
1b A	1,3	1	131,2	1,3	1	129,4	1,4	1	137,4	1	1,2	83,1
1b B	1,5	1	152,9	1	1,7	59,3	1,6	1	163	1,1	1	112,9
1c A	1	1,4	71,8	1	3,1	32	2,3	1	227,2	1	2,5	39,2
1c B	1,2	1	118,6	1	1,7	57,9	4,0	1	402,8	1	1,7	59
2b A	2,2	1	223,7	1,6	1	161,7	1,6	1	163	1,6	1	164,8
2b B	3,0	1	295,2	2,3	1	231,4	1,2	1	124,7	1,3	1	125,7
2c B	1	1,7	57,2	1	3,5	28,9	1	2,4	42,3	1	3,0	33,9
3a A	2,5	1	251	2,2	1	219	1	1,2	86,7	1,4	1	135,3
3a B	2,5	1	253,1	2,4	1	242,1	1	1,1	94,3	1,9	1	190
3b A	1,7	1	170,6	1,8	1,	177,7	1,5	1	146,5	1,2	1	122,7
3b B	4,7	1	466,1	12,3	1	1231,5	1,1	1	109,8	2,8	1	281,2
3c A	1,7	1	173,3	1	1,1	87,6	1	1	104,3	1,1	1	110,7
3c B	2,5	1	246,7	1,5	1	151,4	1,1	1	109	2,0	1	197,2
3c C	1,3	1	132,2	1	1,2	82,7	1	1,1	87,4	1	1,4	72

	Ag			Zn			As		
	Soil	Slag	%	Soil	Slag	%	Soil	Slag	%
1a B	1	1,1	89,7	1	1,4	73,3	3,1	1	308,7
1b A	1	1	99,9	1	3,0	33,5	3,1	1	310,8
1b B	1	1,5	64,9	1	2,0	50,5	2,1	1	213,3
1c A	1,5	1	149,1	1	5,7	17,5	2,2	1	222,8
1c B	1,2	1	122	1	4,3	23,1	2,2	1	218,2
2b A	1	1	97,7	1	1,4	72,2	3,4	1	344
2b B	1	1,3	79,6	1	1,7	59,2	8,6	1	861,8
2c B	1	2,0	50,3	1	9,4	10,6	ND	ND	ND
3a A	1	1,2	82	1	1,6	63,8	6,6	1	664,4
3a B	1	1,2	86,2	1	1,4	72,7	6,7	1	667,6
3b A	1	1,2	83,4	1	3,3	30	3,5	1	349,2
3b B	1,1	1	109,8	1	1,7	59,7	2,1	1	210,4
3c A	1	1,2	83,4	1	1,9	35,6	8,2	1	821,6
3c B	1,1	1	111,1	1	2,1	46,6	4,2	1	416,2
3c C	1	1,2	86,4	1	3,3	30,1	2,4	1	243

On quick visual inspection it is clear that Pb, Mn, Cu and As are accumulating in the soils into which the slags are weathering, whereas Ag and Zn are showing definite lower concentrations in the soils compared to the slags, suggesting that they are being readily leached out of the soils.

By presenting the data in this way, it is possible to compare different soil characteristics in a statistical Chi-Square test. This will statistically prove the hypothesis that there is or is not any dependence between soils which accumulate metals and the chosen soil characteristic.

For the characteristic of organic matter, values from samples were split into high and low Corg content, (less than or above 20% of Corg respectively), and tested in a contingency table against samples that accumulate or leach metals respective to the slag concentrations as shown in Table 7.3.1.

H_0 = There is no association between soils which accumulate metals and organic matter content in soil

H_1 = There is an association between soils which accumulate metals and organic matter content in soil

Table 7.3.2 Chi-square test for risk elements (from Table 7.3.1) to test for any association between soils that accumulate metals and soil organic carbon content, method from Taylor (2007)

	Accumulating	Losing	total
organic soil	14(18)	16(12)	30
mineral soil	28(24)	12(16)	40
total	42	28	70
Observed	Expected	O - E^2 /E	
14	18	0.888889	
16	12	1.333333	
28	24	0.666667	
12	16	1	
	Sum	3.888889	
X^2 CV	3.84		
test statistic	3.89		

Test statistic is greater than the critical value (CV) so H_0 is rejected

By comparison of the X^2 critical value with the ‘test statistic’ it is clear that although the null hypothesis is rejected, the significance is very marginal.

For pH the values were categorized between 4 – 5.49 and greater than 5.5. It is practical to keep two more distinct categories for the purpose of the statistical test.

H_0 = There is no association between soils that accumulate metals and soil pH
H_1 = There is an association between soils that accumulate metals and soil pH

Table 7.3.3 Chi square test for risk elements (from Table 7.3.1) to test for any association between soils that accumulate metals and soil pH, method from Taylor (2007)

	Accumulating	Losing	total
pH 4 – 5.49	19(24)	21(16)	40
pH > 5.5	26(21)	9(14)	35
total	45	30	75
Observed	Expected	O - E^2 /E	
19	24	1.041667	
21	16	1.5625	
26	21	1.190476	
9	14	1.785714	
	Sum	5.580357	
X^2 CV	3.841		
test statistic	5.58		

Test statistic is greater than the critical value so H_0 is rejected

Due to the greater difference between X^2 critical value and test statistic for pH, compared to the very close X^2 critical value and test statistic values for organic carbon content, it suggests that pH is a stronger factor controlling the accumulation of REs in soils.

It has been determined that there is dependence between soils that accumulate metals and the soil characteristics (pH, Corg). The following graphs illustrate the trend.

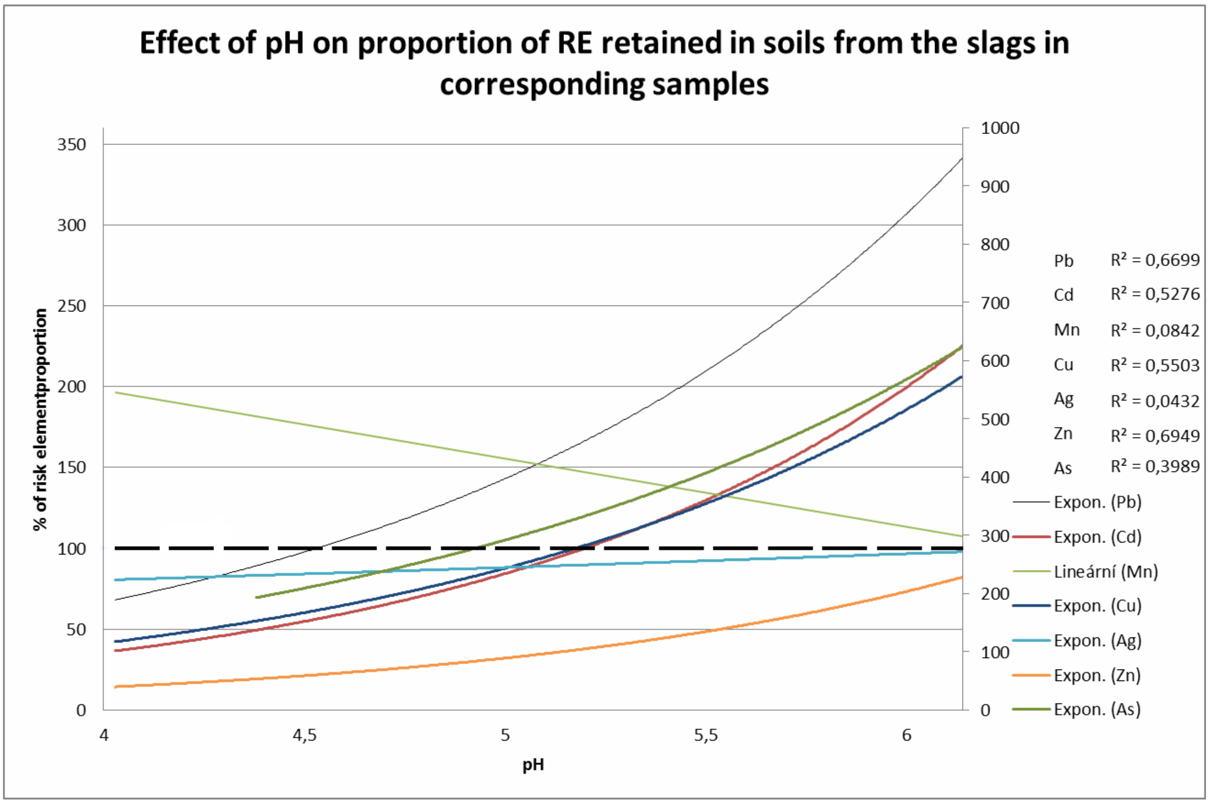


Figure 7.3.12 RE in soils proportional to RE in slags, correlated with pH (5% CV = 0.514), (As = right axis)

What is seen in Figure 7.3.12 is the same trend as with Figure 7.3.9 whereby REs are accumulating in the soils with higher pH with the exception of Mn, which now shows a decreasing proportionality with increasing pH. It also has very low significance (Mn R = 0.29) and poor correlation so the trend cannot be accepted. Significance for correlation of each element occur in the following decreasing order (Pb, Zn > Cu, Cd > As >> Mn, Ag).

The dashed line indicates the transition value (at a slag:soil ratio 1:1 or 100%) whereby any value above indicates accumulation in the soil and any value below indicates losses from the soil. The following graph shows the same data as Figure 7.3.12 but only for data with strong statistically significant correlation.

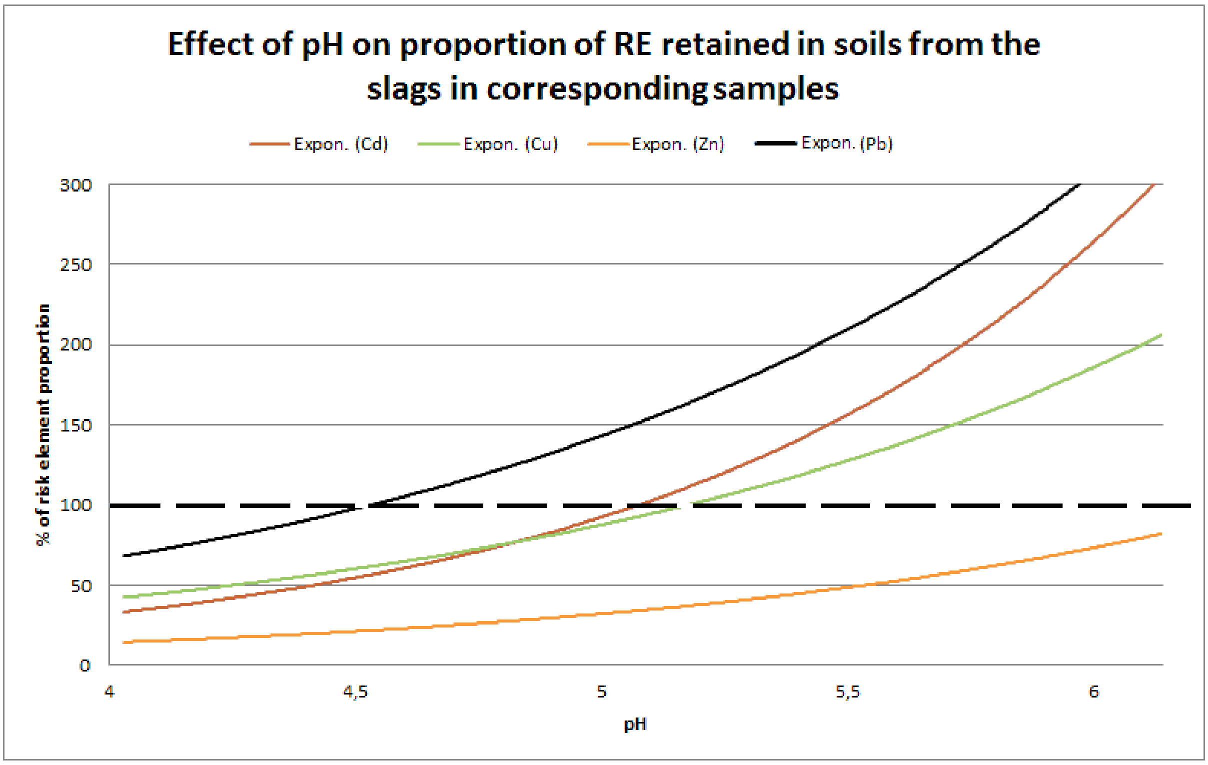


Figure 7.3.13 Pb, Cd, Cu and Zn in soils proportional to their concentrations in slags, correlated with pH

From Figure 7.3.13 conclusions can be made that, irrespective to other soil properties, Pb starts to accumulate in soil above pH of 4.5. Cd and Cu start to accumulate in soils above approximately pH 5.1 - 5.2, and Zn appears to be readily leached from soils up to approximately pH 7. This is not entirely true however, as the results actually revealed extremely high total contents of Zn in soils (particularly in the mineral soils) see Figure 7.3.8. The reason for this is that the amount of Zn that was solubilised in the 2M HNO_3 from the slag samples was so high (as high as 10:1 slag:soil) that the result will always be shown as <100% (1:1), despite the fact that the Zn concentrations in soil are excessive. This does raise some questions on the validity of the test, although the trends are very strong and significant for most of the elements analysed, and the chi-square is significant. What it suggests is that firstly, not all of the elements are detached at the same rate or so easily from the minerals in slag in which they were contained, and secondly, it is possible that the CEC of the soils with the higher pH and lower Corg content are fully saturated with Zn and therefore cannot match the concentrations that are contained within the slags. The higher range of pH is also likely to be causing precipitation of Zn which may not be fully detectable by a 2M HNO_3 extract. So, even though the soils accumulate HNO_3 extractable Zn within the upper pH range, it is not displayed on the graph as exceeding 100% (1:1 ratio) (Figure 7.3.13) because the cation exchange capacity of soil could be exceeded or insoluble precipitates have formed, and yet the slag sample still contains the higher concentrations. Rather than referring to the metals as ‘accumulating’ or ‘losing’, it would be more accurate to say that they are retained in soils to a ‘greater’ or ‘lesser’ extent respective of the slag concentrations from which they are weathered. Another criticism could be that the HNO_3 extract is not a true total extract and that it is not able to dissolve all of the compounds in the strong minerals. This would result in a ratio which shows higher soil concentrations compared to slag concentrations. It is not the case however, as many of the analysed samples show both higher and lower slag:soil ratios and the statistics show a great deal of significance, too much to be an accidental good fitting of data. It was also shown in an experiment by Borůvka and Drábek (2000) that aqua regia (extract representing a powerful pseudo-total extract) forms a very significant linear correlation with 2M HNO_3 extract on a range of heavy metal polluted soils (Cd R = 0.991; Pb R = 0.982; Zn R = 0.977).

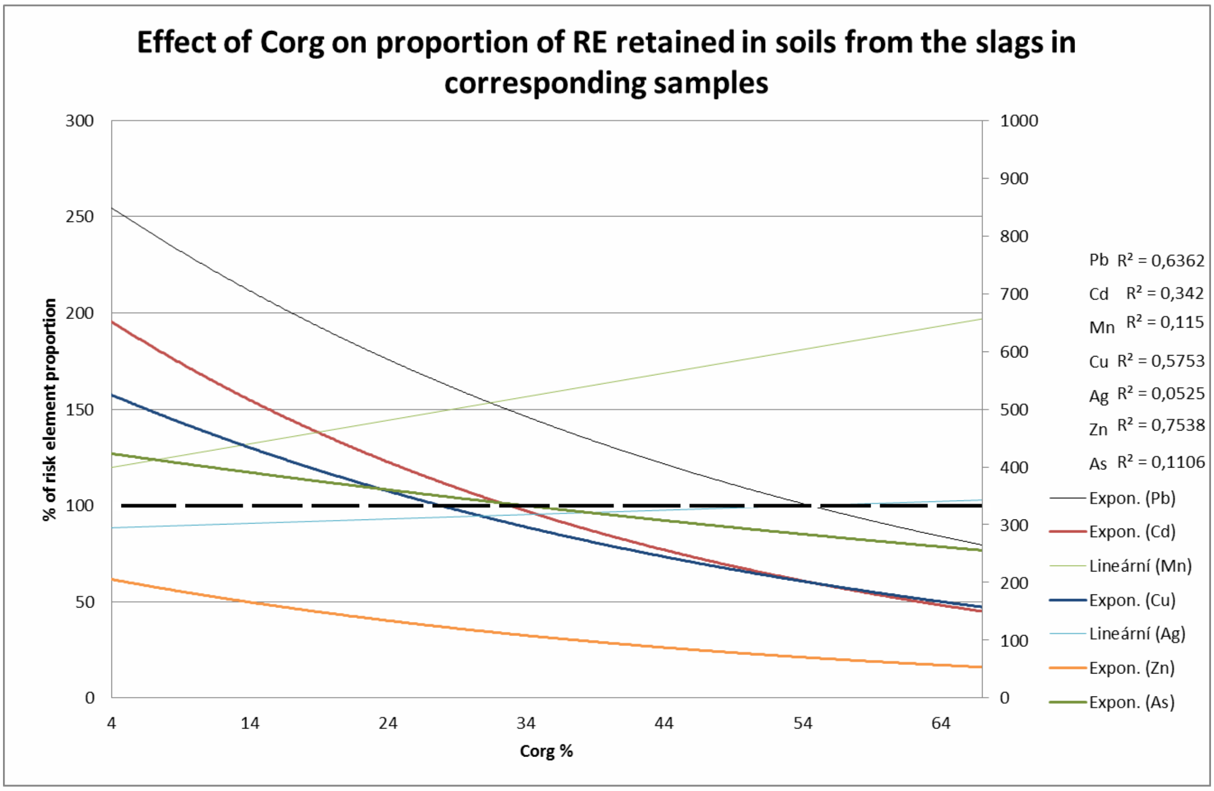


Figure 7.3.14 RE in soils proportional to RE in slags, correlated with organic matter (5% CV = 0.514), (As = right axis)

The graph shows that REs are accumulating in the soils that contain the lowest amount of organic matter (probably because higher OM correlates with acidic soil). Again, Mn shows an opposite (but insignificant) trend. The low R value for Mn, As and Ag indicates that correlation for these data cannot be reliable for interpretation. Reasons for the non-uniform results may be attributed to the heterogeneous occurrence of Mn and Ag within the slags, or due to the fact that Mn is naturally occurring in most soils.

7.3.4 Risk elements in the Vrchlice River sediments

The observed RE concentrations have been plotted onto 3 separate graphs to keep the scales in perspective. The following figures (7.3.15; 7.3.16; 7.3.17) show the sediment RE concentrations at the 3 different locations 1s, 3s and lagoon (as shown on the map in Figure 5.1.1).

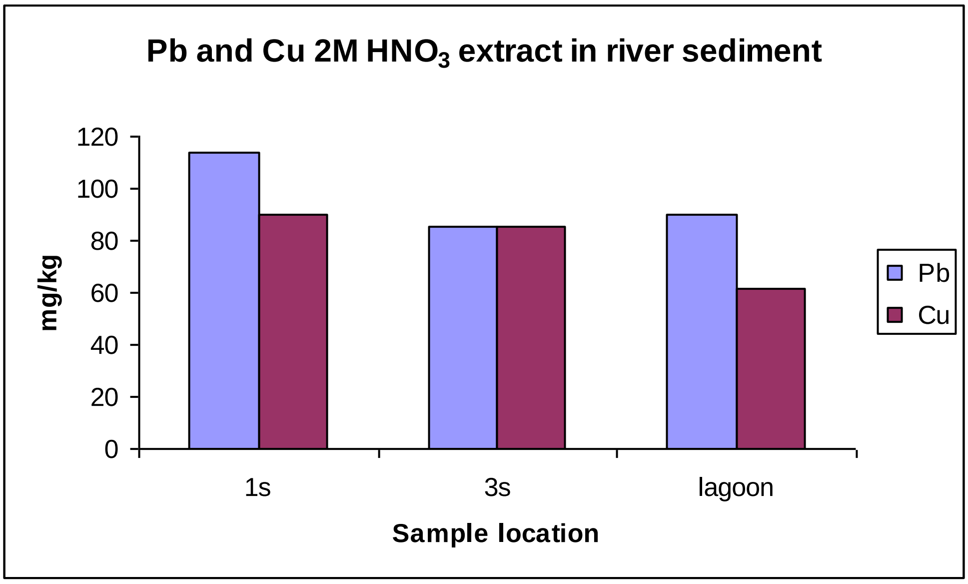


Figure 7.3.15 2M HNO_3 extractions for Cu and Pb in river sediments

U.K and Czech SGVs are 450 and 50 mg/kg respectively for Pb and the Czech SGV for Cu is 50 mg/kg. None of the values for Pb reach the limit set by U.K SGVs yet all of the samples exceed the Czech SGV for sandy soils. Cu also exceeds the SGV in every case although not excessively.

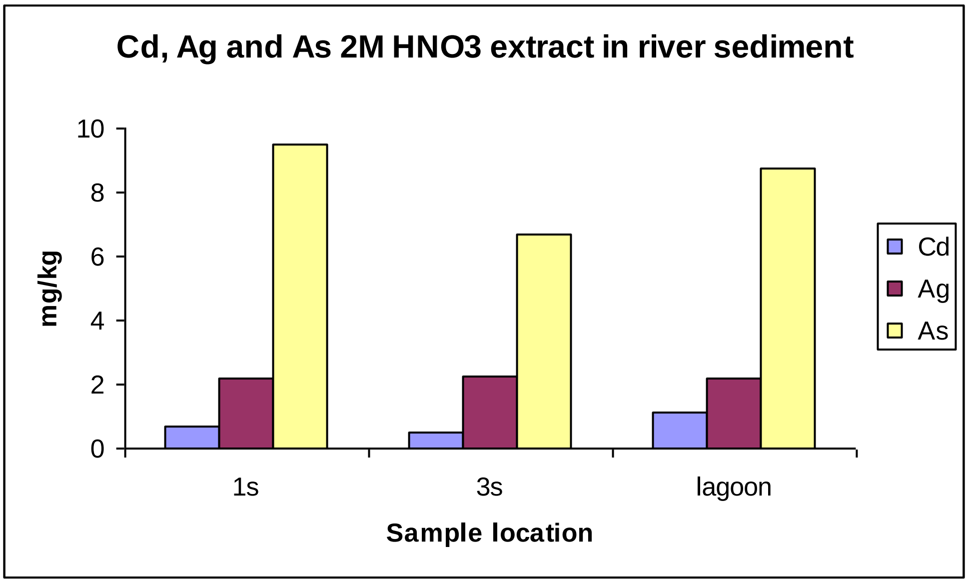


Figure 7.3.16 2M HNO_3 extractions for Cd, Ag and As in river sediments

SGVs for Cd are 8 and 1 mg/kg for U.K and Czech SGVs respectively, and are not exceeded by the 2M HNO_3 extract in sediment samples. SGVs for As are 20 and 4.5 mg/kg by U.K and Czech authorities respectively. These As concentrations in sediment are approximately double the allowable SGV for Czech Republic, but again, do not reach the U.K guideline value.

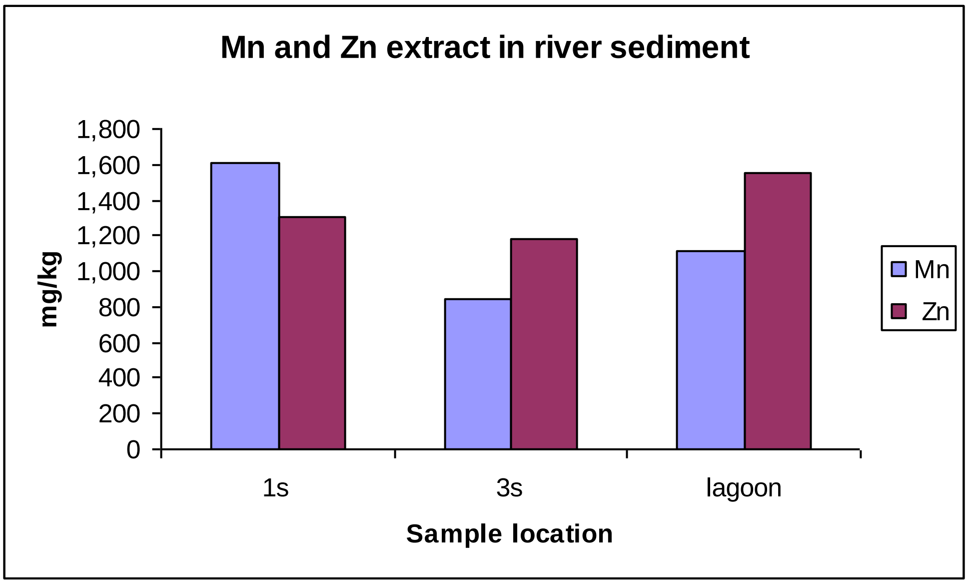


Figure 7.3.17 2M HNO_3 extractions for Mn and Zn in river sediments

Mn is very concentrated in all of the sampled sediments. In fact, sample 1s represents the highest value for Mn found in the entire study. These findings are consistent with the behaviour of Mn as this element is known for having precipitating and settling properties in aerobic waters (EPA 2004). The excessive RE concentrations in the sediments is a sound indication that REs are entering the Vrchlice River. Czech authorities set the SGV for Zn at 100 mg/kg. As the figure shows, this value is far exceeded in every sample.

The REs appear to be mostly concentrated in the 1s sample, contrary to what was expected, as the direction of flow is from 1s to 3s. However, the reality of the situation is that these slag deposits are scattered all along this stretch of the river so identifying a pattern in their distribution is unlikely.

7.4 Leaching experiment

7.4.1 Change in solvents risk element concentration over one month of leaching experiment

Citric acid (pH 3.2) showed the highest amount of Pb to be extracted of all the solutions, although the actual amount is very low <1.5 mg/kg. There is a trend of decreasing Pb with increasing time with the exception of sample 3a. The rainwater simulation solution (RSS) with pH 4.6 appears to extract some amount of Pb at the start of the experiment, but then the concentration decreases after a week followed by an increase again at the end of the experiment. However, at such low concentrations it is difficult to draw on any conclusions with confidence other than that all of these solutions did not extract any significant amount of Pb in this experiment.

No control samples (except for citric acid control in 2a) were included as the results were below determination limit.

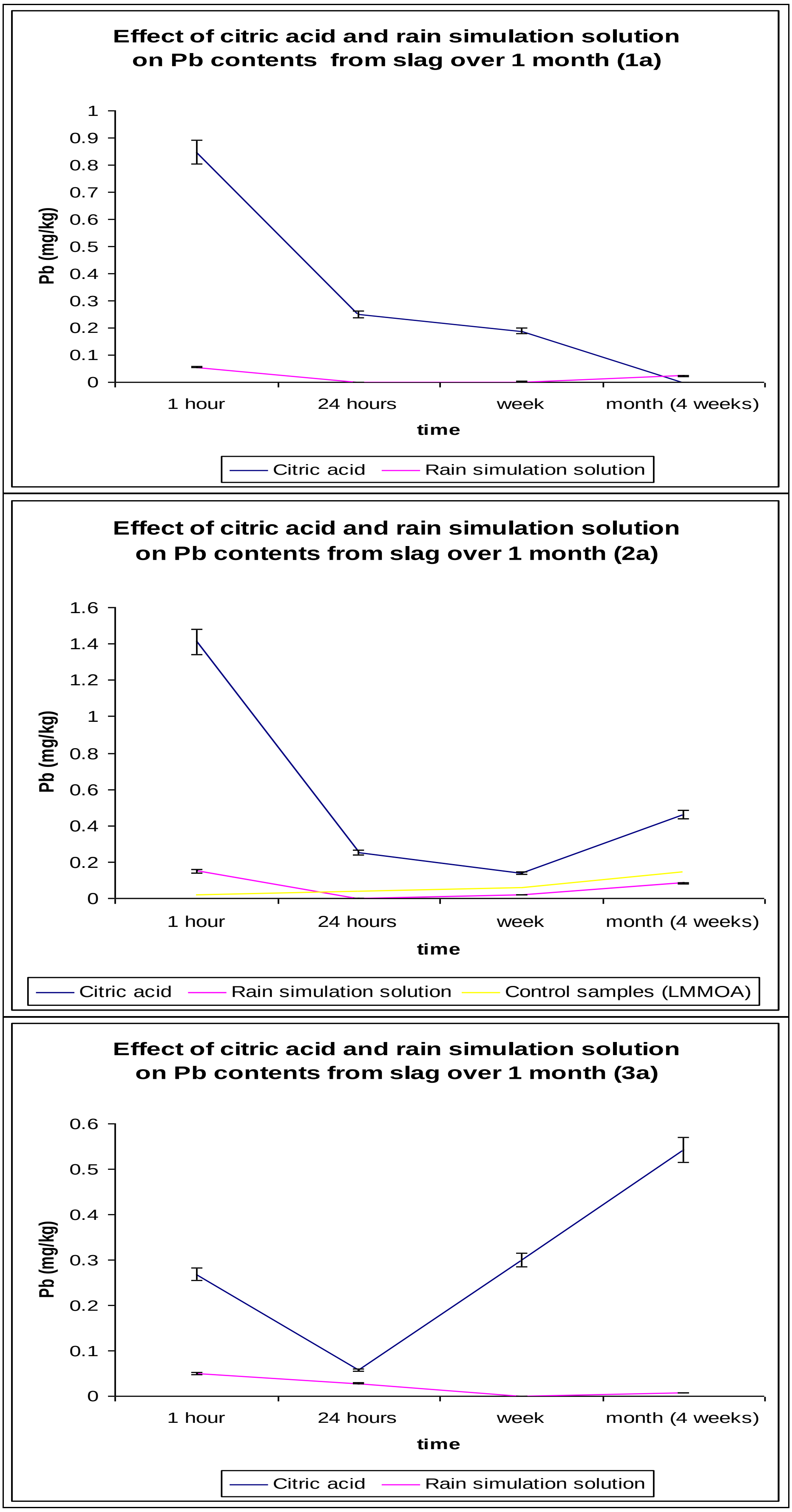


Figure 7.4.1 Change in Pb concentration in solvents during leaching experiment

Figure 7.4.2 shows precise results with a mostly uniform trend for all three sample locations. The citric acid solution appears to extract some quantity of Zn initially and increasingly over the first hour but then after 24 hours the trend is of a static or decreasing nature.

The RSS is able to increasingly dissolve Zn for the duration of the experiment. The RSS with pH slightly lower than that of the control samples does not appear to be any more effective in its extraction of Zn with the exception of the 3a samples. Due to the fact that the trend is increasing exponentially, the possibility that further extraction may be achieved after a greater amount of time cannot be ruled out.

For all of the samples, RSS and control solutions are effective solvents in the dissolution of Zn from ground slag samples. Citric acid is effective only up to 24 hours. The extractability of these solvents is only a fraction of the extracting power of the 2M HNO_3 extract (no more than 2%)

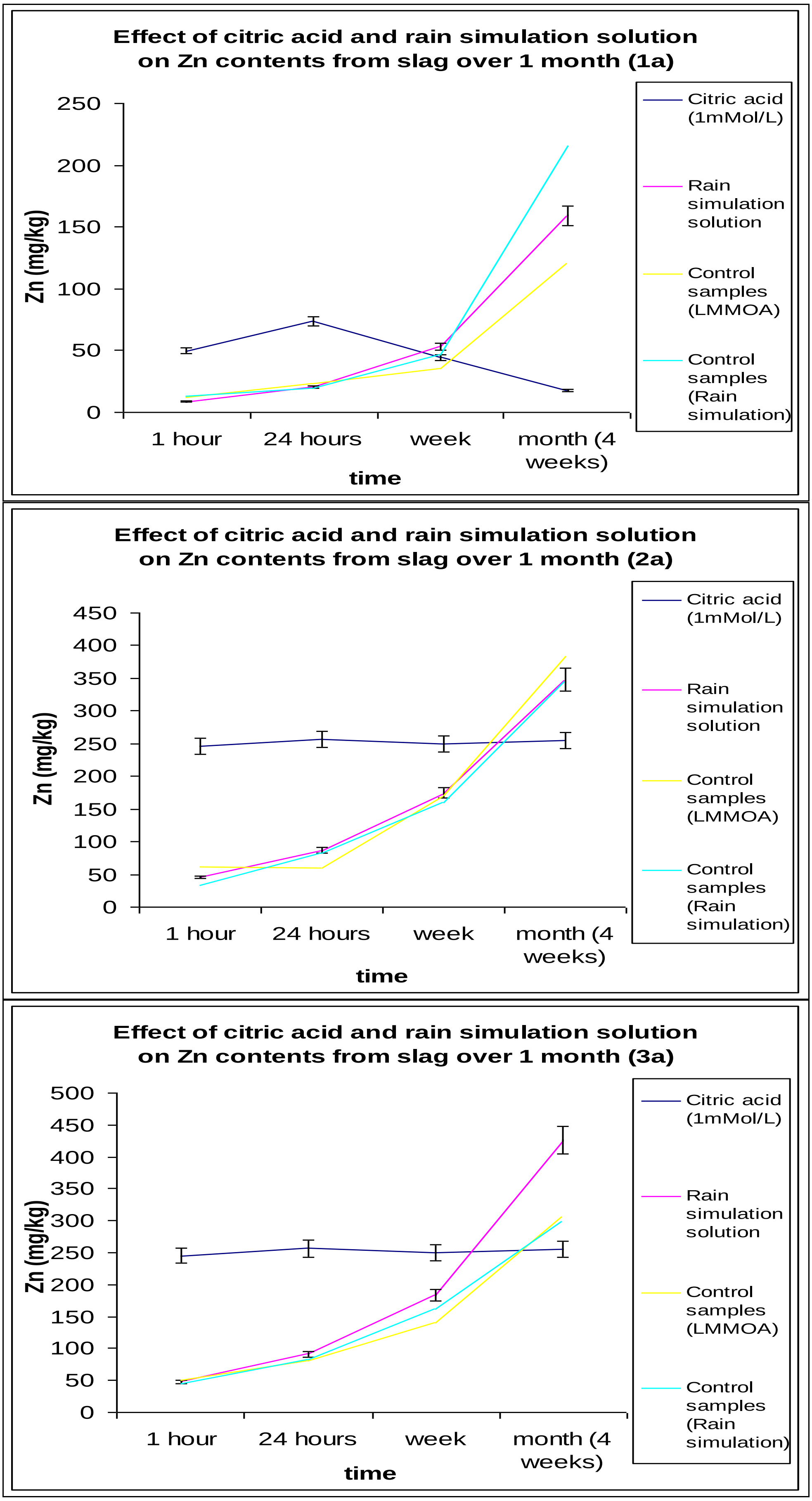


Figure 7.4.2 Change in Zn concentrations in solvents during leaching experiment

The citric acid solution is effective in dissolving a small quantity of Cd, and much like the trend for Zn, the initial extraction is followed by either a decrease or a plateau in the trend (see Figure 7.4.4). The inability of the citric acid solution to maintain an increasing trend is attributable to either the degradation of the acid itself as the experiment progresses or due to the buffering effect that the slags produce, or a combination of both factors (discussed later in this chapter).

The RSS also proves to be effective in the dissolution of Cd from slag as the concentrations in solution continually increase for the duration of the experiment. There appears to be little difference in the extraction strength between RSS and the control solution as Figure 7.4.3 illustrates (R = 0.967).

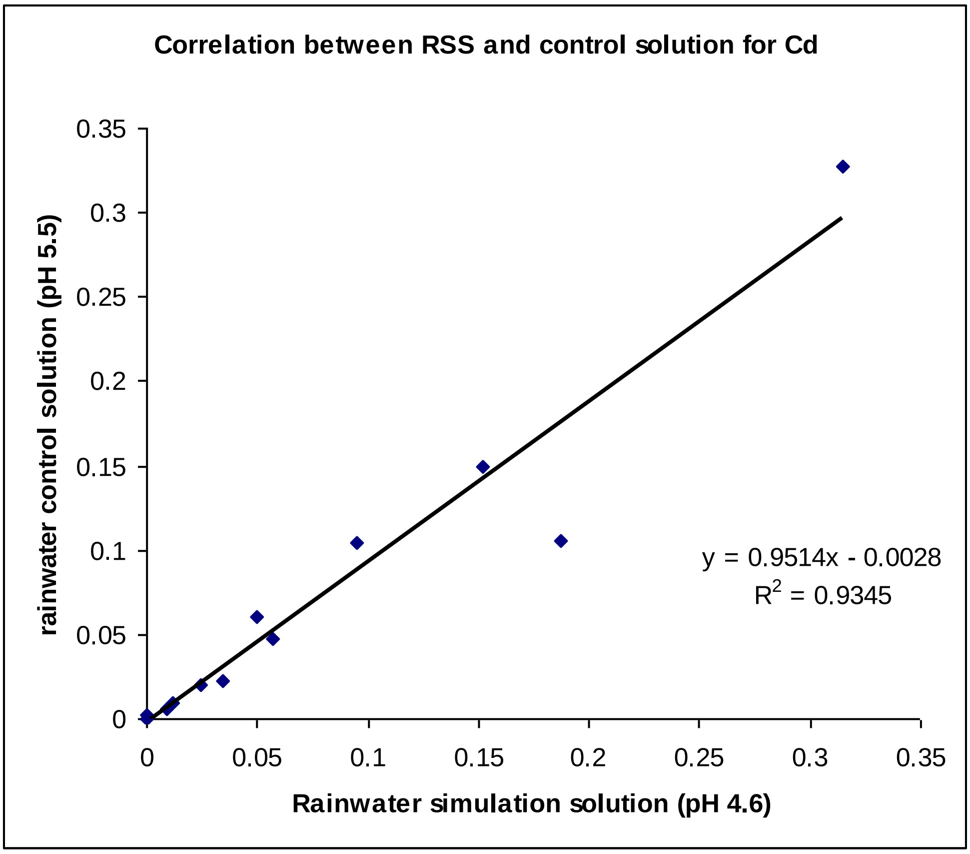


Figure 7.4.3 RSS and rainwater control solution correlation

The correlation between RSS and control solution was equally significant for Zn (R = 0.955). This is in alignment with the findings by Piatak *et al.* (2004), whereby Zn extractable from smelter slag by a solvent designed to represent precipitation of the Eastern United States (pH 4.2) has linear correlation with deionised water.

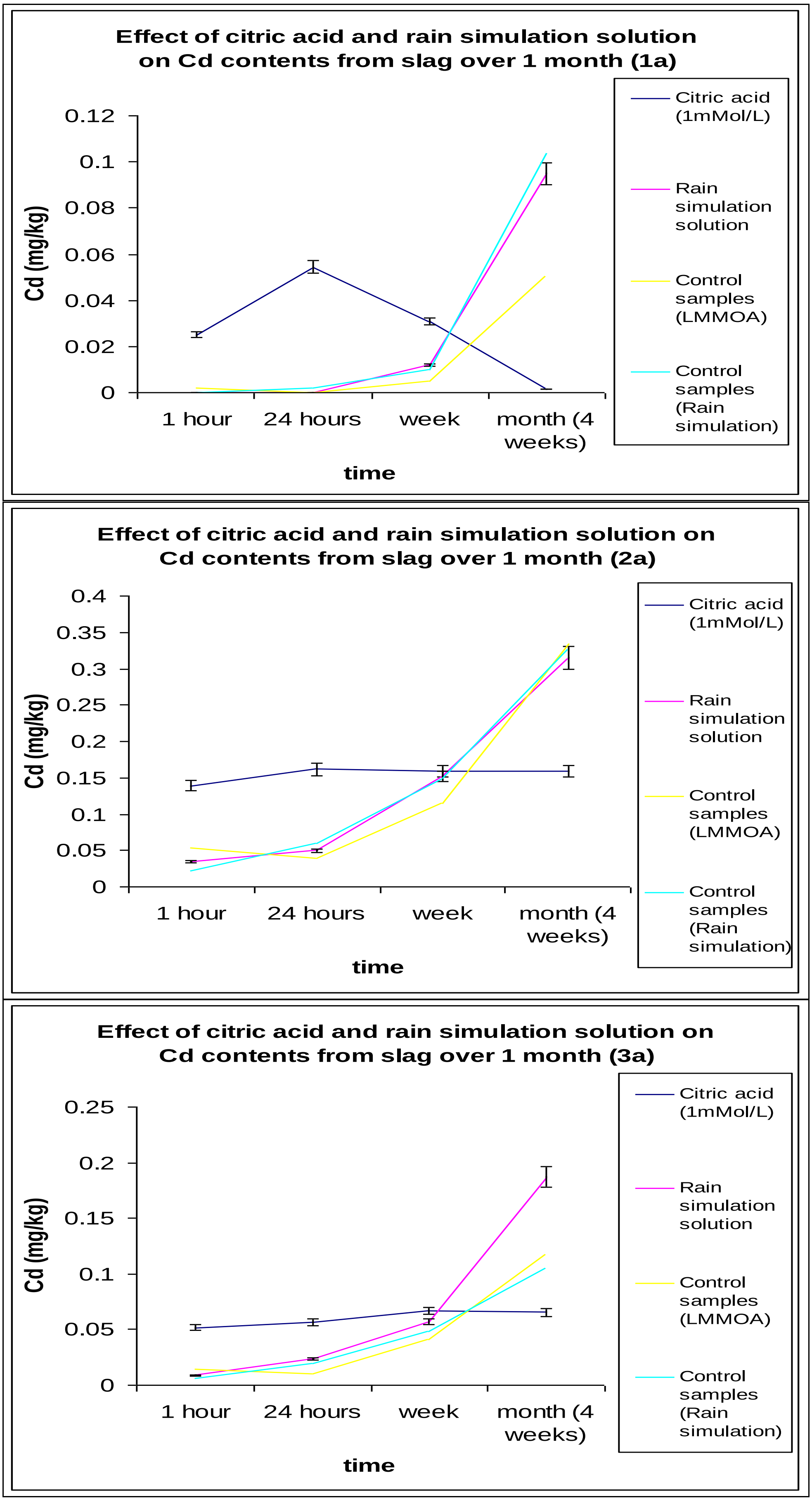


Figure 7.4.4 Change in Cd concentration in solvents during leaching experiment

Table 7.4.1 2M HNO_3 extractable risk element concentrations in slag samples 1a, 2a and 3a

Sample location	Horizon/ soil layer	Fraction	mg/kg **Pb**	mg/kg **Zn**	mg/kg **Cd**
1a	surface	slag	684.4	21135.3	10.9
2a	surface	slag	848.4	19540.5	10.66
3a	surface	slag	320.2	24389.5	8.97

By comparing results from the leaching experiment with Table 7.4.1, it is clear that even after one month, none of the solvents (citric acid, rain simulation and controls) were comparable to the extracting power of 2M HNO_3 on slag samples. However, Due to the permeability of the slag (Table 6.3.1), any dissolved elements are likely to be transported through the slag during rain events and may enter the river via seepage as well as surface runoff..

Ag and Cu have been omitted from the discussion as too many values were below determination limit, and due to the low values observed for Mn, this element is listed in the chapter as a nutrient as opposed to a contaminant.

7.4.2 Change in solvents nutrient element concentration over one month of leaching experiment

The commonly observed trend continues for Mn whereby the citric acid solution is able to extract Mn initially but cannot maintain this increase and maximum extraction peaks sometime between 1 and 24 hours. Concentrations of Mn in solution then decreased after a week. Concentrations of Mn extracted by RSS and control solutions are low initially but an exponential increase was observed in most cases as the experiment progressed.

Despite the nature of the trend, after the one month duration of the experiment, citric acid solution had extracted higher amounts of Mn than RSS.

Table 7.4.2 extractable nutrient element concentrations in slag samples 1a, 2a and 3a

Sample location	Horizon/soil layer	Fraction	mg/kg **Mn**	mg/kg **Ca**	mg/kg **Mg**	mg/kg **K**	mg/kg **Na**
1a	surface	slag	742.2	2335.1	1313.1	677.8	357.3
2a	surface	slag	554.1	3124.9	1026.3	1067.4	342.8
3a	surface	slag	897.4	3850.1	1476.2	769.5	304.1

Mn extracted by the tested solvents in the leaching experiment is very low comparable to the 2M HNO_3 extract.

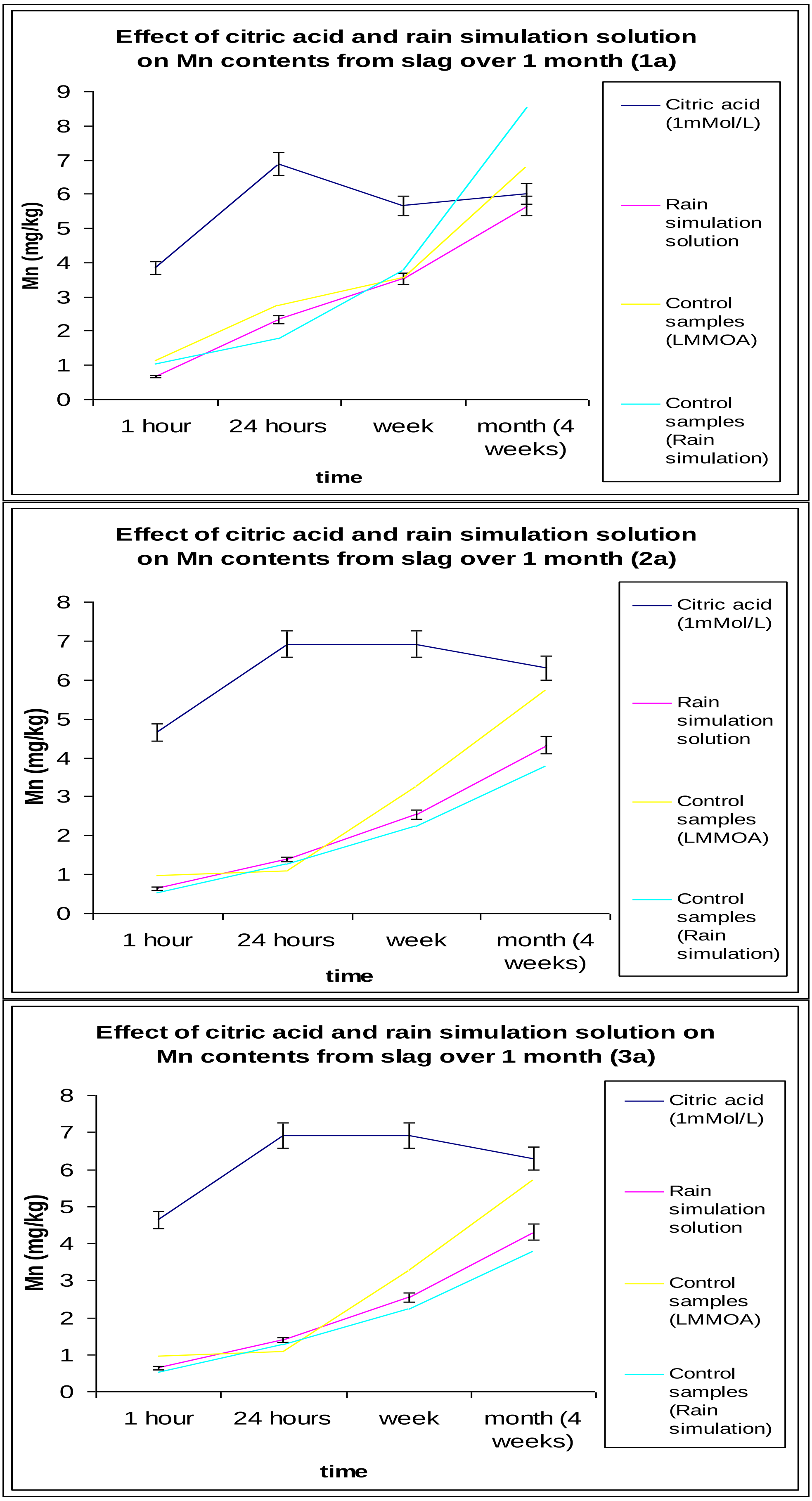


Figure 7.4.5 Change in Mn concentration in solvents during leaching experiment

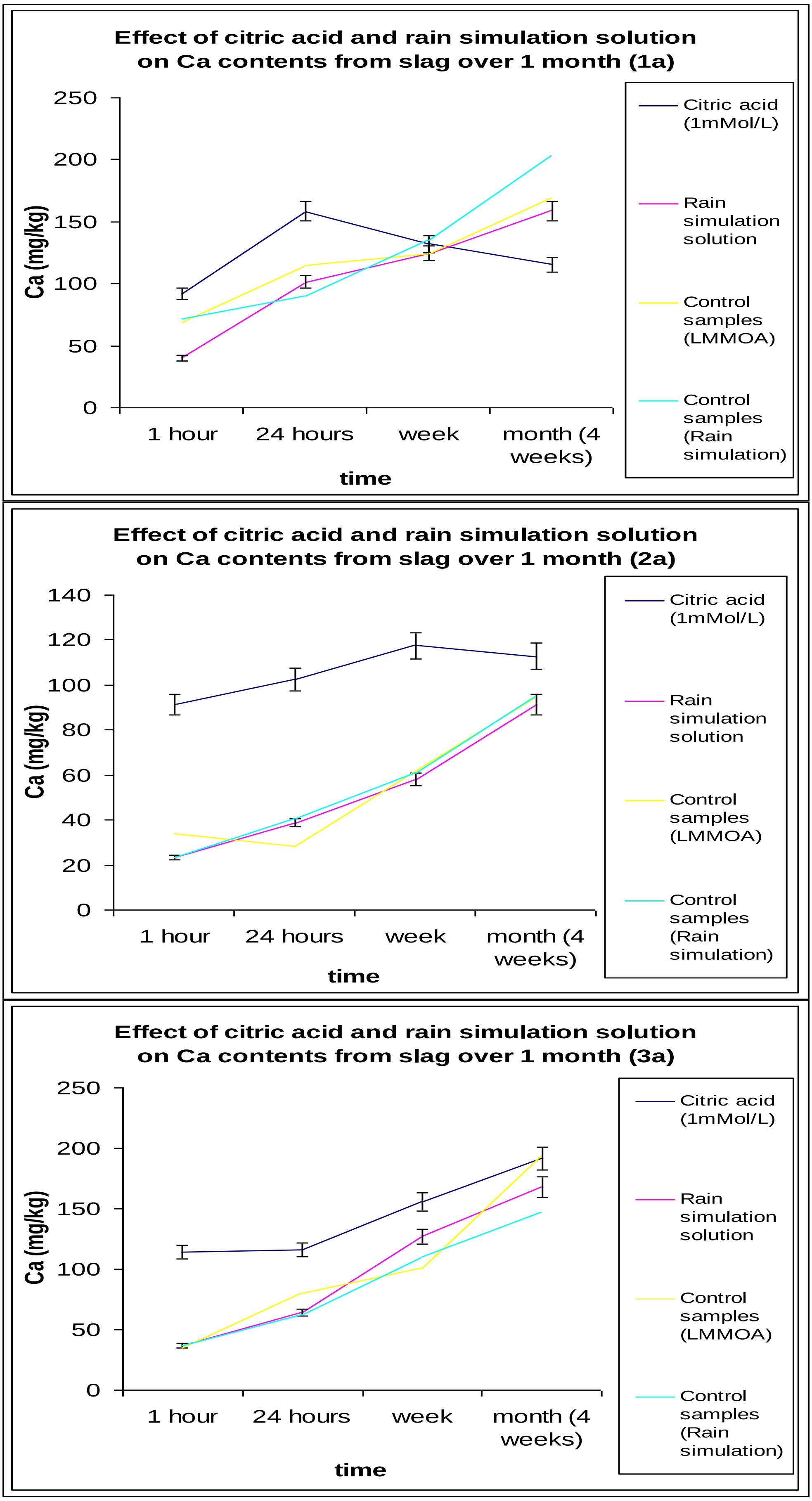


Figure 7.4.6 Change in Ca concentration in solvents during leaching experiment

In Figure 7.4.6 the trend is somewhat inconsistent for Ca in the citric acid extract, as there are decreasing and increasing tendencies at different times throughout the experiment. What is consistent is that the final concentration is greater than the initial concentration, albeit only slightly in the case of 1a and 2a. Ca is one of the elements that exhibit greater availability with increasing pH, as shown in the Figure by Atwell *et al.* (1999) in Appendix G. At this point it is necessary to refer to the observations made from analysis of the citrate in the citric acid samples during the experiment. Figure 7.4.7 illustrates the variation in soluble Ca compared with the changes in citrate concentration and pH over one month.

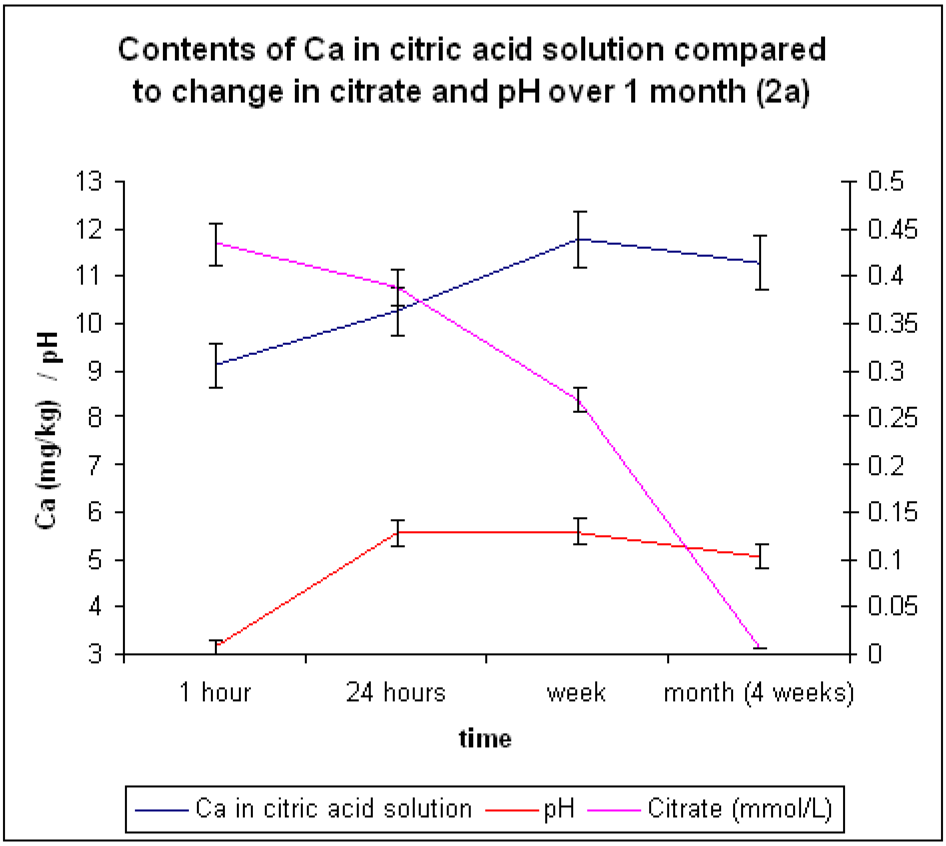


Figure 7.4.7 Comparison of change in soluble Ca with citrate and pH in citric acid solution samples 2a (right axis = citrate mmol/L). Note that values for Ca have been divided by 10 to keep all data to a scale suitable for viewing

What the graph shows is that over the one month duration of the experiment, the citrate has almost fully decomposed. As a consequence of this, the pH has risen from the initial value of 3.15 up to the value of ~ 5.0. The values for Ca dissolved in solution then vary to some degree in accordance to pH value (as pH increases, so does the dissolved Ca, and when pH is lower the dissolved Ca is also lowered).

RSS extracts Ca increasingly step by step at each time interval, but not in an exponential manner with the exception of 2a. Only in sample 1a does the RSS extraction of Ca exceed that of the citric acid solution. The RSS results run parallel with the control solution almost exactly for sample 2a.

Mg behaves somewhat similarly to Ca in that the overall elemental content in the citric acid solution is higher at the end of the experiment than the initial concentration. The response of Ca to pH in Figure 7.4.7 is replicated for Mg (Figure 7.4.8).

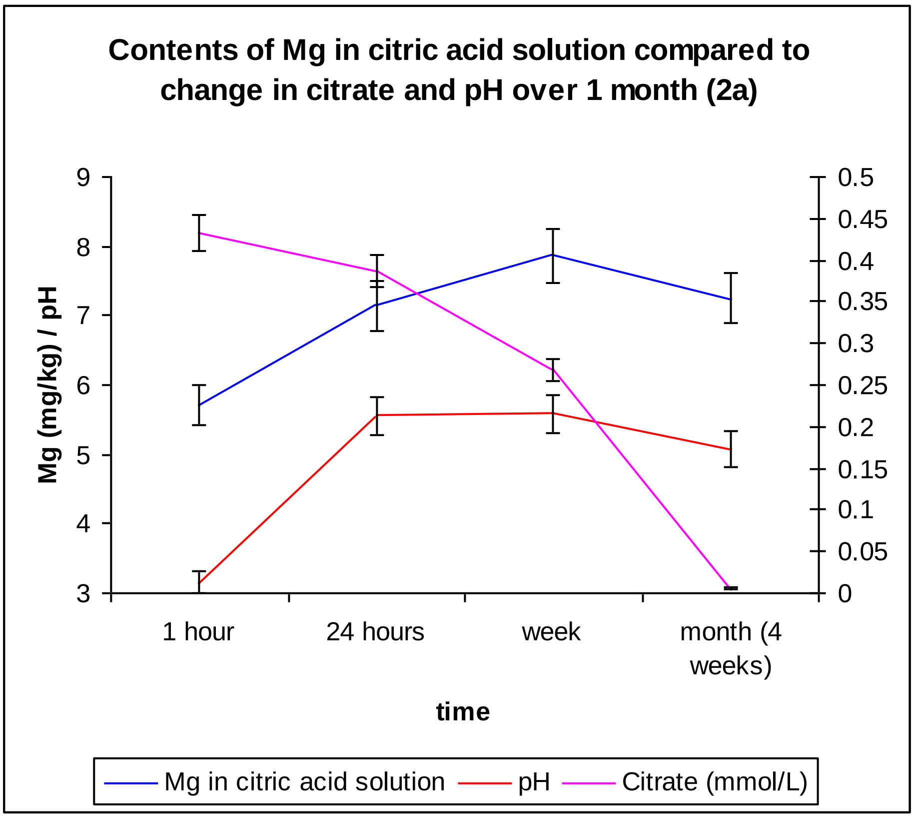


Figure 7.4.8 Comparison of change in soluble Mg with citrate and pH in citric acid solution samples 2a (right axis = citrate mmol/L)

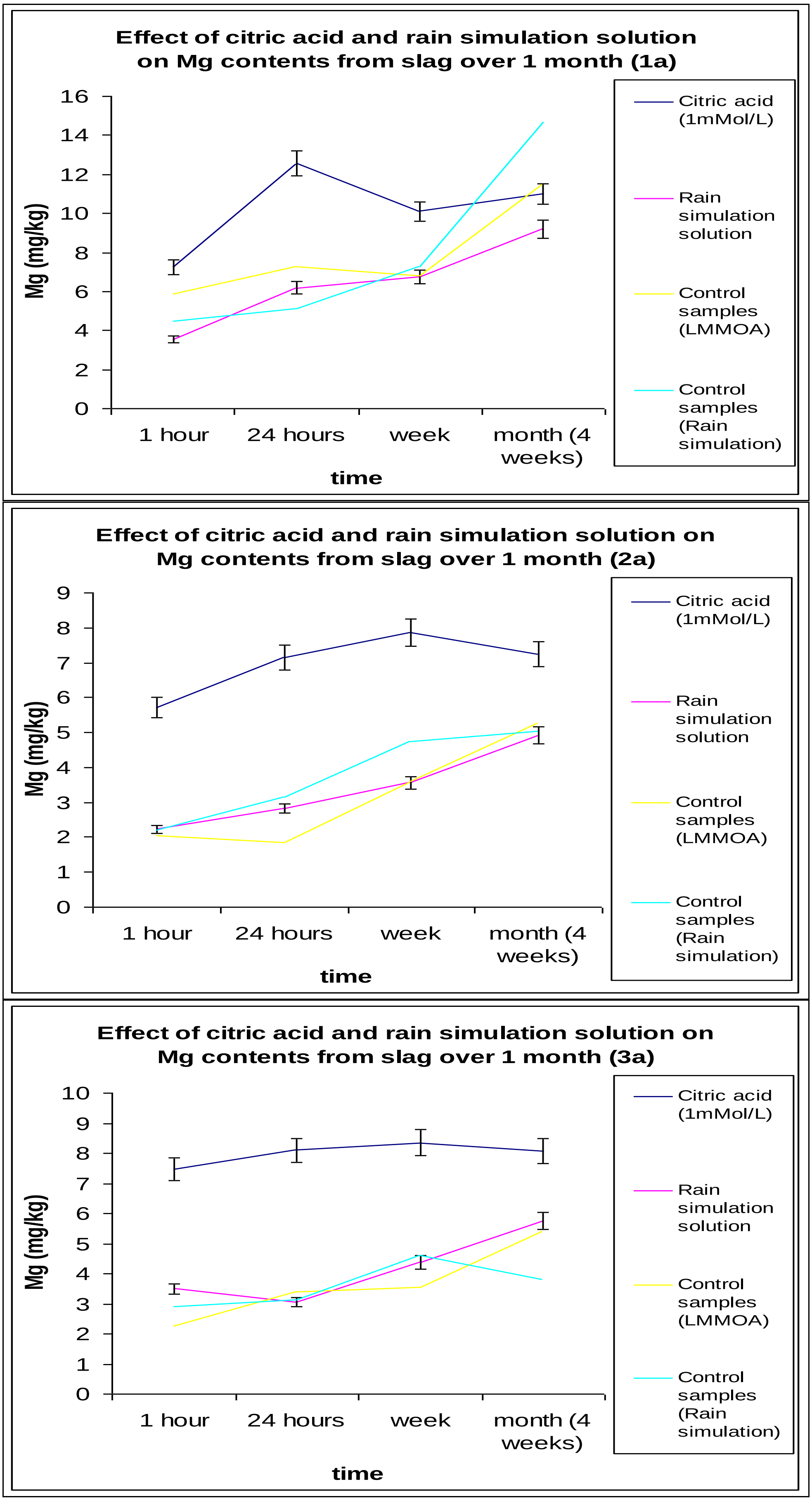


Figure 7.4.9 Change in Mg concentration in solvents during leaching experiment

The citric acid samples were dissolving Mg far more effectively than the control samples in this experiment and so irrespective of pH there is some property of the organic acid which is favouring the release of Mg into solution.

The RSS shows a positive trend with higher concentrations of Mg obtained in the solution at the end of the experiment than in the start, although the values are not particularly high < 10mg/kg.

In Figure 7.4.9 the shape of the trend is deviating between increases and decreases for K in the citric acid solution, however, despite the non-uniform pattern in the trend, there is an overall increase in K obtained from the citric acid solution from the start to the end of the experiment. The citric acid solution is more effective than the control sample.

The RSS proves to be an effective solution for the extraction of K from slag samples. Samples 1a and 3a show a continued increasing trend for RSS, which is also significantly higher than the control sample. In sample 2a however the control sample matches the RSS closely with RSS being a little more effective after one month.

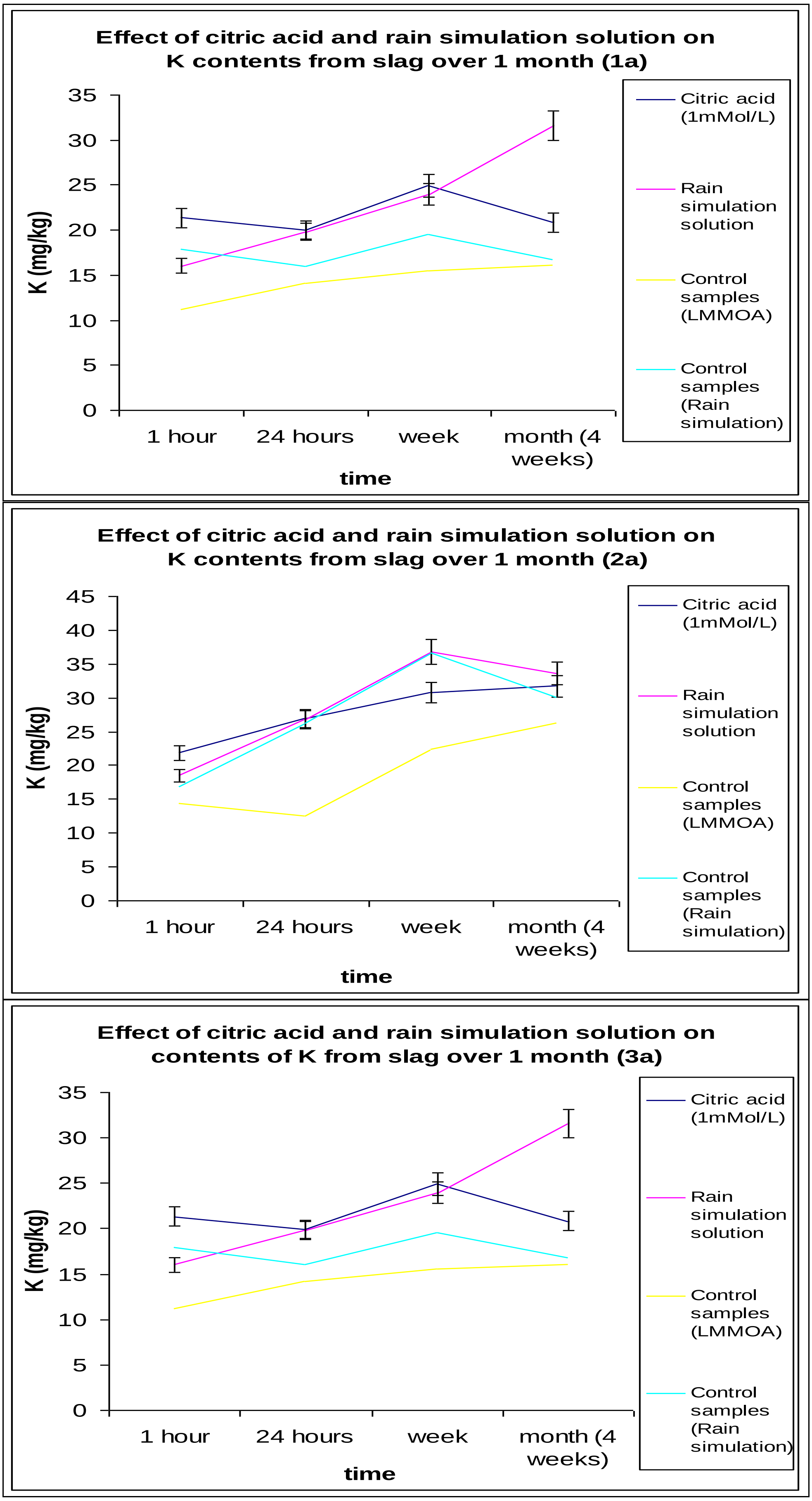
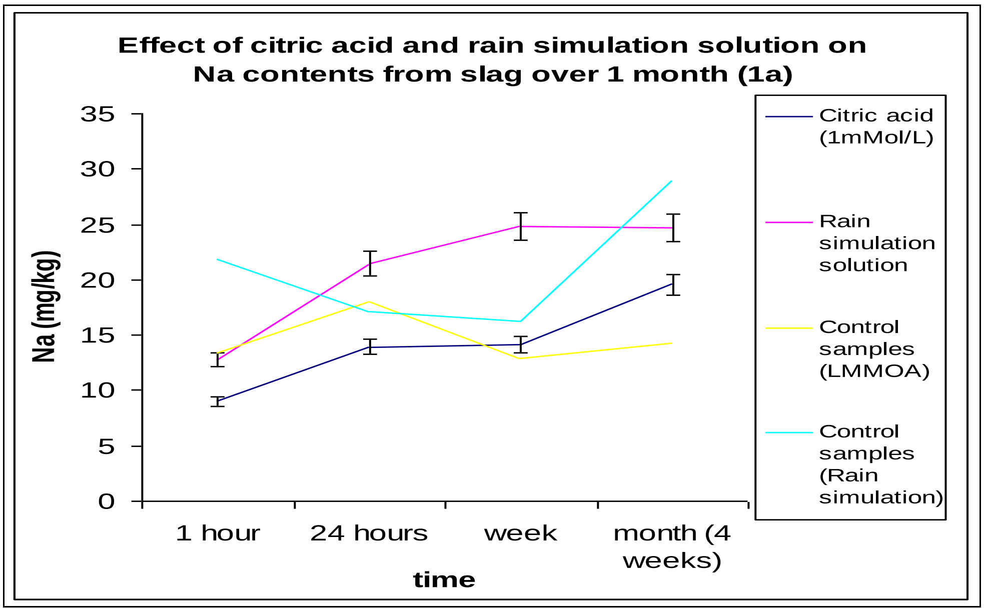
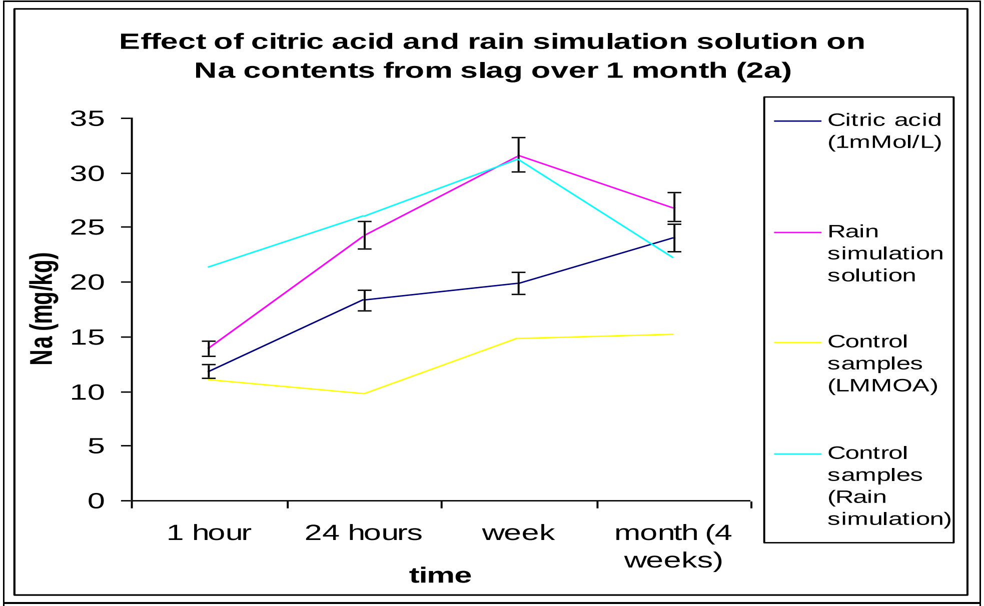


Figure 7.4.9 Change in K concentration in solvents during leaching experiment





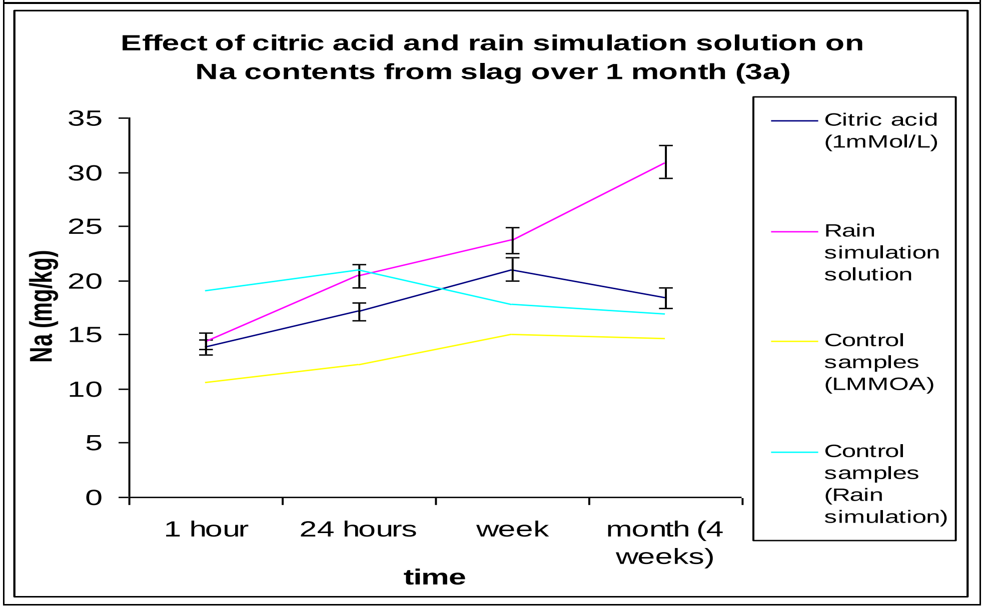


Figure 7.4.10 Change in Na concentration in solvents during leaching experiment

The extraction of Na into citric acid solution is positive over time for all three samples. After the first hour, the citric acid did not extract any significantly higher amounts of Na than the control sample. The control sample actually exceeds the citric acid in sample 1a, however, after the one month duration of the experiment, the citric acid solution was more effective in dissolution of Na from slag than the control sample.

The RSS is an effective extractant of Na up to one week, after which, in samples 1a and 2a the Na contents in solution has decreased. RSS proved to be more effective in the dissolution of Na than the citric acid solution in all cases. The maximum observed values for Na extracted by RSS are approximately 10% of the 2M HNO_3 "total" amounts suggesting that Ca is easily leached from slag.

The correlations of RSS with the control solution for the nutrients listed in this section are as follows: Mn R = 0.881, Ca R = 0.935, Mg R = 0.879, K R = 0.769, Na R = 0.253. Therefore, the more acidic rain simulation solution (pH 4.6) is not largely different in its extraction power than the less acidic control solution (pH 5.5) for Mn, Mg and Ca in particular. Greater variation between the two extractants can be seen in the case of K and Na.

7.4.3 Citrate analysis in citric acid solution over one month of experimentation

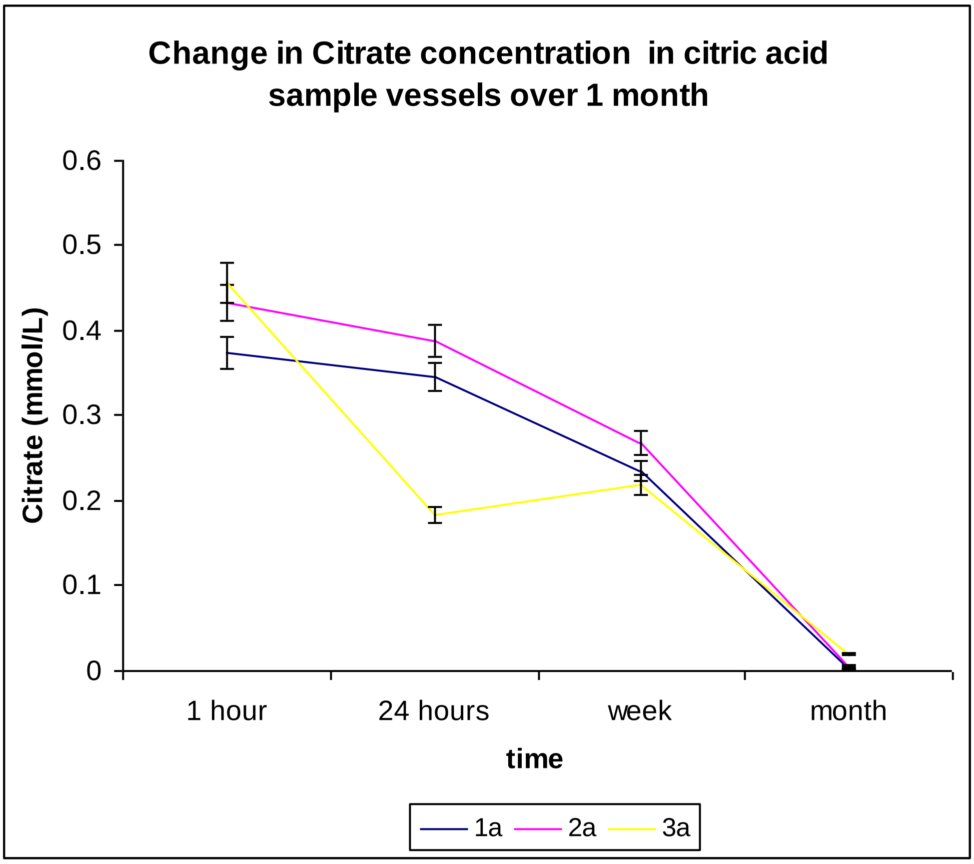


Figure 7.4.11 Citrate change over one month in citric acid solution

The evolution of citrate was observed for all three samples in the study, and each responded more or less the same to the presence of the slags. The citrate concentration decreased over the duration of the experiment to the point where it was either extremely low or undetectable after one month duration. Ettler *et al.* (2004) had similar experiences with their leaching experiment of slags whereby citric acid solutions made up to 20mM and 8mM had decreased after 24 hours to 15.5 and 5mM respectively. After 168 hours (week) the 8mM solution had dropped below determination limit. The decomposition of citrate in the experiment by Ettler *et al.* (2004) was slightly faster because the citrate in this experiment was still detectable after one week. However, this may be attributable to the sensitivity of different equipment used (capillary electrophoresis as opposed to ion chromatography).

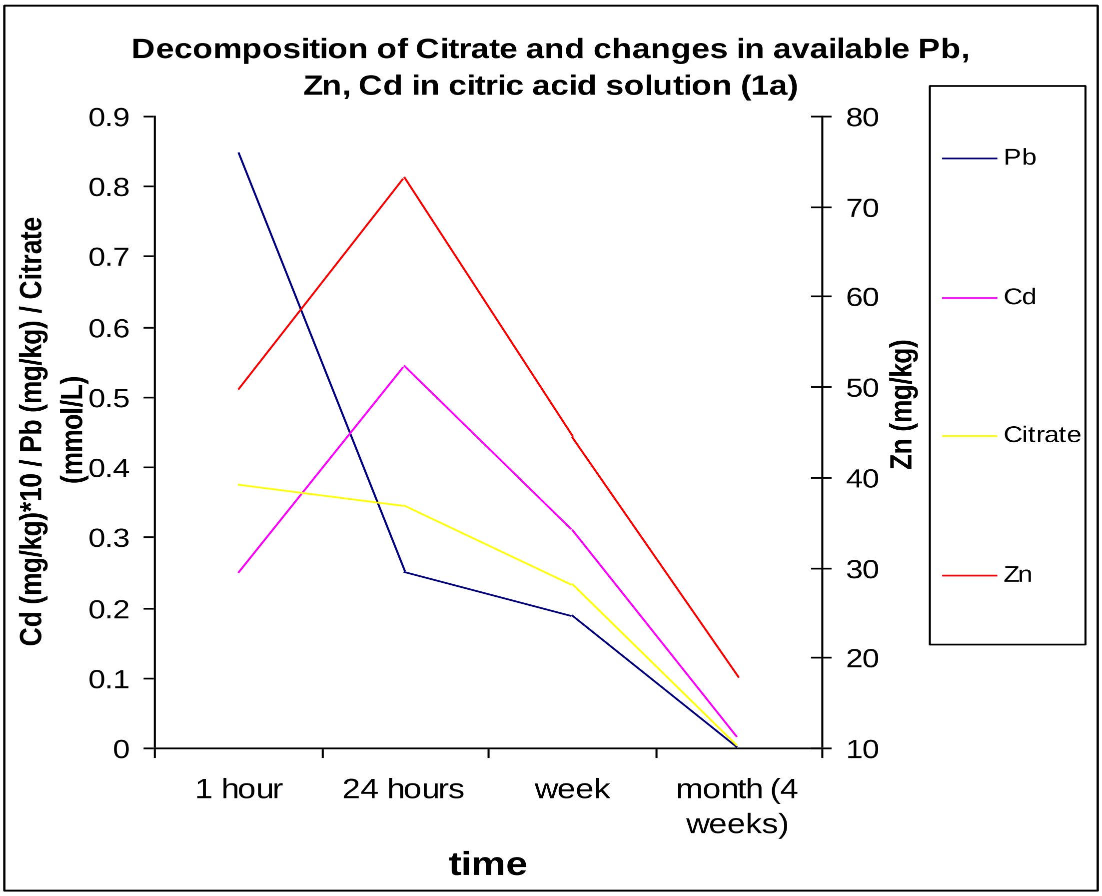


Figure 7.4.12 Graph showing the decomposition of citrate compared with the change in concentrations of Pb, Zn and Cd in citric acid solution from sample 1a

Heavy metals Pb, Zn and Cd all exhibited a decreasing trend with the progression of time during the experiment. As Figure 7.4.12 shows, that after an initial increase, the decreasing trend runs parallel with the decrease in citrate. These results are agreeable with the results from the leaching experiment on smelter slag by Ettler *et al.* (2004). For Pb and Zn, these authors observed an initial increase in metals concentration in the 8mM citric acid solution followed by a drop with undetectable levels for the rest of the experiment. The stronger solution on the other hand sustained the increased levels of Pb and Zn (see Figure 7.4.13). However, these citric acid concentrations are higher than those which are designed to mimic environmental solutions and therefore the lower strength citric acid solutions (such as the 1mM solution used in this thesis) may give a better representation of the behaviour of metals in the river bank soils of the KH slags.

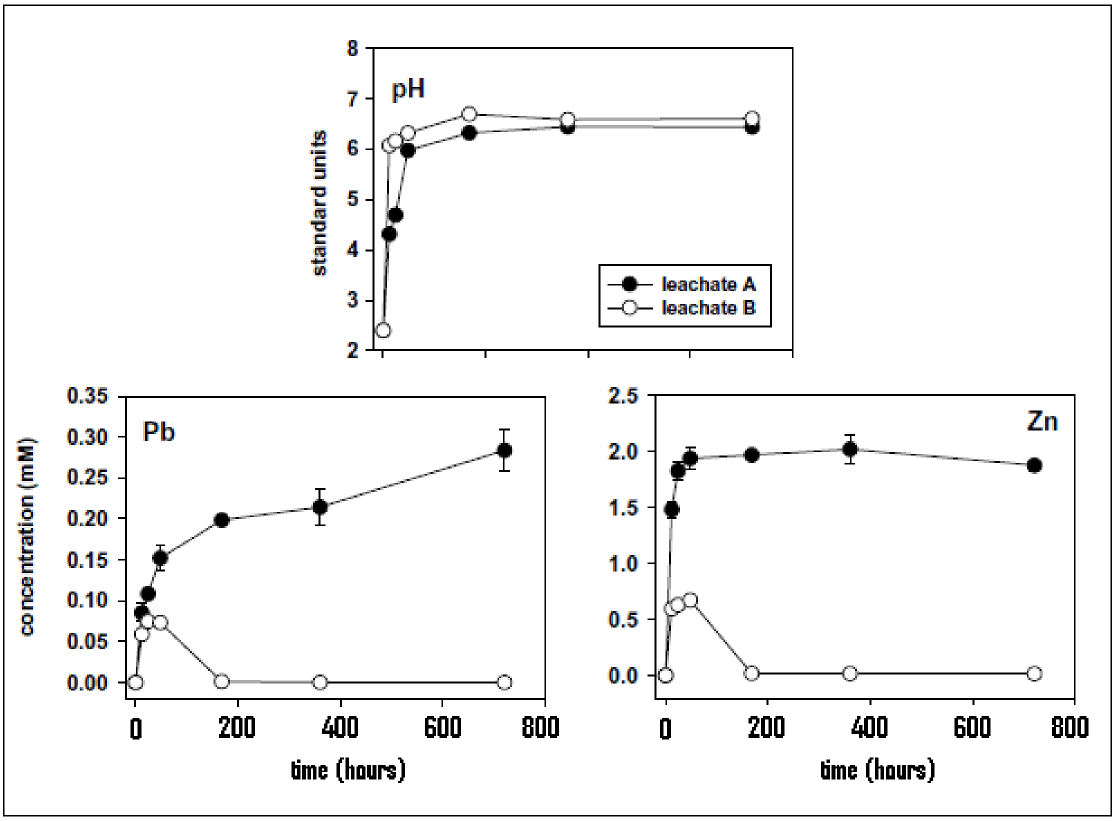


Figure 7.4.13 Results for comparison in the leaching experiment by Ettler *et al.* (2004). Leachate A refers to 20mM citric acid and leachate B 8mM

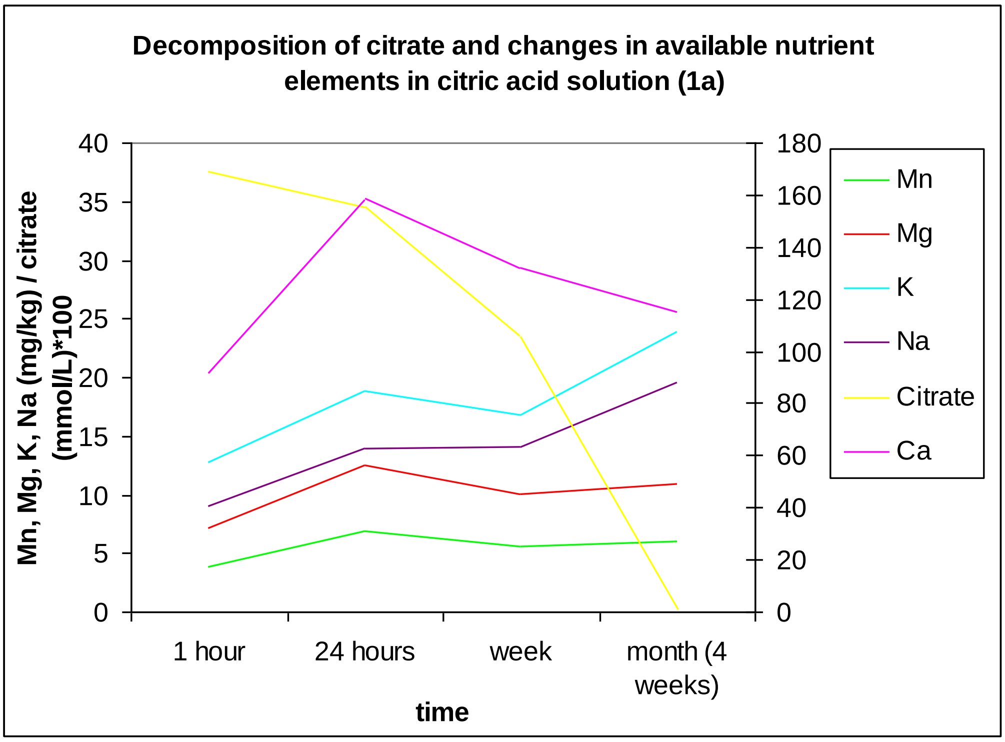


Figure 7.4.14 Graph showing the decomposition of citrate compared with the change in concentration of nutrient elements in citric acid solution from locality 1a (right axis = Ca)

What Figure 7.4.14 shows is that all of these elements have an increased available concentration at the end of the one month compared to at the start. It may be a result of preferential dissolution at a higher pH range (although this is in contrast to the results from the correlation with pH for these elements in soils as seen in section 7.2). All of these elements respond positively initially with an increased concentration in citric acid solution after 24 hours, followed by a reduced rate of increase or even a decrease, possibly as a consequence of the decomposing citric acid. The available nutrient elements in solution were in almost every case higher in the citric acid solution, compared to the control solution. Therefore, because pH in all experimental solutions were buffered to within a narrow range in the latter part of the experiment, there are likely to be properties in the citric acid which are influencing the dissolution of elements which are independent to pH.

7.4.4 pH analysis of solutions over one month of experimentation

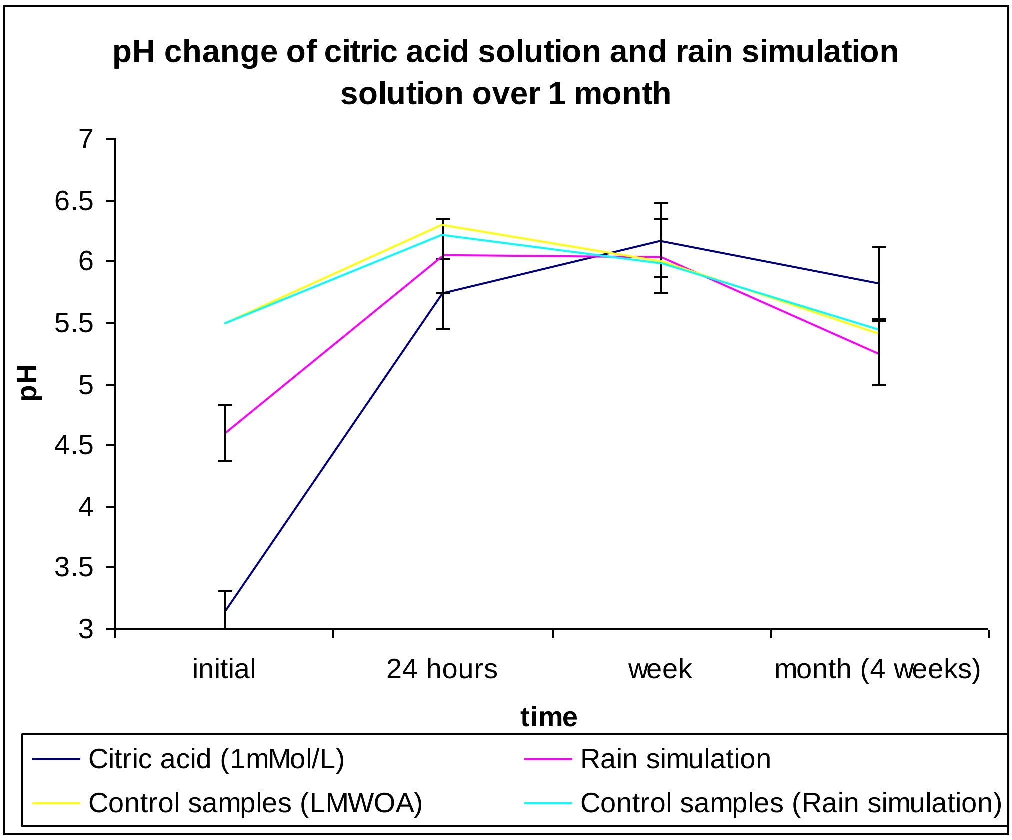


Figure 7.4.15 pH change over one month for leaching experiment solutions

The different solvents (citric acid, rain simulator and control) had a wide ranging pH variation at the beginning of the experiment (pH value range = 2.4). However, after one month of exposure to the ground slags, the mean pH (from three slag samples with two replicates) for each solvent had shifted to within a range of 0.4 of each other. This narrow pH range between solvents around 5.2 – 5.6 is indicative that the slags have a strong buffering potential to approximately 5.5. Ettler *et al.* (2004) had similar results (see Figure 7.4.13). The buffering of pH to this range between 5.2 – 5.6 will have the implications that mobility of each element will either increase or decrease according to the species in which the element exists and its availability at this pH range. Metals like Pb and Zn for example exhibit an overall decreasing or static trend in the citric acid solution which is probably due to the decomposition of citric acid and subsequent increase of pH as Figure 7.4.15 shows. This pH buffering effect is reflected in the soils to some degree as Table 6.1.2 shows, whereby the mean pH values of soils in and around the slag pile are within the range of 4.65 – 5.53.

8. Conclusions

The study identifies very high risk element contents extractable by 2M HNO_3 (levels that represent extreme contamination) in soils in and around the slag, however, the bioavailable fraction of REs remains minimal. Cd was shown to have highest overall availability. Respective maximum and mean available risk element contents (% of total) are as follows: Pb 7.17_0.9; Cd 51.9_18.9; Mn 46.83_12.8; Cu 11.32_1.8 Ag 1.67_0.8; Zn 4.36_1.6; As 1.11_0.6. Bioavailability of risk elements is generally increased in samples containing higher contents of organic matter and lower pH.

There is a trend of decreasing “total” risk element metals in soils with an increase in organic matter, most likely due to the correlation between organic matter and acidity. There is evidence that plant life can become established on the slags where small patches of pioneer plants have colonised and even large trees growing where an O horizon has developed. Increased organic matter input is correlated with the increased bioavailability of essential nutrients which are contained in the slags (K, Mg, Ca). This is the likely reason why these slags have been historically used as a fertiliser.

Mobilisation/dissolution of metals is more heavily dependent on pH rather than on the binding potential of clays and organic matter. Pb appears to accumulate in soil above pH of approximately 4.5. Cd and Cu accumulate in soils above approximately pH 5.1 -5.2, and Zn does not accumulate in soils with a pH of less than approximately 7 (proportional to the concentration in the slags from which they are weathering). The soils which have formed from weathering of the slags, and the organic horizons that occur at the site are likely to be influenced by the buffering potential of the slags, to which solvents digesting the slags will shortly be buffered to an increased pH, influencing the mobility or retention of risk elements that are present in the slag. As observed during the leaching experiment, the mineralogy of the slag caused this buffering effect to a range of pH 5.2 - 5.6 on the three experimental solvents (rain simulation, citric acid and deionised water) within 24 hours of contact.

Analysis of the of the Vrchlice River sediments revealed excessive concentrations of risk elements As, Mn and Zn (observed maximum = 9.48, 1,607. and 1,556. mg/kg respectively). This is a clear indication that REs from the slag are entering the surrounding surface waters.

Leaching experiment:

The effectiveness of citric acid as a solvent varies between elements. Solubility of heavy metals Pb, Zn and Cd respond negatively (decreasing trend) overall to the decrease in citrate concentration and subsequent increase in pH, whereas other ‘non-risk elements’ were shown to increase overall despite a decrease in citrate. This suggests that Pb, Zn and Cd are more reactive in citric acid than other elements in the study. It is probable that the increased mobility of Pb, Zn and Cd under increased citric acid solution is due to the acidic nature of citric acid (pH 3.15). However, the observed overall concentrations are relatively low and therefore low strength organic acids in the environment are not likely to be mobilising significant amounts of risk elements that could cause significant harm to vegetation. This is evident at the study area due to the fact that the riverbank soils are host to a healthy dense canopy of vegetation.

For the rain simulation solution (deionised water amended with HCl to pH 4.6), with every analysed element, except for Pb, an increasing trend was observed. In the majority of samples, it was an exponential increase with the elapsing duration of the experiment, in a few cases the increase was less significant, but in all samples, the final RSS contained a greater concentration than the RSS which was sampled after 1 hour. Due to the permeability of slag, sustained periods of rain are likely to be mobilising elements in the environment, Zn in particular (max ~450 mg/kg after one month). However, very low concentrations of Pb and Cd are likely to be mobilised in rainwater. RSS forms a linear correlation with the control solution (deionised water with pH 5.5) for risk elements Cd (R = 0.967) and Zn (R = 0.955), and to a lesser extent but still significantly for Mn (R = 0.881), Ca (R = 0.935) and Mg (R = 0.879). Water is an equally effective solvent in the extraction of Zn and Cd from slags over a pH range of at least 1.0, and probably more.

9. Recommendations

Due to the fact that the bioavailable concentrations of risk elements are so small, there is no significant threat to the environment. The study area is also listed with historical preservation status and therefore no remediation is possible. If it were required that risk elements were to be contained so as not to enter the river, then it may be feasible to either mix a liming amendment into the riverbank soils (may negatively affect vegetation), or to create some engineered barrier between the river and the slag (e.g. an alkaline clay slurry or concrete).

Re-vegetation of slag could be achieved by importing topsoil and applying it at the surface. Over time a succession of plants will occur, and as the soil develops, nutrients contained in the slag will be made available to larger trees and shrubs. The availability of risk elements is not likely to be sufficient enough to prevent growth of trees on the slag, although rooting depth will probably be limited to the upper horizons due to the high permeability and gravely structure of the slag.

The study can be extended by preparing a leaching experiment which replicates conditions in the Vrchlice River as this thesis only focuses on precipitation. Investigations can also be made on the fields surrounding the villages near to Kutná Hora that are used for growing crops and to examine the soil-plant transfer of risk elements.

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Appendix A:

Table A1 Human health effects associated with risk elements

Element	Exposure pathways	Health implications	Reference
As	ingestion and dermatological contact	cancers, peripheral neuropathy and anaemia	(ATSDR 2009)
Be	Inhalation	Chronic beryllium disease (lung condition, and Be sensitisation	(DOE 1999)
Cd	Inhalation and ingestion	Lung cancer, kidney toxicity and renal damage	(Defra 2011)
Co	Ingestion, inhalation and dermal contact	Cardiomyopathy, nerve and thyroid problems	(Medlineplus 2011)
Cr	Inhalation	Carcinogen	(Defra 2011)
Cu	Ingestion	Neurotoxin, causing Alzheimer’s and Wilson’s disease	(Parmar and Daya 2001)
Hg	Ingestion	Highly potent neurotoxin	(Defra 2011)
Mn	Inhalation	Neurological disorders	(ATSDR 2008)
Mo	Ingestion and inhalation	Pneumoconiosis, anemia and diarrhoea	(ExpertGroup 2003)
Ni	Dermal contact, ingestion and inhalation	Potent skin sensitiser	(Defra 2011)
Pb	Inhalation and ingestion	Anemia, neural and brain disorders	(Medlineplus 2011)
Sb	Inhalation and ingestion	Eye and skin irritation, breathing disorders and stomach pains	(ATSDR 1992)
Se	Ingestion	Lowered haemoglobin, skin lesions and nervous system abnormalities	(Defra 2011)
V	Inhalation	Respiratory and digestion diseases	(Expertgroup 2003)
Zn	Ingestion and inhalation	Metal fume fever, anemia and pancreas diseases	(EnvironmentAgency 2011)

Appendix B:

Table B1 Macro and micro nutrients function in plants

Nutrient	Soil content		Function in plants
	%	mg/kg	
N	0.1 – 0.2	-	Essential for growth and a component of many organic compounds
P	0.02 – 0.15	-	Component of organic compounds, Phytin, DNA, phospholipids, ATP
K	0.5 – 3.2	-	Affects osmotic pressure in cells, activates many enzymes, transports photosynthetic products
Ca	0.15 – 6	-	Stabilises cell walls, important for root development
Mg	0.4 – 0.6	-	Important component of chlorophyll, activates enzymes
S	-	50 – 500	Molecular building blocks for proteins
B	-	-	Regulates sugar metabolism, RNA development and cell division
Fe	0.01 - 10	-	Electron transfer, enzyme activity
Co	-	8 – 45	Nitrogen fixation, atom in vitamin B12
Mn	-	100 – 1200	Electron transfer, catalyses water photolysis
Zn	-	38 – 110	Synthesis of Tryptophan, chlorophyll development
Cu	-	7 – 45	Synthesis of lignin, stabilises cell walls
Mo	-	0.5 – 2	Catalyst in nitrate reduction, nitrogen fixation

Appendix C:

Figure C1 Photo showing sparsely growing waves of grasses on the flatter areas of the slag

Figure C2 Photo showing a succession of vegetation on the fringes of the slag

Appendix D:

- 1a – Large slag samples collected from surface by hand. A Small pit was dug where grass is growing to exposes A and B horizons from which samples were both taken.

Figure D1 Sample pit 1a (left) and 1b (right).

- 1b – On the flat area of the slag heap where there is no significant vegetation growing, a sample from A and B horizons were taken. At this location, 3 x infiltration tests were conducted using a mini-disk infiltrometer.
- 1c – In the area under the canopy on the bank which lines the river, A and B horizon samples were collected. Here the conditions are constantly moist.

Figure D2 Sample pit 1c

- 2a – mixed sized slag pieces only were taken from the steep sloped bank of the main pile.

Figure D3 slag pile (left) and sample pit 2b (right).

- 2b – A and B horizon samples were collected from the level part of the slag pile.
- 2c – Under the tree canopy A and B horizon samples were taken from the moist soil which is dark and rich in organic matter.

Figure D4 Sample pit 2c

- 3a – Slag samples were taken from the upper banks of the slag heap. In addition, samples were taken from A and B horizons at the foot of the pile where some vegetation had colonised the slag. The upper A horizon layer consisted mostly of gravel, with the layer below containing more soil, but still heavily laden with gravel.

Figure D5 Area where loose slag was collected (left) and sample pit 3a (right)

- 3b – A and B horizons are visible on this flat section of the slag pile. Samples from both layers were collected.

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Figure D6 Sample pit 3b

- 3c – Sample was taken below the tree canopy under moist conditions. Here samples were taken from 3 horizons. The lower C horizon is visibly different from the overlaying organic matter rich horizon delineated by an abrupt change.

Figure D7 Sample pit 3c (left) and Vrchlice River where sediments were collected (right)

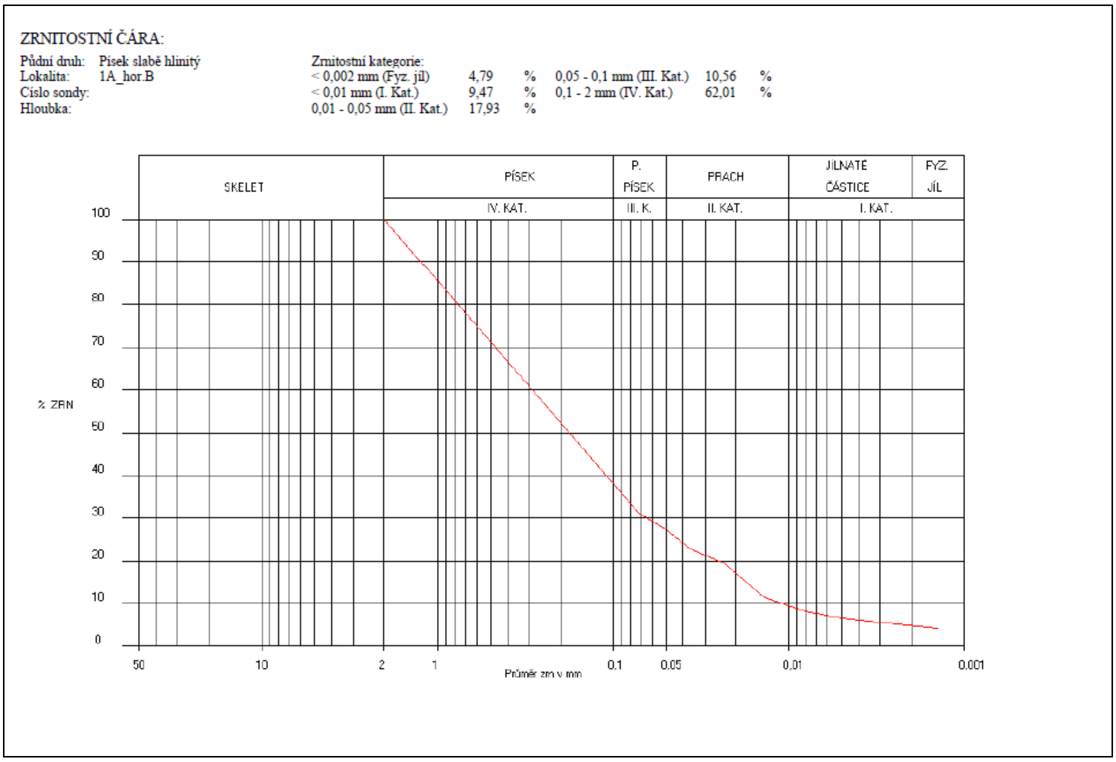
Figure D8 Typical fragments of slag material

Appendix E:

ICP-OES: inductively coupled plasma-optical emission spectrometer(ICP-OES, iCAP 6500 Radial ICP, Thermo Scientific, GB)

Ion chromatograph ICS 1600 (Dionex, USA) equipped with IonPac AS11-HC Dionex, USA) guard and analytical columns. Eluent composition was 1-37,5 mM KOH with gradient 1-50 min; and flow rate was set to 1 mL min-1. To suppress eluent conductivity the ASRS 300 – 4 mm suppressor (Dionex, USA) and The Carbonate Removal Device 200 (Dionex,USA) were used.

Appendix F:



ZRNITOSTNÍ ČÁRA:

Půdní druh: Písek slabě hlinitý
Lokalita: 1A_hor.B
Císlo sondy:
Hloubka:

Zrnitostní kategorie:
< 0,002 mm (Fyz. jíl) 4,79 %
< 0,01 mm (I. Kat.) 9,47 %
0,01 - 0,05 mm (II. Kat.) 17,93 %
0,05 - 0,1 mm (III. Kat.) 10,56 %
0,1 - 2 mm (IV. Kat.) 62,01 %

Figure F1 Texture curve: sample 1a B

ZRNITOSTNÍ ČÁRA:

Půdní druh: Písek jílnatohlinitý
Lokalita: 1B_hor.B
Císlo sondy:
Hloubka:

Zrnitostní kategorie:
< 0,002 mm (Fyz. jíl) 0,38 %
< 0,01 mm (I. Kat.) 16,71 %
0,01 - 0,05 mm (II. Kat.) 23,19 %
0,05 - 0,1 mm (III. Kat.) 8,19 %
0,1 - 2 mm (IV. Kat.) 51,89 %

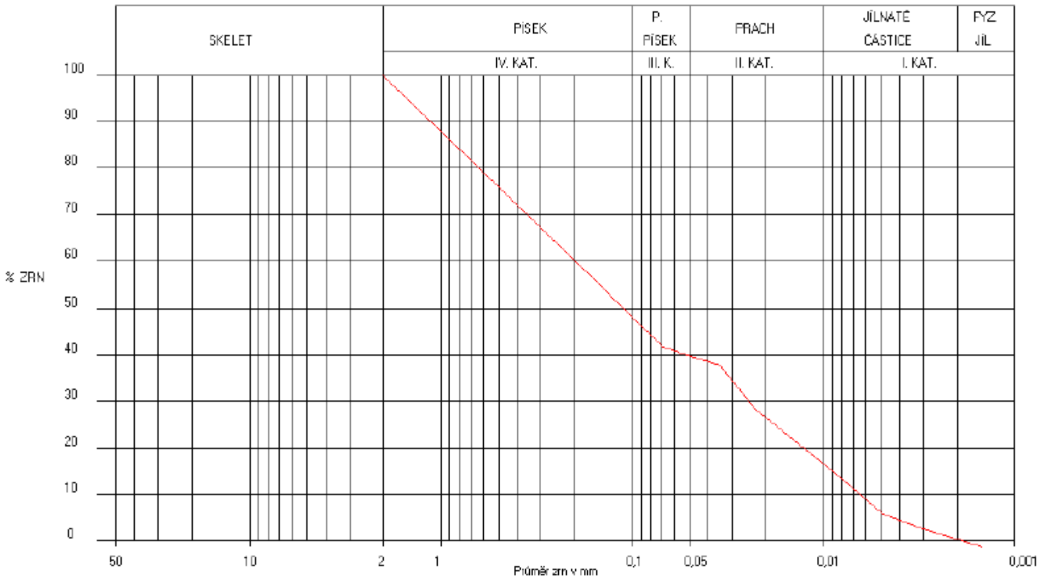


Figure F2 Texture curve: sample 1b B

ZRNITOSTNÍ ČÁRA:

Půdní druh: Písek slabě hlinitý
Lokalita: 1C_hor.B
Císlo sondy:
Hloubka:

Zrnitostní kategorie:
< 0,002 mm (Fyz. jíl) 3,26 %
< 0,01 mm (I. Kat.) 8,68 %
0,01 - 0,05 mm (II. Kat.) 11,88 %
0,05 - 0,1 mm (III. Kat.) 16,64 %
0,1 - 2 mm (IV. Kat.) 62,78 %

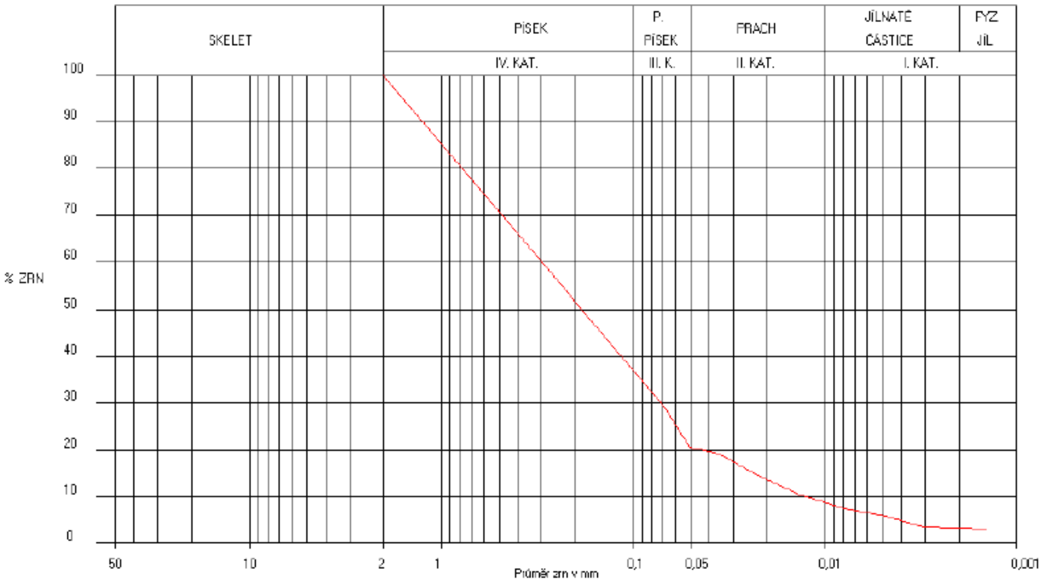
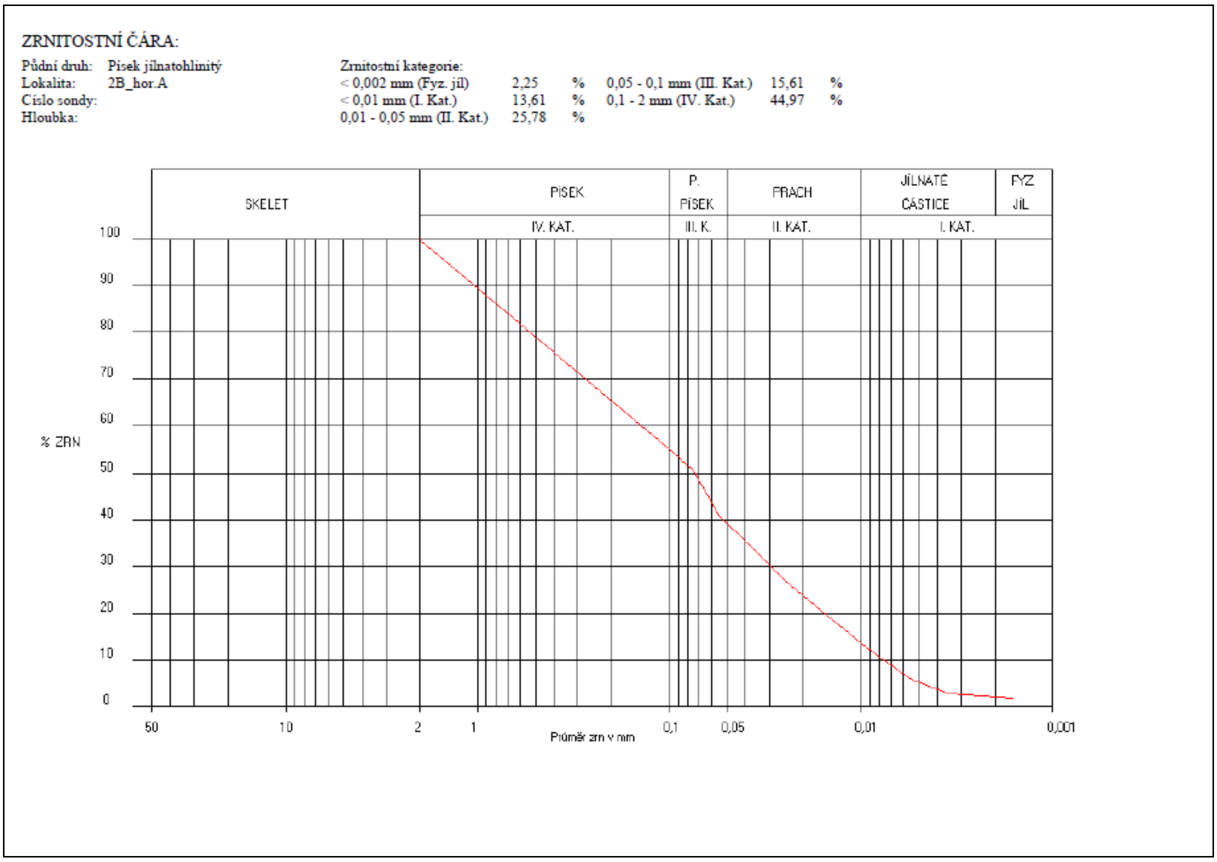


Figure F3 Texture curve: sample 1c B

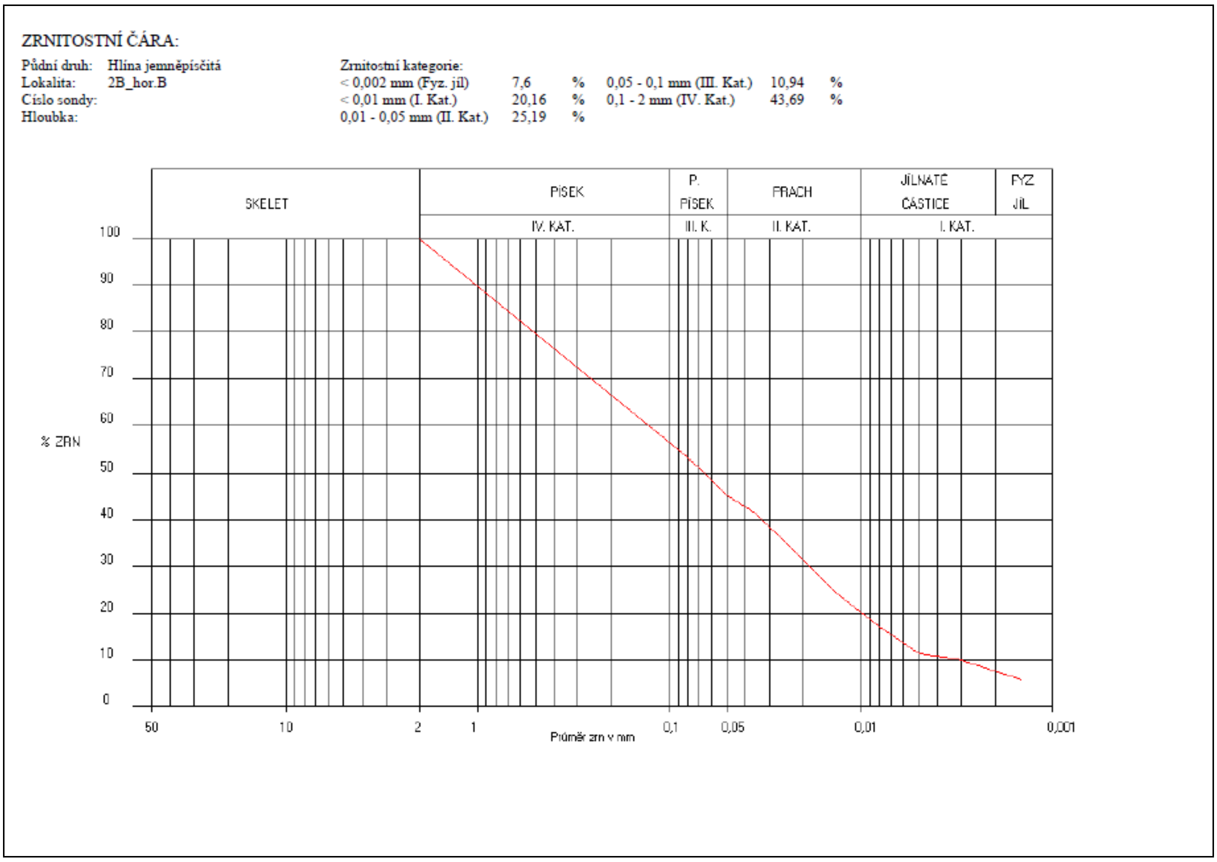


ZRNITOSTNÍ ČÁRA:

Půdní druh: Písek jílnatohlinitý
Lokalita: 2B_hor.A
Císlo sondy:
Hloubka:

Zrnitostní kategorie:
< 0,002 mm (Fyz. jíl) 2,25 %
< 0,01 mm (I. Kat.) 13,61 %
0,01 - 0,05 mm (II. Kat.) 25,78 %
0,05 - 0,1 mm (III. Kat.) 15,61 %
0,1 - 2 mm (IV. Kat.) 44,97 %

Figure F4 Texture curve: sample 2b A



ZRNITOSTNÍ ČÁRA:

Půdní druh: Hlína jemněpísčitá
Lokalita: 2B_hor.B
Císlo sondy:
Hloubka:

Zrnitostní kategorie:
< 0,002 mm (Fyz. jíl) 7,6 %
< 0,01 mm (I. Kat.) 20,16 %
0,01 - 0,05 mm (II. Kat.) 25,19 %
0,05 - 0,1 mm (III. Kat.) 10,94 %
0,1 - 2 mm (IV. Kat.) 43,69 %

Figure F5 Texture curve: sample 2b B

ZRNITOSTNÍ ČÁRA:

Půdní druh:	Písek jílnatohlinitý	Zrnitostní kategorie:					
Lokalita:	2C_hor.A	< 0,002 mm (Fyz. jíl)	2,41	%	0,05 - 0,1 mm (III. Kat.)	12,3	%
Císlo sondy:		< 0,01 mm (I. Kat.)	10,49	%	0,1 - 2 mm (IV. Kat.)	48,52	%
Hloubka:		0,01 - 0,05 mm (II. Kat.)	28,66	%			

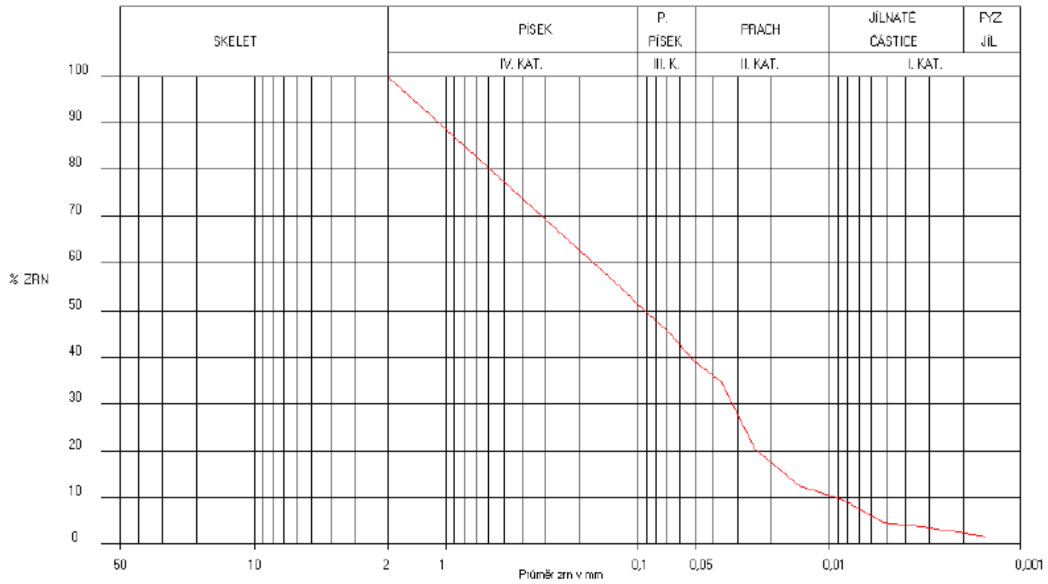


Figure F6 Texture curve: sample 2c A

ZRNITOSTNÍ ČÁRA:

Půdní druh:	Písek jílnatohlinitý	Zrnitostní kategorie:					
Lokalita:	2C_hor.B	< 0,002 mm (Fyz. jíl)	3,5	%	0,05 - 0,1 mm (III. Kat.)	16,26	%
Císlo sondy:		< 0,01 mm (I. Kat.)	12,02	%	0,1 - 2 mm (IV. Kat.)	44,53	%
Hloubka:		0,01 - 0,05 mm (II. Kat.)	27,18	%			

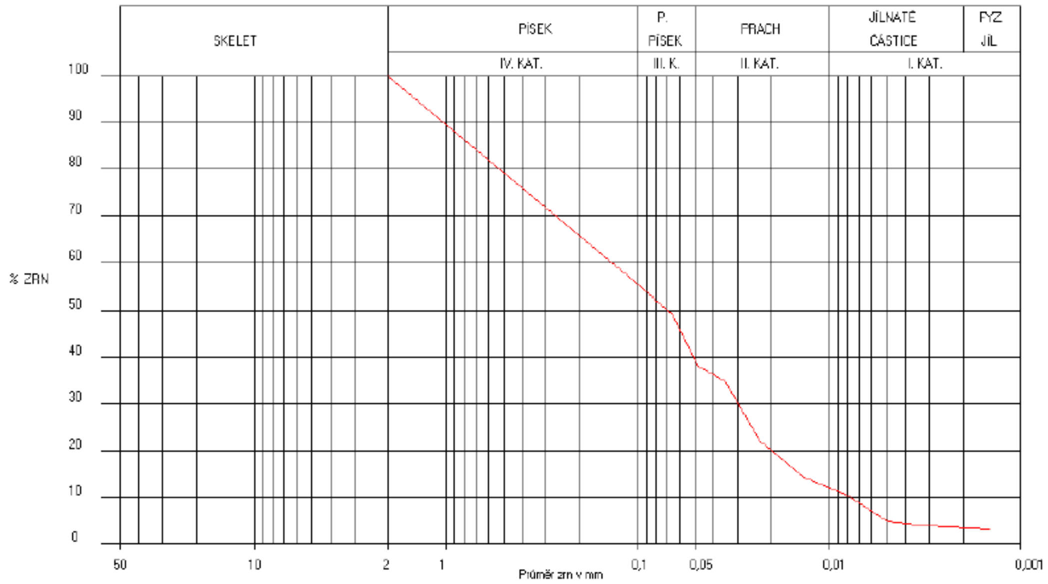
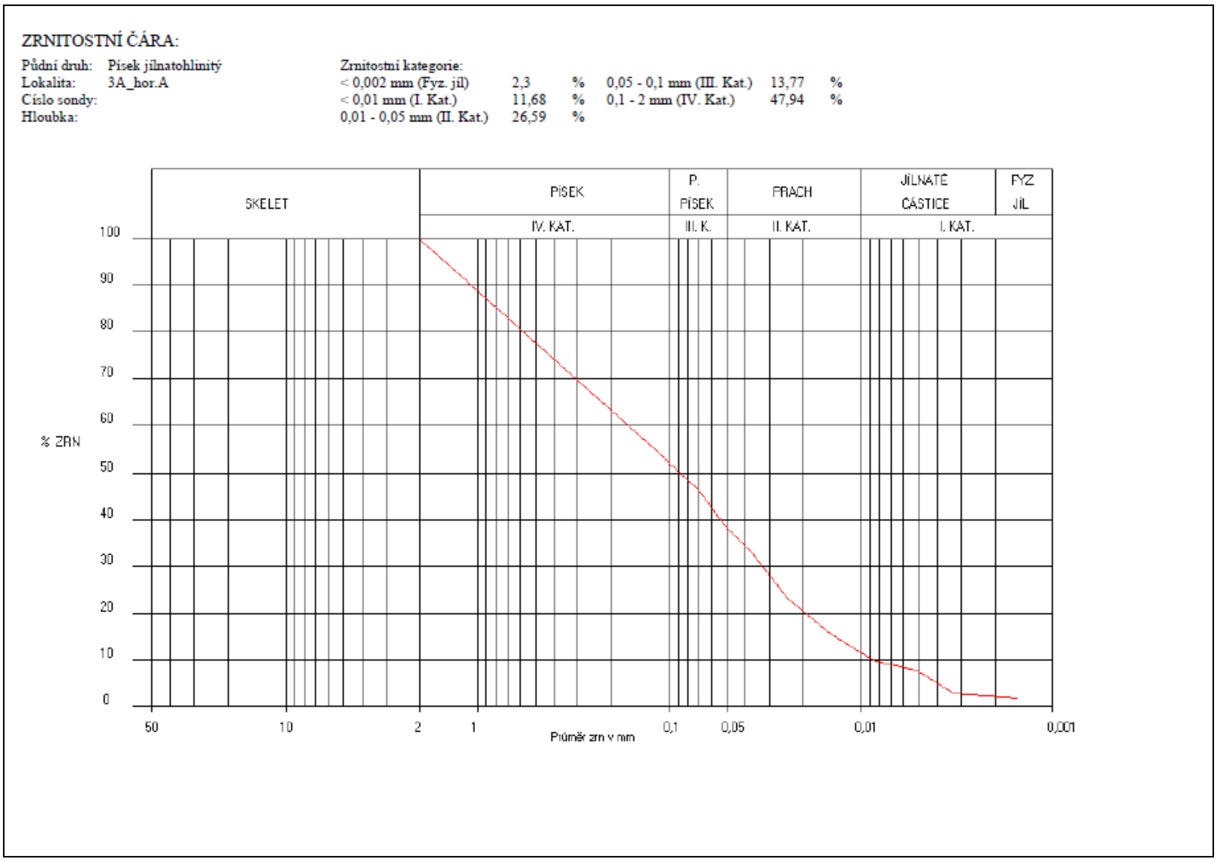


Figure F7 Texture curve: sample 2c B

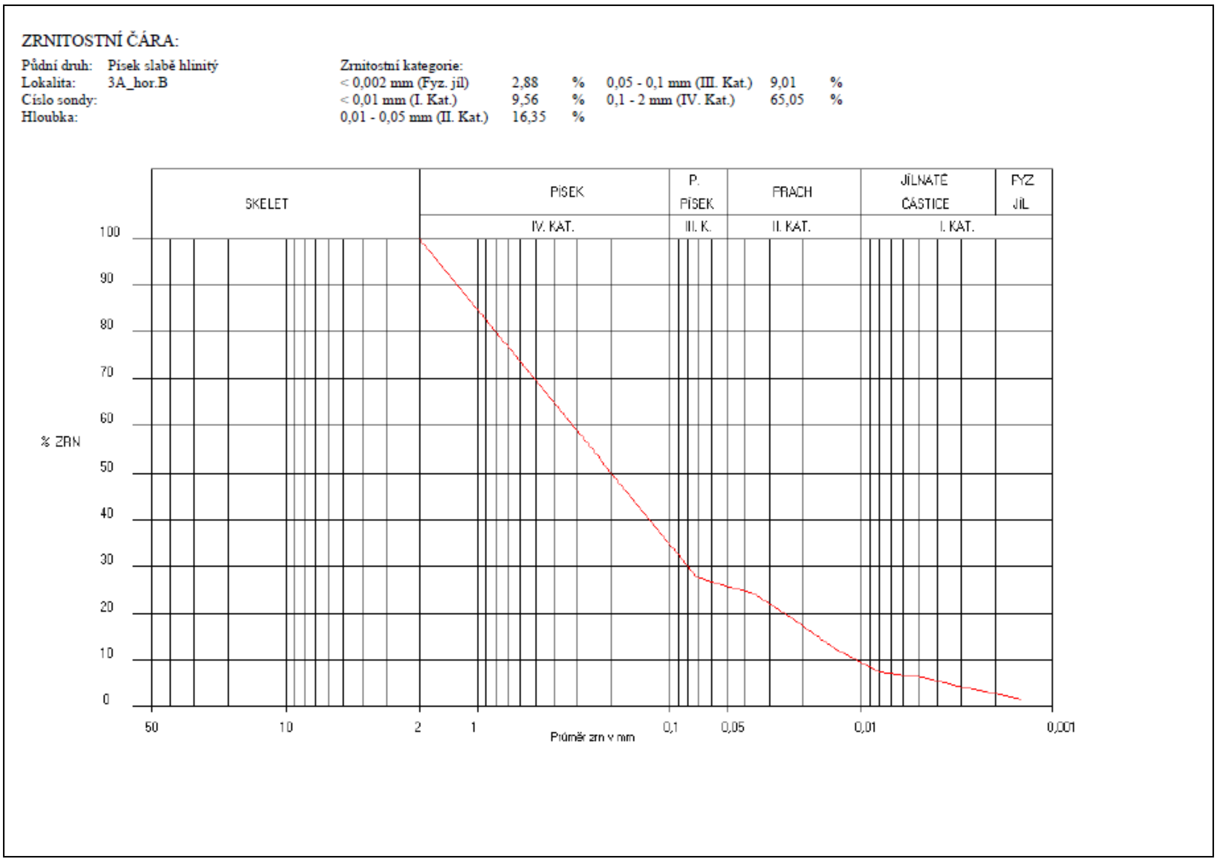


ZRNITOSTNÍ ČÁRA:

Půdní druh: Písek jílnatohlinitý
Lokalita: 3A_hor.A
Cislo sondy:
Hloubka:

Zrnitostní kategorie:
< 0,002 mm (Fyz. jíl) 2,3 % 0,05 - 0,1 mm (III. Kat.) 13,77 %
< 0,01 mm (I. Kat.) 11,68 % 0,1 - 2 mm (IV. Kat.) 47,94 %
0,01 - 0,05 mm (II. Kat.) 26,59 %

Figure F8 Texture curve: sample 3a A

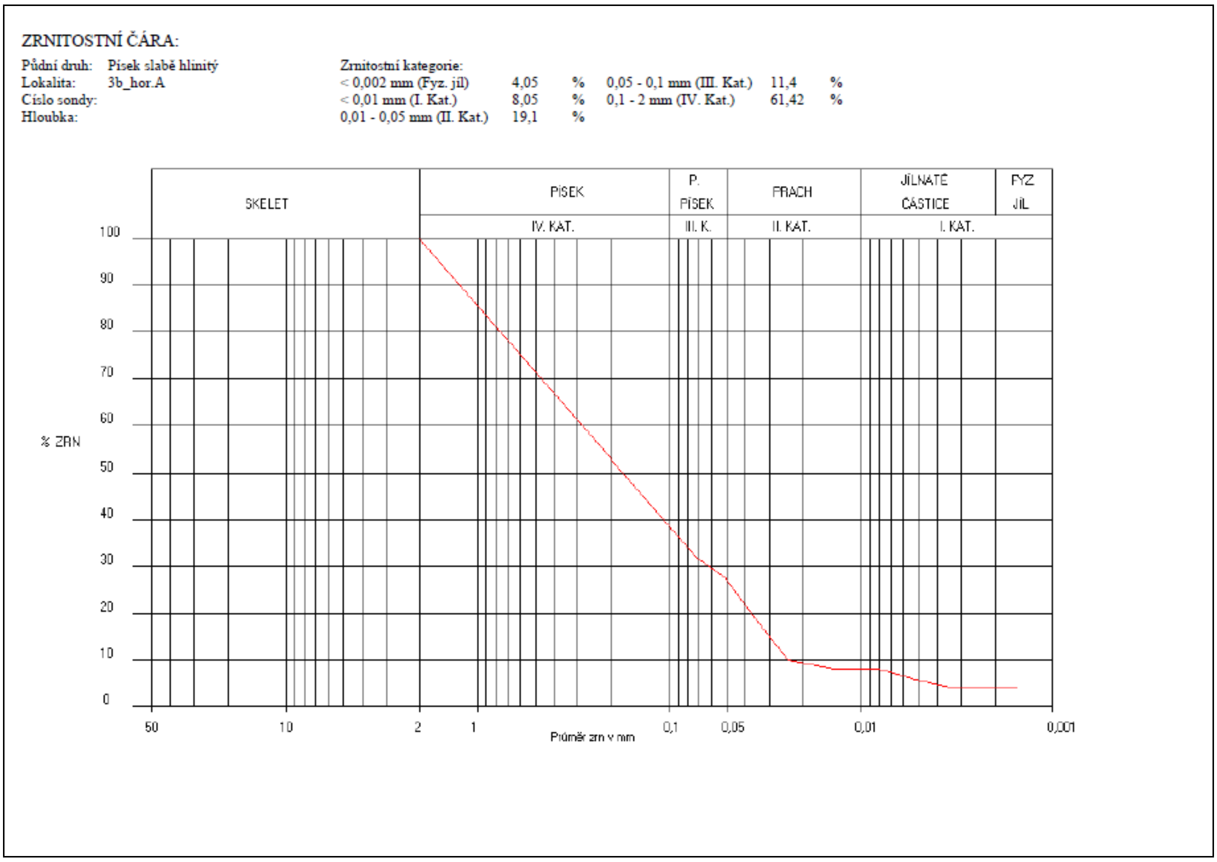


ZRNITOSTNÍ ČÁRA:

Půdní druh: Písek slabě hlinitý
Lokalita: 3A_hor.B
Cislo sondy:
Hloubka:

Zrnitostní kategorie:
< 0,002 mm (Fyz. jíl) 2,88 % 0,05 - 0,1 mm (III. Kat.) 9,01 %
< 0,01 mm (I. Kat.) 9,56 % 0,1 - 2 mm (IV. Kat.) 65,05 %
0,01 - 0,05 mm (II. Kat.) 16,35 %

Figure F9 Texture curve: sample 3a B

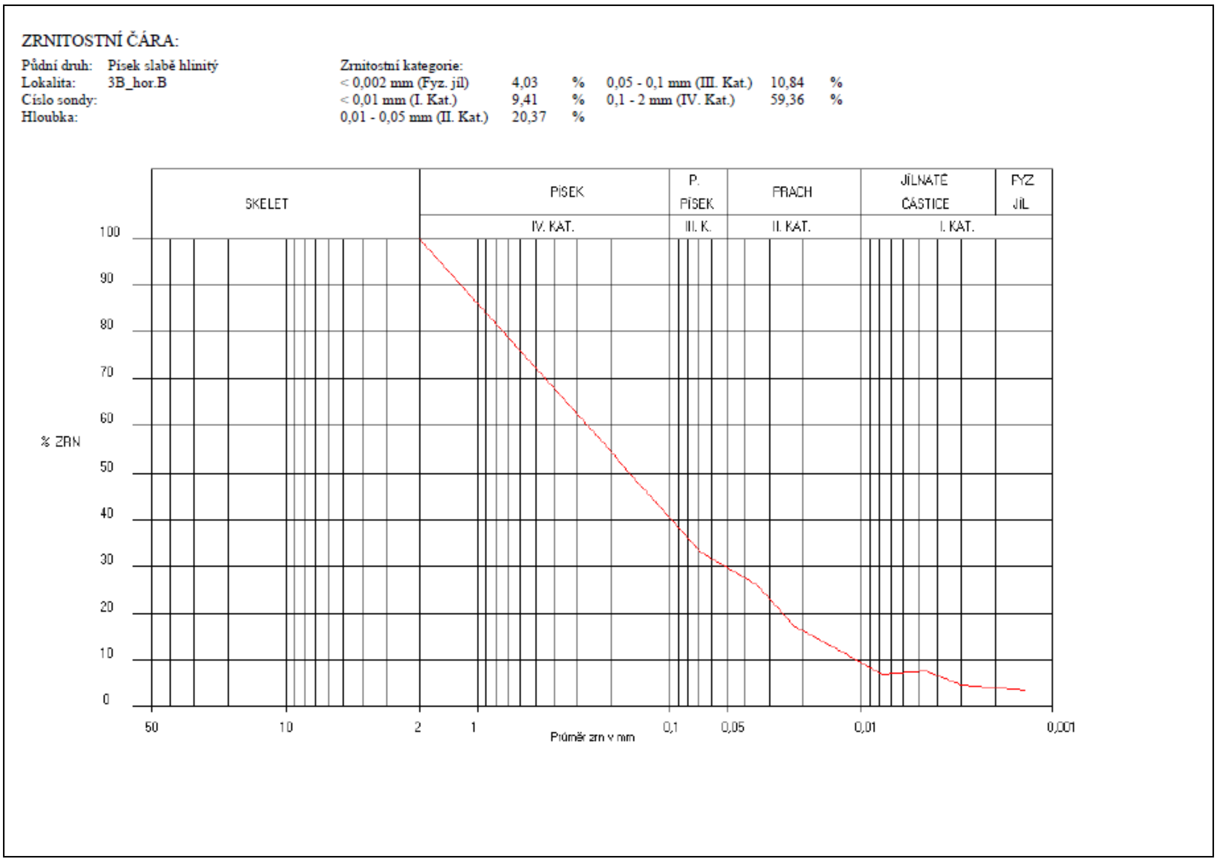


ZRNITOSTNÍ ČÁRA:

Půdní druh: Písek slabě hlinitý
Lokalita: 3b_hor.A
Císlo sondy:
Hloubka:

Zrnitostní kategorie:
< 0,002 mm (Fyz. jíl) 4,05 %
< 0,01 mm (I. Kat.) 8,05 %
0,01 - 0,05 mm (II. Kat.) 19,1 %
0,05 - 0,1 mm (III. Kat.) 11,4 %
0,1 - 2 mm (IV. Kat.) 61,42 %

Figure F10 Texture curve: sample 3b A

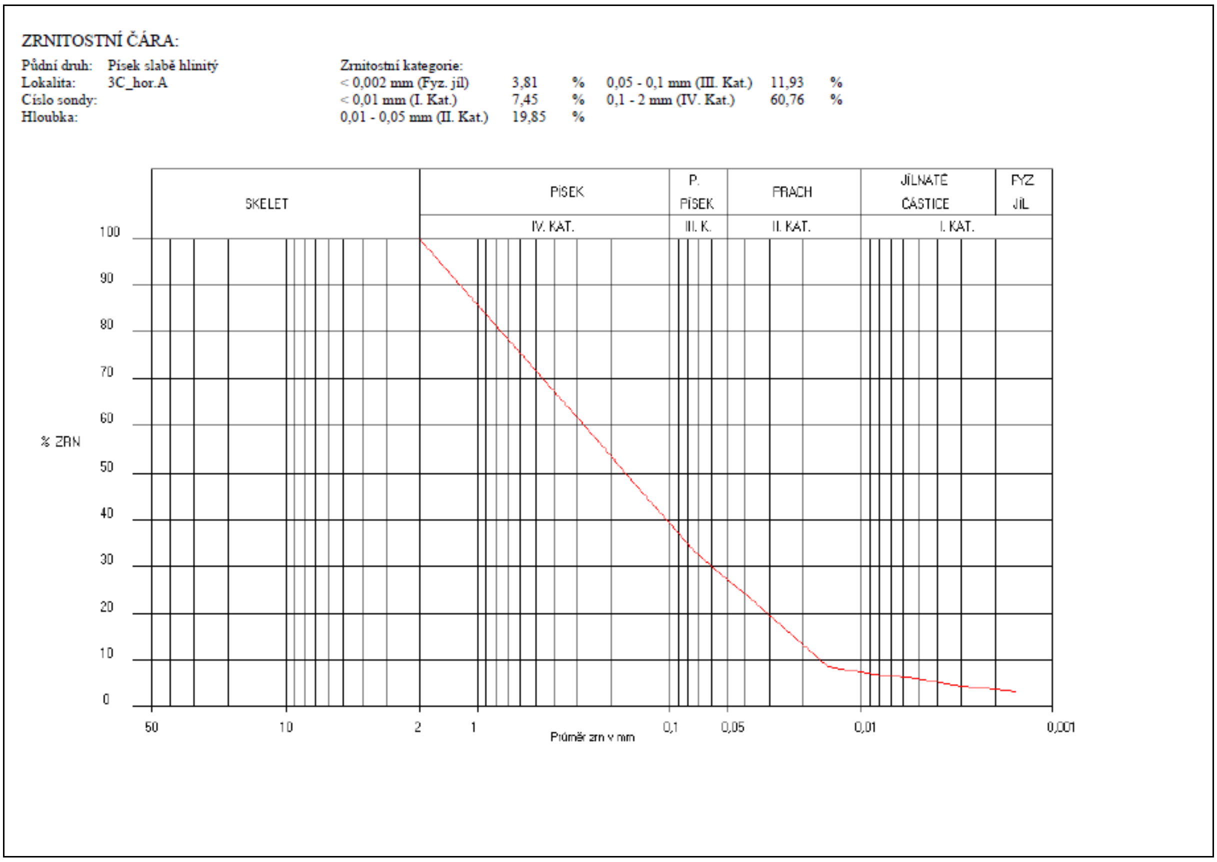


ZRNITOSTNÍ ČÁRA:

Půdní druh: Písek slabě hlinitý
Lokalita: 3B_hor.B
Císlo sondy:
Hloubka:

Zrnitostní kategorie:
< 0,002 mm (Fyz. jíl) 4,03 %
< 0,01 mm (I. Kat.) 9,41 %
0,01 - 0,05 mm (II. Kat.) 20,37 %
0,05 - 0,1 mm (III. Kat.) 10,84 %
0,1 - 2 mm (IV. Kat.) 59,36 %

Figure F11 Texture curve: sample 3b B

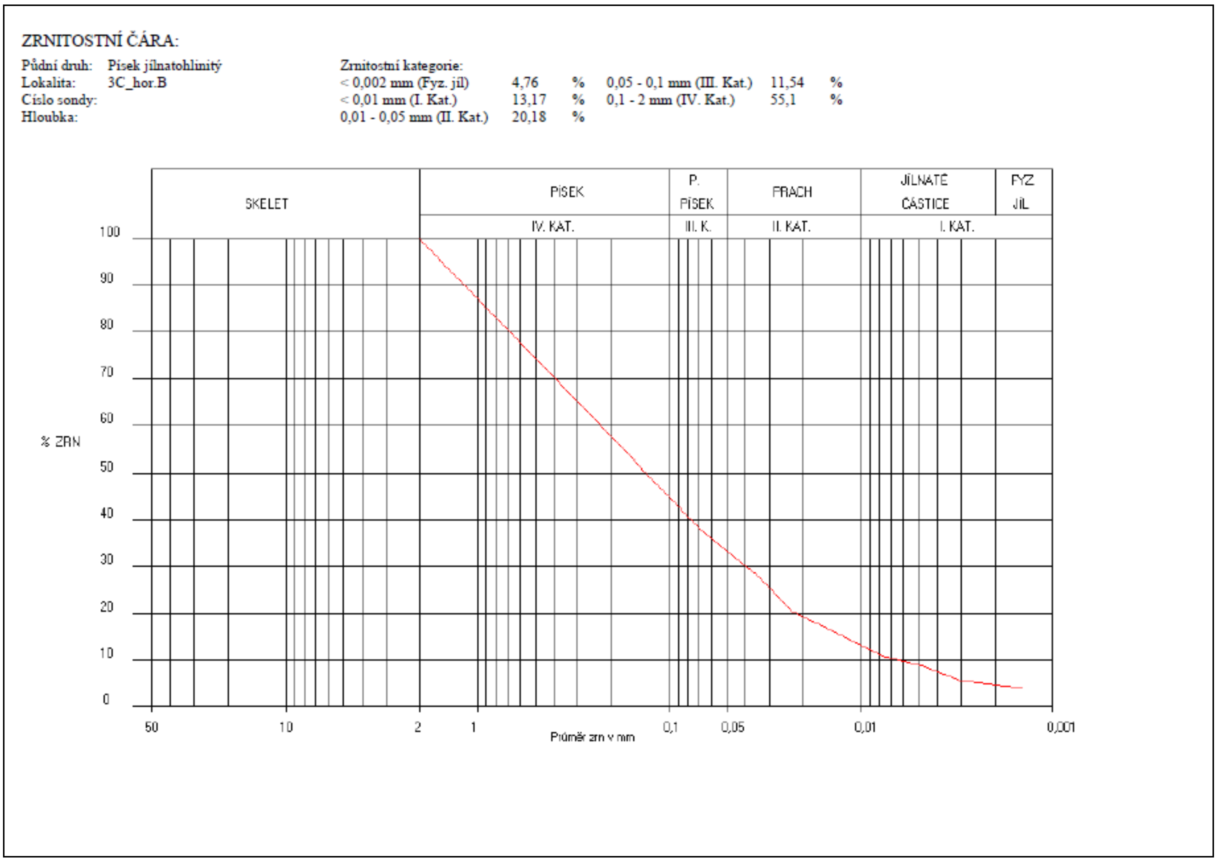


ZRNITOSTNÍ ČÁRA:

Půdní druh: Písek slabě hlinitý
Lokalita: 3C_hor.A
Císlo sondy:
Hloubka:

Zrnitostní kategorie:
< 0,002 mm (Fyz. jíl) 3,81 %
< 0,01 mm (I. Kat.) 7,45 %
0,01 - 0,05 mm (II. Kat.) 19,85 %
0,05 - 0,1 mm (III. Kat.) 11,93 %
0,1 - 2 mm (IV. Kat.) 60,76 %

Figure F12 Texture curve: sample 3c A



ZRNITOSTNÍ ČÁRA:

Půdní druh: Písek jílnatohlinitý
Lokalita: 3C_hor.B
Císlo sondy:
Hloubka:

Zrnitostní kategorie:
< 0,002 mm (Fyz. jíl) 4,76 %
< 0,01 mm (I. Kat.) 13,17 %
0,01 - 0,05 mm (II. Kat.) 20,18 %
0,05 - 0,1 mm (III. Kat.) 11,54 %
0,1 - 2 mm (IV. Kat.) 55,1 %

Figure F13 Texture curve: sample 3c B

Appendix G:

Figure G1 Nutrient availability and pH (Atwell *et al.* 1999)