CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE

FACULTY OF ENVIRONMENTAL SCIENCES

EFFICIENCY OF NANO ZERO-VALENT IRON APPLICATION IN SOIL
UNDER DIFFERENT INCUBATION CONDITIONS

DIPLOMA THESIS

GEORGE KOFI GORDOR

SUPERVISOR OF THE THESIS: Mgr. Martina Vítková, Ph.D.

PRAGUE 2017

# CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE

Faculty of Environmental Sciences

# DIPLOMA THESIS ASSIGNMENT

George Kofi Gordor

Environmental Geosciences

Thesis title

**Efficiency of nano zero-valent iron application in soil under different incubation conditions**

## Objectives of thesis

The main objectives of the thesis are (i) to assess the effect of different moisture content and liquid-to-solid ratio on the leaching behaviour of contaminants in soil amended with nano zero-valent iron (nZVI), (ii) to evaluate the changes in pH-Eh conditions and (iii) to assess the optimal incubation conditions for metal stabilisation in soils.

## Methodology

Based on recommended literature and other sources found by the student the theoretical part will be elaborated. It will include a brief description of iron nanoparticles (nZVI), the potentials and drawbacks when applied into soils, the effect of different experimental conditions on the release of risk elements and organic matter, the use of speciation models to estimate the contaminant behaviour etc.

In the methodological part the student will describe the soil samples tested, the experimental setting (incl. incubation and laboratory experiments), methods of sample treatment and analyses (incl. instruments) as well as methods of data treatment (incl. statistics and geochemical modelling).

The practical part will include (i) 3-month incubation of nZVI/control soil at different water content, (ii) determination of pH/Eh/EC and leaching experiments at different liquid-to-solid ratio and (iii) geochemical modelling. Laboratory experiments, sample preparation, analytical data treatment and model data treatment will be performed by the student independently under control of the thesis supervisor. The results will be presented in written and graphical forms. The discussion will be elaborated carefully based on the main results and with reference to relevant literature. The conclusion will be brief and concise. The text will be spell-checked and grammar checked before sent to the supervisor.

March-August 2016: Sample preparation, incubation and laboratory experiments, data treatment

5th September 2016: Submission of the outline of the thesis

September-November 2016: Data treatment, geochemical modelling

5th December 2016: Submission of the theoretical part

January-February 2017: Completing results and discussion

31st March 2017: Submission of final version of the thesis

**The proposed extent of the thesis**

50-60 pages

**Keywords**

Nanoiron, Chemical stabilisation, Soil contamination, Liquid-to-solid ratio

**Recommended information sources**

BOLAN N., KUNHIKRISHNAN A., THANGARAJAN R., KUMPIENE J., PARK J., MAKINO T., KIRKHAM M.B., SCHECKEL K., 2014: Remediation of heavy metal(loid)s contaminated soils – To mobilize or to immobilize? Journal of Hazardous Materials 266: 141–166

BONTEN L.T.C., GROENENBERG J.E., WENG L., VAN RIEMSDIJK W.H., 2008. Use of speciation and complexation models to estimate heavy metal sorption in soils. Geoderma 146: 303–310

CRANE R.A., SCOTT T.B., 2012: Nanoscale zero-valent iron: Future prospects for an emerging water treatment technology. Journal of Hazardous Materials, 211–212: 112–125

FEST E.P.M.J., TEMMINGHOFF E.J.M., COMANS R.N.J., VAN RIEMSDIJK W.H., 2008. Partitioning of organic matter and heavy metals in a sandy soil: Effects of extracting solution, solid to liquid ratio and pH. Geoderma 146: 66–74

KIM K.-R., OWENS G., 2009. Chemodynamics of heavy metals in long-term contaminated soils: Metal speciation in soil solution. Journal of Environmental Sciences 21: 1532–1540

KOMÁREK M., VANĚK A., ETTLER V., 2013: Chemical stabilization of metals and arsenic in contaminated soils using oxides- A review. Environmental Pollution, 172: 9-22

KUMPIENE J., LAGERKVIST A., MAURICE C., 2008: Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments – A review. Waste Management, 28: 215–225

KUMPIENE J., ORE S., RENELLA G., MENCH M., LAGERKVIST A., MAURICE C., 2006: Assessment of zerovalent iron for stabilization of chromium, copper, and arsenic in soil. Environmental Pollution, 144: 62–69

MUELLER N.C., NOWACK B., 2010: Nanoparticles for remediation: Solving big problems with little particles. Elements 6: 395-400

VÍTKOVÁ M., RÁKOSOVÁ S., MICHÁLKOVÁ Z., KOMÁREK M., 2016. Metal(loid)s behaviour in soils amended with nano zero-valent iron as a function of pH and time. Journal of Environmental Management. In press.

**Expected date of thesis defence**

2017/18 SS – FES

**The Diploma Thesis Supervisor**

Mgr. Martina Vítková, Ph.D.

**Supervising department**

Department of Environmental Geosciences

Electronic approval: 15. 8. 2016

**prof. RNDr. Michael Komárek, Ph.D.**

Head of department

Electronic approval: 17. 8. 2016

**prof. RNDr. Vladimír Bejček, CSc.**

Dean

Prague on 11. 12. 2017

## DECLARATION

I hereby declare that the present Diploma Thesis entitled "Efficiency of nano zero-valent iron application in soil under different incubation conditions" is my own work and the literature and other sources, which I used, are stated list of references which are attached to this work.

In Prague, 15$^{th}$ of December 2017

………….……………………

George Kofi Gordor

## ACKNOWLEDGEMENT

# ABSTRACT

Nano zero-valent iron (nZVI) is continuously being studied as its use as a stabilising chemical agent for remediating contaminated water and soils evolves. This study is focused on the efficiency of nZVI application in soil as a potential sorbent of the risk elements in soils under different incubation conditions. A set of leaching experiments in combination with geochemical modelling has been performed, with the emphasis on the leaching behaviour of contaminants and their release as a function of the liquid-to-solid ratio (L/S). The behaviour of zinc (Zn), lead (Pb), cadmium (Cd), and arsenic (As) was investigated in control soils and test samples (amended with 1% (w/w) of nZVI) and the results were evaluated.

Firstly, both the control and nZVI-treated soil samples were subjected to incubation in order to reach pseudo-equilibrium conditions under various moisture content. The pots were maintained at 0%, 30%, 60%, 90% and 130% of water holding capacity (WHC) for 3 months. The samples were dried and subjected to a set of laboratory experiments at L/S 2, 5, and 10 ml/g, respectively. The test included physico-chemical measurements and metal concentrations analyses.

The influence of moisture content on the leaching behaviour was element specific. The best result for the stabilisation of Pb was observed at 60% moisture content, while 90% moisture content was the best condition for the stabilisation of Zn, Cd and As. The addition of nZVI to the soil generally increased pH across the various samples used and decreased the amount of metal(loids) leached from the samples. The effectiveness of immobilisation of contaminants by nZVI depends on several factors and as such deep analysis should be carried out before its use in the field.


**Key words:**

Nano-iron, Chemical stabilisation, Soil contamination, Liquid-to-solid ratio.

# TABLE OF CONTENTS

# 1. INTRODUCTION

## 1.1 Background

Restoring contaminated soils to pristine conditions is one of the main concerns for environmental scientists today (Mueller and Nowack, 2010). Of the many innovative techniques, environmental scientists are using nano zero-valent iron (nZVI) as they are cost effective and a less distractive method (Mueller and Nowack., 2010; Komáreket al., 2013). Also, due to its high reactivity, nZVI shows high potential for environmental remediation as was shown in numerous laboratory and field studies (Nurmi et al., 2005; Kumpiene et al., 2006; Komárek et al., 2013; O'Carrol et al., 2013.

Many studies have looked at nZVI and reported successful treatment of soils contaminated with metal(loid)s (Gil-Díaz et al., 2014a, b; Vítková et al., 2017). Nanoiron, being a strong reducing agent, oxidizes into secondary oxides that trap metal(loid)s and effects the speciation of redox-sensitive elements like As (Gil-Díaz et al., 2014b).

Various factors affect the leaching behaviour of metalloids in the soil including but not limited to liquid-to-solid ratio, time, pH-Eh, leaching available fraction, particle size and morphology (Evanko and Dzombak., 1997). Generally, the leaching of most metals increases at low pH and increasing redox potential (Kumpiene et al., 2008; Schulin et al., 2010; Antoniadis et al., 2008; Vítková et al., 2017)

This diploma thesis focuses on the study of nZVI as a sorbent and its behaviour in soils under simulated site-specific conditions, as information on this aspect is still limited. The results of this work and its further developments will provide valuable information about the performance of nZVI in remediating contaminated soils under different environmental conditions and the influence of pH-Eh on the behaviour of nZVI as an intensively studied agent in decontamination technology.

## 1.2 Purpose and aims of the study

The overall aim of this study is to determine the efficiency of nano zero-valent iron (nZVI) application in soil under different conditions. To accomplish this aim, the following specific objectives are addressed;

(i)     Assess the effect of different moisture content and liquid-to-solid ratio on the leaching behaviour of contaminants in soil amended with nZVI.

(ii)    Evaluate the effect of different moisture content on the changes in pH-Eh conditions.

(iii)   Assess the optimal conditions for efficient metal stabilisation in soils by nZVI.

## 2. REVIEW OF LITERATURE

### 2.1 Soil contamination with risk metal(loid)s

A soil is said to be contaminated if the present concentration of contaminant in the soil is above the background level and causes the loss of some soil functions (ec.europa.eu). Metals abound naturally in the soil, some of which are needed for plants and other soil living organisms, but rarely in toxic levels with their concentrations spatially variable (Pierzynski et al., 2005). Table 1 illustrates common and geochemically anomalous levels of selected metals/metalloids. Risk metals represent the highest percentage of various types of contaminants found in contaminated sites in the European Union as seen in Figure 1 (Huber and Prokop, 2012). Contamination sources range from industrial activities, poor waste disposal, mining, military activities to accidents (ec.europa.eu). The most discussed metalloid contaminants include As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn (Dermont et al., 2008). This study is focused on Pb, Zn, As, and Cd, which are described in chapter 2.2

Table 1. Selected metal(loid)s with their common and anomalous concentrations in soils (Pierzynski et al., 2005)

| Element | Normal range [mg/kg] | Metal-rich range [mg/kg] |
|---|---|---|
| Arsenic (As) | <5 to 40 | Up to 2500 |
| Cadmium (Cd) | <1 to 2 | Up to 30 |
| Copper (Cu) | 2 to 60 | Up to 2000 |
| Molybdenum (Mo) | <1 to 5 | 10 to 100 |
| Nickel | 2 to 100 | Up to 8000 |
| Lead (Pb) | 10 to 150 | 10000 or more |
| Selenium (Se) | < 1 to 2 | Up to 500 |
| Zinc (Zn) | 25 to 200 | 10000 or more |
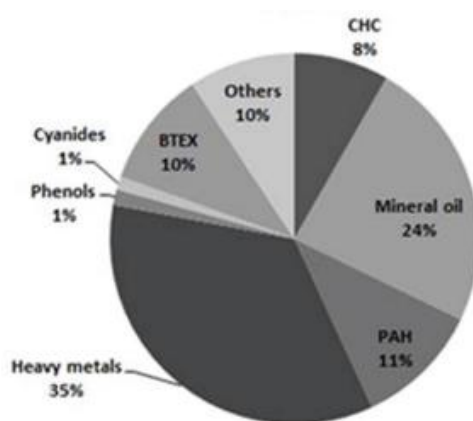
Figure 1. Most frequently occurring contaminants in soil (Huber and Prokop, 2012). BTEX = Benzene, toluene, ethylbenzene and xylene. PAH = Polyaromatic hydrocarbons. CHC = Chlorinated hydrocarbons.

The Příbram region represents one of the most polluted sites with sources from mining and smelting activities. The known risk metals in the area include Zn, Pb and other risk elements like Cd and As (Vítková et al., 2017).

## 2.2 Characteristics of risk metals and arsenic

Risk metals in soils is often present in several forms with different levels of solubility as follows: (i) dissolved (in soil solution), (ii) exchangeable (in organic and inorganic components), (iii) structural components of the lattices in soils and (iv) insolubly precipitated with other soil components (Aydinalp and Cresser, 2003; Ur Rehman et al, 2012).

### 2.2.1 Zinc (Zn)

Zinc is a transition metal that occurs in ores such as sphalerite (ZnS), the principal Zn ore, and wurtzite ((Zn,Fe)S), a less encountered mineral. Zinc exhibits only one oxidation state of +2. At low concentrations in the soil, Zn is essential for plant growth as well as in animal nutrition (Schulin et al., 2010).

### 2.2.2 Lead (Pb)

Lead is a naturally occurring, bluish-grey metal usually found as a mineral combined with other elements, such as sulphur, i.e., galena (PbS), anglesite (PbSO$_4$), or oxygen, i.e., cerussite (PbCO$_3$). However, there is little evidence for nutritive role of Pb in

plants and animals (Hooda, 2010). Lead has three naturally occurring oxidation states: Pb (0), Pb(II) and Pb(IV). However, Pb(II) is important over the wide range of environmental conditions that exist in soils.

### 2.2.3 Cadmium (Cd)

Cadmium is a soft, silver-white metal that occurs as oxides, sulphides, and carbonates complex in Zn, Pb, and Cu ores (UNEP, 2010). It may be present in sphalerite as a solid solution of ZnS (Chaney, 2010). The average concentrations of cadmium in soils range from $0.1 \, \text{mg kg}^{-1}$ to $11 \, \text{mg kg}^{-1}$ (Bradl, 2004). In solution, Cd occurs largely as a divalent ion $Cd^{2+}$ (Wuana and Okeimen, 2011).

### 2.2.4 Arsenic (As)

Arsenic is a metalloid that occurs naturally in many mineral ores including Cu, Zn, Ag and Au ores. Arsenic can be present in several oxidation states ($-3$, $0$, $+3$ and $+5$) (Smedley and Kinniburgh, 2002). Compared to Cd, Pb and Zn it forms oxyanion species, such as: $AsO_4^{3-}$ or $AsO_3^{3-}$ (Wuana and Okieimen, 2011) and occurs together with Fe and S (Frumkin and Thun, 2008).


### 2.3 Factors that affect mobility of metals in soils.

As has been already indicated, the mobility and availability of risk metals in the soil is affected by some soil properties like; pH, organic matter, cation exchange capacity (CEC), oxidation-reduction status (Eh), clay mineral content, calcium carbonate, Fe and Mn oxides (Kashem and Singh, 2001; Antoniadis et al., 2008; Schulin et al., 2010).

### 2.3.1 pH

pH is considered as the key factor of metal mobility and bioavailability due to its strong influence on the speciation and solubility of metals in the soil especially under oxidising conditions (Kumpiene et al., 2008; Schulin et al., 2010; Gil-Díaz et al., 2014; Vítková et al., 2017). Risk metal sorption onto soil constituents is known to decrease with decreasing pH and vice versa (Antoniadis et al. 2008; Zeng et al. 2011). Metal cations are mostly mobile under acidic conditions while anions sorb to oxide minerals in acidic environments. On the other hand, at high pH ranges, cations precipitate or adsorb to mineral surfaces while anions are mobile (Zeng et al., 2011). The availability

of Zn and Pb increases with a decrease in soil pH as observed by Chaney (2010), UNEP(2010) and Vítková et al. (2017). At higher pH values, Zn can form carbonate precipitate ($ZnCO_3(s)$) and hydroxide ($Zn(OH)_2(s)$) (Evanko and Dzombak, 1997). At pH above 6 units, Cd is adsorbed by the soil solid phase or is precipitated, and thus lowering the concentrations of dissolved cadmium (UNEP, 2010).

Conversely, As, an anion-forming element, shows a different leaching trend. No significant leaching is observed at low pH with leachability increasing at higher pH values (Cappuyns and Swennen, 2008; Wuana and Okieimen, 2011; Vítková et al., 2017).

### 2.3.2   Oxidation-reduction status (Eh)

Redox potential has been well documented in many studies as a critical factor in metal mobility in soils. Considerable quantity of Zn is released to solution under well oxidised conditions, whereas low abundances are present under moderately and intense reducing conditions (Gambrellet al., 1991; Schulin et al., 2010). Lead concentrations are low at low Eh and rise when the Eh increase, which can be attributed to interactions with dissolved organic carbon and manganese and precipitation such as sulphide (Husson 2013).

Arsenic can mobilise over a range of redox conditions (Smedley and Kinniburgh, 2002). Under aerobic conditions and at low pH values arsenate co-precipitates with or is adsorbed onto iron hydroxides. Pentavalent forms of As (e.g. arsenate $AsO_4^{3-}$), which are dominant in aerobic conditions, has less toxicity than trivalent compounds (e.g. arsenite $AsO_3^{3-}$) (Ampiah-Bonney et al., 2007). Kumpiene et al. (2009) reports that under anoxic conditions, arsenate can be easily reduced to mobile arsenite.

### 2.3.3   Presence of organic matter

Organic matter (OM) contributes to the soils ability to retain risk metals (Tack., 2010; Zeng et al., 2011). Risk metal adsorption onto soil constituents lowers with less organic matter in soils and vice versa (Dai et al., 2004; Antoniadis et al., 2008). Organic matter enhances adsorption of As in agricultural soils (Cao and Ma, 2004). Organic matter effect on metal mobility has shown to be pH dependent with slight acidic (pH 5.5) conditions, fostering low As leaching, whereas at neutral soil pH, chemical reduction of As(V) to As(III) and consequent leaching was induced by compost (Shiralipour et al, 2002). Lead may form insoluble, highly stable complexes

with organic matter reducing its lability (Usman et al., 2006). Cadmium solubility decreases with organic matter inputs because of the induced decrease in Eh (Husson, 2013). Dissolved organic matter in soils could increase risk metal release and subsequent uptake to plant roots (Du Laing et al., 2009).

### 2.3.4 The effect of liquid-to-solid ratio (L/S) on risk metals

The liquid-to-solid ratio of risk metals largely affects their mobility and bioavailability in soils (AlAbed et al., 2004; Degryse et al., 2009; Tang and Steenari, 2016). Metal concentrations decrease in most cases with increasing L/S ratio (AlAbedet al., 2004; Astrup et al., 2006; Silva et al., 2018). For instance, in the work by Tang and Steenari (2016), Pb concentrations decreased significantly from more than 90% to about 20% with increasing L/S ratio. Zinc and Cd in the same studies showed little differences in concentrations after samples were extracted at different L/S ratios. Negative correlation between concentrations of As and Cd with L/S ratio was reported by Silva et al. (2018).

## 2.4 Soil remediation

To remediate contaminated soils, it is essential to know both the physical and chemical properties of the contaminant as these strongly influence the selection of the applicable remediation approach (Wuana and Okieiman, 2011). Moreover, a detailed site characterisation must be performed to assess the mobility of risk elements and set the optimal remediation conditions, and the final use of the contaminated medium needs to be considered as well (Mulligan et al., 2001).

### 2.4.1 Remediation technologies for metal(loid) contaminated soil

There are various technologies available for the remediation of soils contaminated with risk metals. Different approaches include isolation, immobilisation, toxicity reduction, physical separation and extraction (Mulligan et al., 2001; Khalid et al., 2016). Usually, a combination of two or more of the approaches increases the feasibility and efficiency (Evanko and Dzombak, 1997). The next paragraph focuses

on chemical stabilisation for this study. For an overview of remediation technologies, their description and applicability see Mulligan et al. (2001) and Khalid et al. (2016).

### 2.4.2 Chemical stabilisation of metal(loid)s in contaminated soils

Chemical stabilisation is a soil remediation technique which involves adding organic or inorganic amendments to contaminated soils to decrease the mobility, bioavailability and bioaccessibility of the target contaminant (Komárek et al., 2013).Such amendments include e.g., phosphates, natural and synthetic aluminosilicates, iron-oxides, bio solids, amorphous manganese oxide (Kumpiene et al., 2008; Hooda, 2010; Ettler et al., 2012; Komárek et al., 2013; Michálková et al., 2016b). Risk metals, unlike organic contaminants, are not degradable and remain in soils indefinitely (Kumpiene et al., 2008; Hooda, 2010; Gil-Díaz et al., 2014). Therefore, the immobilisation of risk elements in the soil is about the feasible, cost effective methods for cleaning up contaminated soils (Kumpiene et al., 2008; Lee et al., 2011). Also, soil deterioration hardly occurs from the use of chemical amendments in the right dose unlike other methods (Kim et al., 2017).

The use of contaminant-immobilising amendments can decrease metal/metalloid bioavailability through sorption processes, which include adsorption to mineral surfaces, formation of stable complexes, and surface precipitation or ion exchange (Kumpiene et al., 2008). Identifying the type of sorption process occurring in a soil is difficult as all the processes may be happening all at once (Lair et al., 2007). The different processes of chemical stabilisation are summarised in Figure 2.
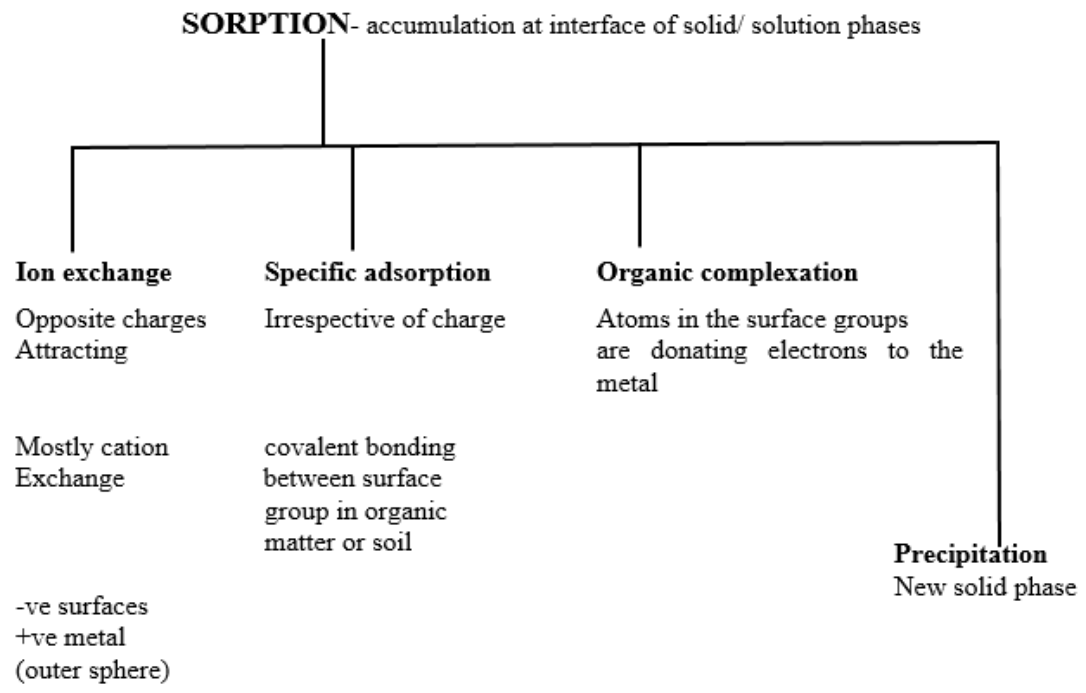
Figure 2. Sorption processes that occur in chemical stabilisation (Nwuchekwa, 2007)

## 2.5 Nano scale zero-valent iron (nZVI)

Nano zero-valent iron is one of the potential amendments used in the chemical stabilisation of contaminated soils. A particle of nZVI as shown in Figure 3, consists of a core and shell (Li et al., 2006).
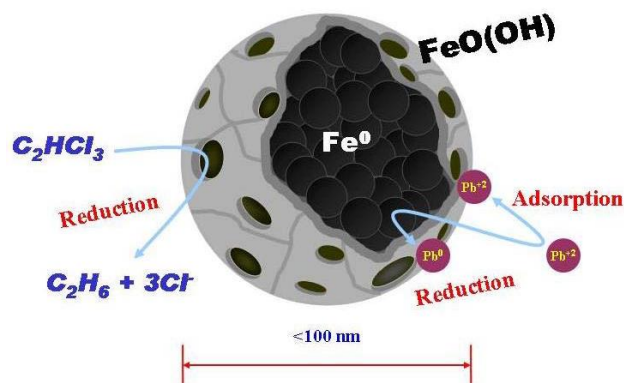


Figure 3. A 3-dimensional core-shell model of nZVI particle (GeoNano Environ. Tech., Inc)

The core is made up of mainly metallic iron that provides the reducing power for reactions, while the shell with mixed valence [$Fe^{2+}$, $Fe^{3+}$] serves as site for complex formation. The shell comprises iron oxides and hydroxides that resulted from the oxidation and hydrolysis of the core (Li et al., 2006; Li et al., 2007; Hooda, 2010).As shown by equation 1, nZVI ($Fe^0$) with zero net charge loses electrons and thus

17

becomes oxidised reducing the metal in the process. The sorption of metalloids onto oxide occurs as a result of the coordinating and electrostatic interactions with metal ions on the surface and can be summarised by the reaction in equation 2 (Li et al., 2007)

Reduction: $Fe^0 + M^{2+} \longrightarrow Fe^{2+} + M^0$ \hfill (1)

Sorption: $\equiv Fe\text{-}OOH + M^{2+} \equiv \longrightarrow Fe\text{-}OOM + H^+$ \hfill (2)

Nano zero-valent iron have high reactivity (Mueller and Nowack, 2010; O'Carroll et al., 2013; Li et al., 2016) as a result of their high specific surface area (tens to hundreds of $m^2\ g^{-1}$) and high sorption capacity (Komárek et al., 2013).

## 2.5.1   Advantages of using nZVI

Include:

I.   They are able to remove various risk metal(loid)s simultaneously(Li et al., 2016). Li et al., (2016) successfully removed multiple risk metals (Cu, Ni, Zn) with over 90% efficiency.

II.   It sorbs both anions and cations owing to its amphoteric nature (Cornell and Schwertmann, 2003). This occurs because of protonation and deprotonation of the functional groups on them (McBrige, 1994).

III.   One other advantage of using nZVI is that, it is one of the few amendments which causes minor changes in pH, preventing pH fluctuations (Kumpiene et al., 2006; Wang et al. 2016).

The concern about this amendment is its limited mobility and the lifetime of nZVI particles (Mueller and Nowack, 2010; Gómez-Pastora et al., 2014). Some studies have reported negative influence of nZVI on plants and microbes. Němeček et al (2014) reported toxicity towards many microbial species.

## 2.5.2   Interaction of nZVI with risk elements

According to O'Carroll et al. (2013) nZVI-metal interactions for the various metalloids can be one of the following processes:

I.   Adsorption; Cr, Pb, Ni, Co, Cd, Zn, Ba, As, Se,

II.   Oxidation/re-oxidation; Se, As, U, Pb.

III.   Reduction; Se, Co, Pd, Pt, Hg, Ag, Cr, As, Cu, U, Pb, Ni,

IV.    Precipitation; Cu, Pb, Cd, Co, Zn
V.    Co-precipitation; Cr, As, Ni, Se.

The type of stabilisation process involved in lowering the amount of risk metals by nZVI depends on the redox potential of the risk metal species (O'Carroll et al. 2013). Cadmium and zinc with more electronegative redox potential than that of the iron are removed by sorption (O'Carroll et al. 2013; Vítková et al. 2017).Studies by Liang et al. (2014) reported that Zn was successfully immobilised by using nZVI due to adsorption and co-precipitation. Work by Boparai et al., (2013) further proved Cd removal by adsorption processes. Metals with slightly more positive redox potential than $Fe^0$ (e.g., Pb and Ni) can be removed by both reduction and adsorption (Li and Zhang, 2007; O'Carroll et al., 2013). Lower levels of Pb were achieved by reduction and adsorption after treatment with nZVI as concluded by Fu et al. (2015) and Wang et al. (2016).

Metalloids such as As with much more positive redox potential than nZVI are favourably removed by reduction and precipitation (Li et al., 2006). The results provided in studies by Kumpiene (2006), Ramos et al. (2009), O'Carroll et al. (2013), Li et al. (2016) or Vítková et al. (2017) have sufficiently documented the effectiveness of nZVI as an amending agent for arsenic. Nano zero-valent iron reduces less toxic arsenate ($As^{5+}$) to arsenite ($As^{3+}$) which is a toxic and mobile form of arsenic (Ramos et al., 2009).  Arsenite is then adsorbed or co-precipitated at the surface of the nanoiron alongside left over $As^{5+}$ (Ramos et al., 2009). Figure 4 shows the interaction of nZVI with some of the risk elements.
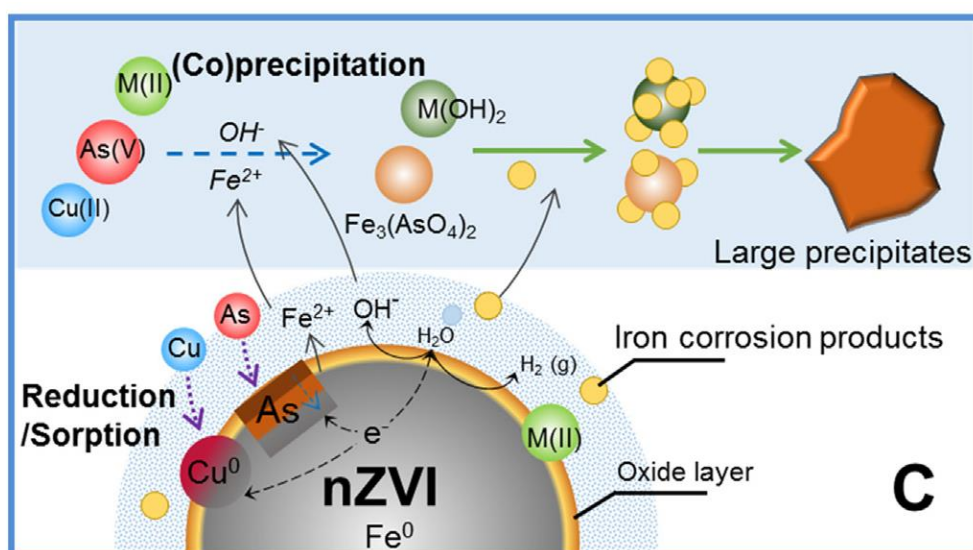


Figure 4. Scheme of removal processes of risk elements using nZVI (Li et al., 2016)

# 3. MATERIALS AND METHODS

## 3.1 Nanoiron

Nano zero-valent iron from NANO IRON, Ltd. (Czech Republic) in the form of surface stabilised air-stable nano powder (NANOFER STAR) was used. Each particle is coated with a thin layer of Fe oxides that protects nZVI from rapid oxidation. Based on the manufacturer's recommendation of 1:4 solid-to-liquid ratio, 10 g of demineralised water was added to 2.5 g of 1% w/w nZVI and intensively mixed to remove the Fe oxide coating (protective layer).

## 3.2 Soil samples

The soil samples were collected from the superficial layer (0-25 cm) of the alluvium of Litavka River (Příbram District, Czech Republic), air-dried, homogenised and sieved through a 2-mm stainless sieve (Vítková et al., 2017).

An experimentally determined water holding capacity ($WHC_{100\%}$) of 47.8 g DEMI water /100 g solid was reported (Vítková et al., 2017, unpublished results). Other basic soil properties are given in table 2.

Table 2. Soil properties of the studied soil type (Vítková et al., 2017)

| Soil type | $pH_{H2O}$ | $pH_{KCl}$ | Particle size distribution (%) | | |
| --- | --- | --- | --- | --- | --- |
| | | | Clay | Silt | Sand |
| Fluvisol | 5.95 | 5.14 | 5 | 20 | 75 |

**Bulk chemical composition (mg/kg)[a]**

| Al | As | Ca | Cd | Fe | K |
| --- | --- | --- | --- | --- | --- |
| $8191 \pm 1542$ | $296 \pm 5$ | $1099 \pm 99$ | $39 \pm 0.90$ | $37408 \pm 159$ | $6583 \pm 239$ |

| Mg | Mn | Na | Pb | Zn |
| --- | --- | --- | --- | --- |
| $675 \pm 142$ | $4276 \pm 28$ | $5571 \pm 306$ | $3539 \pm 306$ | $4002 \pm 55$ |

[a]Mean $\pm$ standard deviation *(n = 3)*

## 3.3 Incubation of studied soil at different water content

A mass of 250 g of soil was weighed and transferred into a plastic pot. In total, nine pots representing nine different incubation conditions (i.e., 0%, 30%, 60%, 70%, 80%, 90% and >100% of WHC, and frozen samples denoted as F1, F2) were prepared. The

activated nZVI was added to the treated sample pots. A specific weight of deionised water was added to each pot based on the WHC of the soil (table 3) and maintained for 3 months. Anaerobic conditions were simulated by adding >100% of WHC so that the sample was approximately 0,5 cm under the water level. Samples F1 and F2 were prepared with 60% WHC and frozen for 3 months (F1) or frozen for last 15 days of the 3-month period (F2), respectively (Figure 5). This treatment should simulate the effect of freeze during winter, in other words, what happens in permanently or temporarily frozen lands.

Table 3. Quantity of deionised water added to each pot

| Pot label | 0 % | 30 % | 60 % | 70 % | 80 % | 90 % | 130% | F1 | F2 |
|---|---|---|---|---|---|---|---|---|---|
| WHC | 0 % | 30 % | 60 % | 70 % | 80 % | 90 % | 130% | 60 % | 60 % |
| DEMI $H_2O$(g) | 0 | 36 | 72 | 84 | 96 | 108 | 155 | 60 | 60 |

WHC (100%) = 47.8g DEMI water /100g solid (*experimentally defined*)
WHC (100%) / 250g solid = 119.5g DEMI water

Moisture content was maintained by regular addition of water (through checking the weight of individual pots) and covering the pots with porous filter to avoid excessive evaporation. The samples were thoroughly mixed occasionally to effectively distribute the nano-irons, homogenise the samples and keep them aerated (except for the flooded sample). After the incubation period, the soil was dried (30°C) and gently homogenised.



Figure 5. Image of samples during incubation.

## 3.4 Determination of physico-chemical parameters (pH/Eh/EC)

To evaluate the changes in pH-Eh conditions dry samples were prepared and used for the determination of pH per ISO standard (ISO 10390:2005). In particular, 5 ml of each soil sample was put in a 50-ml centrifuge tube and 25 ml of either demineralised water ($pH_{H2O}$) or 1 M KCl ($pH_{KCl}$) was added. The suspension was agitated for 60 min using a horizontal shaker (GFL3005, Germany; Figure 6). Then, the suspension was allowed to settle down for 1 hour and after that pH, Eh and electrical conductivity (EC) were measured directly (Figure 7). Measurements were carried out for each of the 9 test samples and their control in duplicates.



Figure 6. Horizontal shaker (GFL 3005, Germany) for continuous mixing of soil and water.



Figure 7. Measurement of pH, Eh and EC of the soil samples.

### 3.4.1 Determination of pH

The pH of the soil was measured using a probe of pH meter (inolab® (pH7310, WTW, Germany)). Standardised buffers 4.00, 7.00, 10.00 (WTW, D- 822362, Germany) were used to calibrate the probe before use.

### 3.4.2 Determination of Eh

The probe of a digital multimeter (multi 3420 WTW, Germany) (value of the reference electrode is 207 mV for 25 °C) was inserted into the soil solution to measure the Eh. The value for the electrode was confirmed with a standard redox buffer solution (220 mV; WTW, RH 28, Germany). The displayed Eh values were recorded as $Eh_{measured}$. The final corrected Eh values were calculated using the equation (3):

$$Eh = Eh_{measured} + Eh_{reference} \tag{3}$$

where $Eh_{reference} = 207$ mV

For subsequent geochemical modelling using the PHREEQC-3 software, the final Eh value was converted to activity of electrons (pe) using the equation (4):

$$pe = \frac{Eh(v)}{0.05916} \tag{4}$$

### 3.4.3 Determination of electrical conductivity

The electrical conductivity was measured using a multimeter (multi 3420 WTW, Germany) equipped with a conductivity cell. The probe was inserted into the supernatant of the solid soil and the value recorded.

During the measurements of the various parameters, the electrodes were carefully cleaned and dried using demineralised water and cellulose paper, respectively, in between different samples.

## 3.5 Leaching experiments at different liquid-to-solid ratio.

To study the effect of liquid-solid ratio (L/S) on the released amount of risk metals, extractions of the soil samples were conducted at different L/Ss. The one stage leaching test also served as basis for geochemical speciation modelling. All extractions for this thesis were performed using demineralised water as the extractant. The use of water as a solvent allows identifying the most mobile and potentially available metal species. The liquid-to-solid ratios used in this study were as follows: L/S = 2 ml/g (EN 12457-1), L/S = 5ml/g, and L/S = 10 ml/g (EN 12457-2) (Table 4). For practical

reasons, the leaching experiments were done for all the soil samples at L/S 10 in duplicates, but selected samples were used for the L/S 2 and L/S 5 experiments as shown in table5and done in triplicates.

Physico-chemical properties (pH, Eh and EC) of the centrifuged solution were measured immediately using an inoLab® pH metre (pH 7310, WTW, Germany) and/or digital multimeter (Multi 3420, WTW, Germany). The solution was filtered using a polycarbonate vacuum filtration apparatus (Sartorius) fitted with 0.45 μm filter paper (Millipore).

Table 4. Mass of soil used and pots selected for the experiments.

| L/S | Mass of soil (g) | Volume (ml) | Selected pots |
|---|---|---|---|
| 2 | 15 | 30 | 0%, 30%, 60%, 90%, 130%, F1, F2 |
| 5 | 6 | 30 | |
| 10 | 3 | 30 | ALL POTS |

### 3.5.1 Determination of major and trace element concentrations

Filtered samples were diluted and acidified (to contain 2% $HNO_3$) and passed to the analytical laboratory of the Department of Environmental Geosciences, FES, CULS Prague to determine bulk concentrations of major and trace elements including the target metal(loid)s using inductively coupled plasma optical emission spectrometry (ICP-OES; Agilent 730, Agilent Technologies, USA).

### 3.5.2 Determination of non-metals concentrations

Filtered solutions were diluted based on the recorded conductivity measured for each sample and passed to the analytical laboratory of the Department of Environmental Geosciences to measure dissolved organic carbon (DOC) and total carbon contents using carbon analyser TOC-L CPH (Shimadzu, Japan) and inorganic anions using Dionex ICS-2000 ion chromatography system (Dionex, USA).

## 3.6 Data treatment and geochemical modelling

The experimental data (means and standard deviations) were statistically treated and graphs plotted using the SigmaPlot 13 (StatSoft Inc., USA). The PHREEQC-3 geochemical code (version 3 for Windows) (Parkhurst and Appelo, 2013) was used to

determine the possible oversaturation with respect to solid phases (saturation indices, SI). The T_H.DAT database was used for all the calculations, which enables the use of DOC in the simulations as documented by Ettler et al. (2012) and Michálková et al. (2016a).

# 4. RESULTS

## 4.1 Changes in the physico-chemical parameters of the soil

### 4.1.1 Soil pH

The natural active and exchangeable pH of the soil was in the range of 5.3-7.1 and 4.9-6.6, units respectively, for all variants (Figure 8). There was initial decline of soil pH (active and exchangeable) as the moisture content increased from 0% till 60%. The trend changed from 60% WHC and increased afterwards with higher water content. For instance, in the nZVI treated sample, $pH_{H2O}$ decreased from 6.0 in the 0% to 5.4 in the 60% moisture sample and then increased to 7.1 in the 130% sample (Figure 8). The flooded sample (>130% WHC) recorded the highest values in active $pH_{H2O}$ of 7.1 and $pH_{KCL}$ of 6.6, while sample with 60% moisture content recorded the lowest pH values (figure 8). For the frozen samples, pH for F1 (frozen for 3 months) was higher than that which was frozen for a 15-day period (F2). The effect of liquid-to-solid ratio on pH was mostly increasing for an increase in liquid-to-solid ratio for all variants of moisture contents with just a few exceptions as seen in Table 5. Liquid-to-solid ratio 2 had the lowest pH values in the range of 5.30- 6.97 units, followed by L/S 5 then L/S 10 for samples that had the same conditions. Overall, the application of the nZVI amendment resulted in a significant increase in soil pH for most of the incubation conditions at various L/S ratios compared to the control (Figure 8, Table 5) except for F1 (3 months frozen) and $pH_{H2O}$ for 0% and 30% WHC.
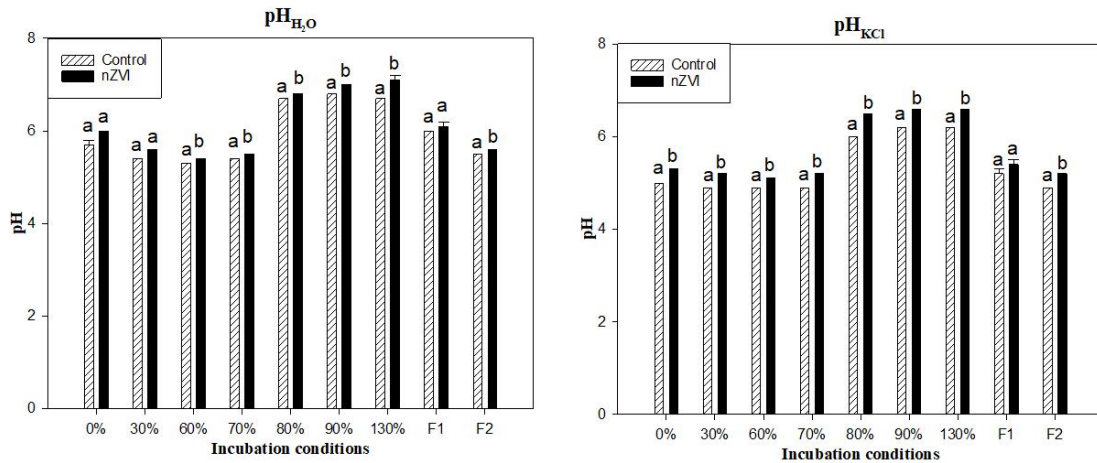
Figure 8. Changes in pH measurements as a function of incubation conditions. (mean ± SD; n = 3) F1= frozen 3 months, F2= frozen 15 days. Statistical evaluation was performed separately for each incubation condition. Data with the same letter represent statistically identical values (P < 0.05).

Table 5. pH ($H_2O$) changes as a function of liquid-to-solid ratio (means; n = 3)

|  | Control |  |  | nZVI |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| L/S | 2 | 5 | 10 | 2 | 5 | 10 |
| 0% | 5.71 ± 0 | 5.74 ± 0 | 5.59 ± 0 | 5.84 ± 0.01 | 5.99 ± 0 | 6.12 ± 0.3 |
| 30% | 5.42 ± 0.01 | 5.54 ± 0 | 5.60 ± 0 | 5.52 ± 0.07 | 5.80 ± 0 | 6.00 ± 0 |
| 60% | 5.36 ± 0.02 | 5.54 ± 0 | 5.52 ± 0 | 5.34 ± 0.08 | 5.51 ± 0 | 6.11 ± 0 |
| 90% | 6.62 ± 0.04 | 6.64 ± 0 | 6.64 ± 0 | 6.90 ± 0.01 | 6.97 ± 0 | 6.94 ± 0.1 |
| 130% | 6.48 ± 0.05 | 6.62 ± 0.01 | 6.81 ± 0 | 6.88 ± 0.01 | 7.02 ± 0 | 6.52 ± 0 |
| F1 | 5.74 ± 0.02 | 5.93 ± 0 | 6.04 ± 0 | 5.88 ± 0.06 | 5.95 ± 0 | 6.23 ± 0 |
| F2 | 5.30 ± 0.04 | 5.51 ± 0 | 5.88 ± 0 | 5.40 ± 0.02 | 5.56 ± 0 | 5.52 ± 0 |

Note; F1= frozen 3 months, F2= frozen 15 days.

### 4.1.2  Soil Eh

The Eh values measured in the soil ranged from 411 - 522 mV as indicated in Figure 9. The Eh value for dry soil (0% WHC) was lower than moist samples except the flooded sample (130%) (figure 9). The Eh values measured for nZVI treated sample increased from 427 mV in sample 0% WHC till a peak at 60% WHC and then declined with increasing moisture content. The lowest Eh of 411 mV was recorded in the flooded sample with over 130% WHC test sample. There is no observable Eh trend with changing liquid-to-solid ratio with values of control samples over 500 mV for all L/S ratios except for 130% WHC. Soils treated with a dose of nZVI were generally

characterised by significant lower Eh values as compared to their controls. For all variants of the tested soil, the highest Eh value of 573 mV was measured at sample with control 30% WHC, and F2 (15-day frozen period). Low Eh up to 435 mV (nZVI 130%) were recorded for treated samples (Table 6).
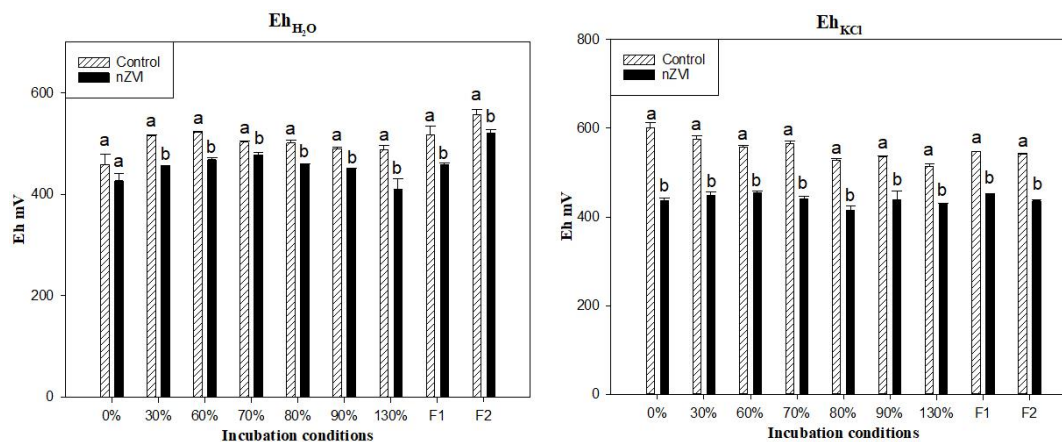


Figure 9. Changes in redox potential as a function of incubation conditions. (mean ± SD; n = 3). Statistical evaluation was performed separately for each incubation condition. Data with the same letter represent statistically identical values (P < 0.05).

Table 6. Eh changes as a function of liquid-to-solid ratio (means; n = 3)

|  | Control |  |  | nZVI |  |  |
|---|---|---|---|---|---|---|
| L/S | 2 | 5 | 10 | 2 | 5 | 10 |
| 0% | 535 | 511 | 568 | 507 | 520 | 547 |
| 30% | 558 | 531 | 573 | 520 | 547 | 545 |
| 60% | 554 | 553 | 572 | 522 | 543 | 535 |
| 90% | 493 | 508 | 521 | 488 | 462 | 441 |
| 130% | 504 | 493 | 513 | 439 | 435 | 492 |
| F1 | 535 | 517 | 560 | 448 | 481 | 517 |
| F2 | 544 | 503 | 573 | 484 | 494 | 562 |

## 4.2 Leaching behaviour of studied metal(loids)

### 4.2.1 Effect of incubation conditions on risk metals and arsenic

The leaching behaviour of the studied metal(loids) with changes in incubation conditions and liquid-to-solid ratios were investigated and shown in Figures 10 and 11, Appendix 2-4). The concentrations of the risk metals and As are in mg/kg to be comparable among different L/Ss. The corresponding physico-chemical properties measured during the leaching experiments at the various L/S ratios are found in Table 5 and 6. Mostly, incubation periods that recorded high pH values, low Eh, had the least leached amounts of the metalloids especially for Zn and Cd. Zinc leached most, followed by Pb, As and Cd, respectively. The leached amounts of Zn ranged between 4.1 mg/kg (90% WHC, L/S 2) at pH 6.62 units to 131.9 mg/kg (F2, frozen 3 months, L/S 2) at pH 5.3 units and Eh 544 mV. For unfrozen soils, Zn concentrations increased from dry sample (0% WHC) till the highest concentration at 121.1 mg/kg at 60% WHC, but leaching decreased with further increase of moisture content (Figure 10). Lead had the second highest amount of its concentration leached, with amounts reaching 43 mg/kg (Figure 10). Unlike Zn, Pb values showed low concentrations for dry sample at 0% WHC as compared to moist soil except for flooded soil extracted at L/S 5 and 10. A decreasing pattern was observed from 0% WHC till minimum values were reached at 60% WHC. The highest Pb concentration leached in soil (43 mg/kg, 130% WHC, L/S 2) represented approximately 1% of total Pb in the soil. The lowest amounts of Pb leached at 60% WHC for all L/Ss ranged between 2.1mg/kg to 15.7 mg/kg. (Figure 10, Appendix 2-4). Arsenic depicted a concave trend like Pb for L/S 5. Their concentrations decreased from 0% WHC till 60% (Figure 11). The highest amount of As leached (90%, control, L/S 5) at pH 6.64 units and Eh 508 mV, represented approximately1% of total As content. Concentrations below detection limit were reported for L/S 2, control 60% WHC and nZVI. Cadmium exhibited leaching trend like that of Zn with the maximum values of Cd released under incubation condition of 60% WHC and frozen for 15 days (Figure 11). A concentration of 1.7 mg/kg representing almost 3.6% of total Cd concentration was leached at this WHC (60%, control, L/S 2) at pH 5.74 units and Eh 535 mV.

In the freezing conditions, metals leaching behaved differently. Whilst Zn and Cd recorded lower concentrations for soil frozen for 3 months, Pb and As yielded higher

amounts for soil frozen for 15 days. The amount of zinc leached in the sample frozen for 15 days (78-141) mg/kg, was almost equivalent to that of its unfrozen counterpart 60% WHC (87-145) mg/kg (Figure 10).

## 4.2.2 Effect of liquid-to-solid ratio on risk metals and arsenic

The influence of liquid-to-solid ratio on metal release has been assessed and their findings are summarised in figures 10, 11 and Appendix 2-4. When the LS ratio was increased from 2 to 10, metal concentrations varied from metal to metal. However, Zn and Cd behaved similarly, yielding their highest concentrations mostly at low L/S of 2 (Figure 10, 11 and Appendix 2-4). For example, highest Zn concentrations of 131.9 mg/kg (nZVI F2), 141 mg/kg (LC F2) and 145 mg/kg (LC 60%) were all measured in the samples with liquid-to-solid ratio of 2. In sample WHC of 90% however, L/S 5 leached the highest amount of 15.34 mg/kg for the nZVI-treated soil (Figure 10). Comparing the different variants, Pb values commonly increased mostly with increasing L/S with few exceptions observed in the dry sample and F1 (15 day frozen). Arsenic tends to yield its highest concentrations at L/S of 5 for most of the incubation conditions with concentrations ranging from 1.02 mg/kg to 2.83 mg/kg (Figure 11).

## 4.2.3 Effect of nZVI on risk metals and arsenic

Generally, lower concentrations of risk metals were released on addition of nZVI. Even though treated samples of Zn, Pb and Cd recorded lower concentrations, significant differences between their means and that of the control were usually recorded for incubation condition 90% WHC (L/S 2 and 5). Samples extracted at L/S of 10 showed very few samples having significant differences between the test samples. Few instances where control sample leached less amount of metals include; (Zn; 0% WHC L/S 2), Pb; 30% WHC L/S 2, 3 and 130% WHC L/S 10, Figure 10, 12). Arsenic behaviour in the samples followed that of the risk metals. Low leachability was observed when soil was treated with nZVI for most variants of incubation conditions. Just like metals, there were significant differences between the treated and control samples at 90% WHC (L/S 2 and 5) mostly.

Figure 10. Leaching of zinc (top row) and lead (down row) as a function of incubation conditions. Statistical evaluation was performed separately for each incubation condition. Data with the same letter represent statistically identical values (P < 0.05).
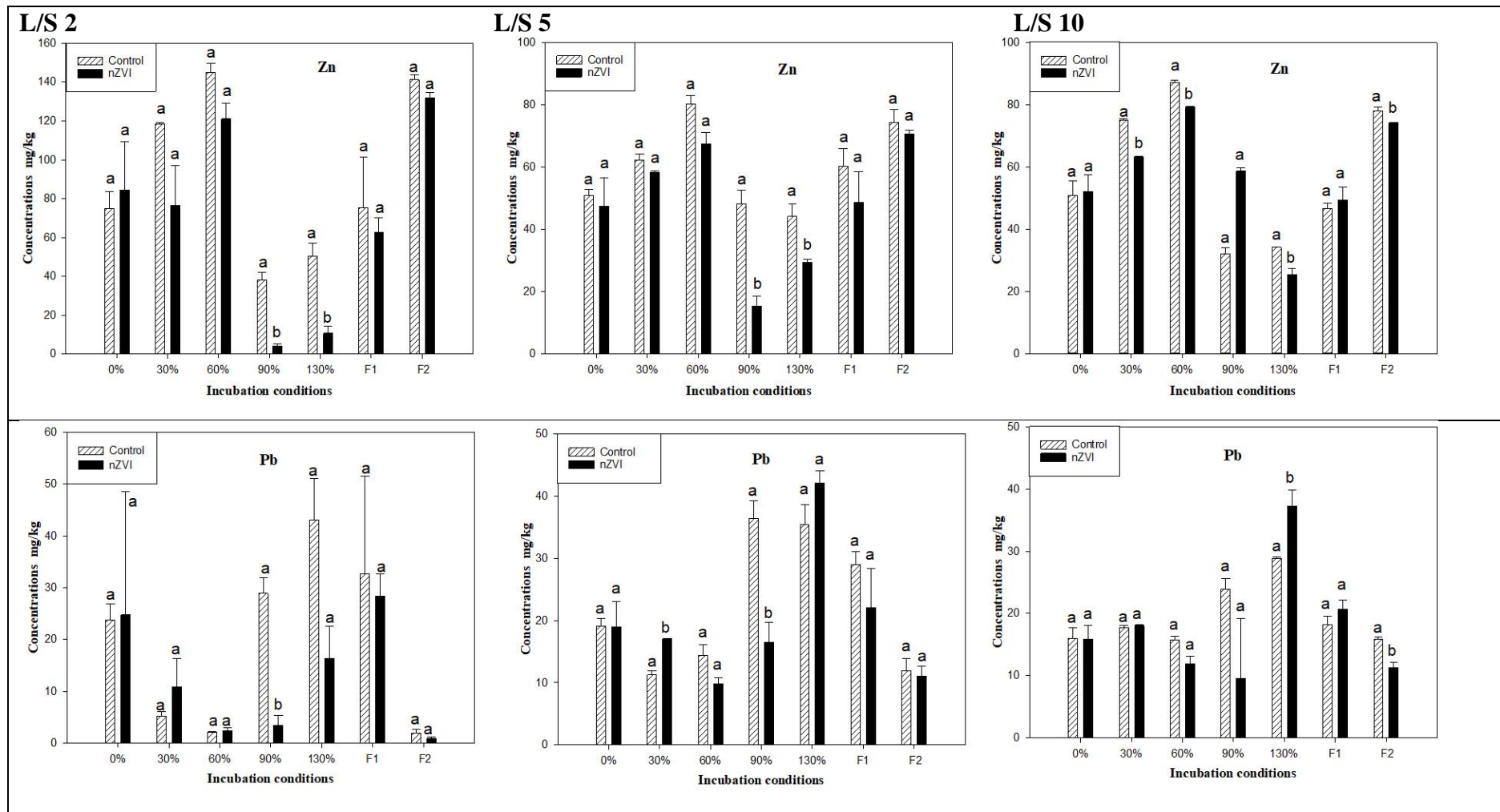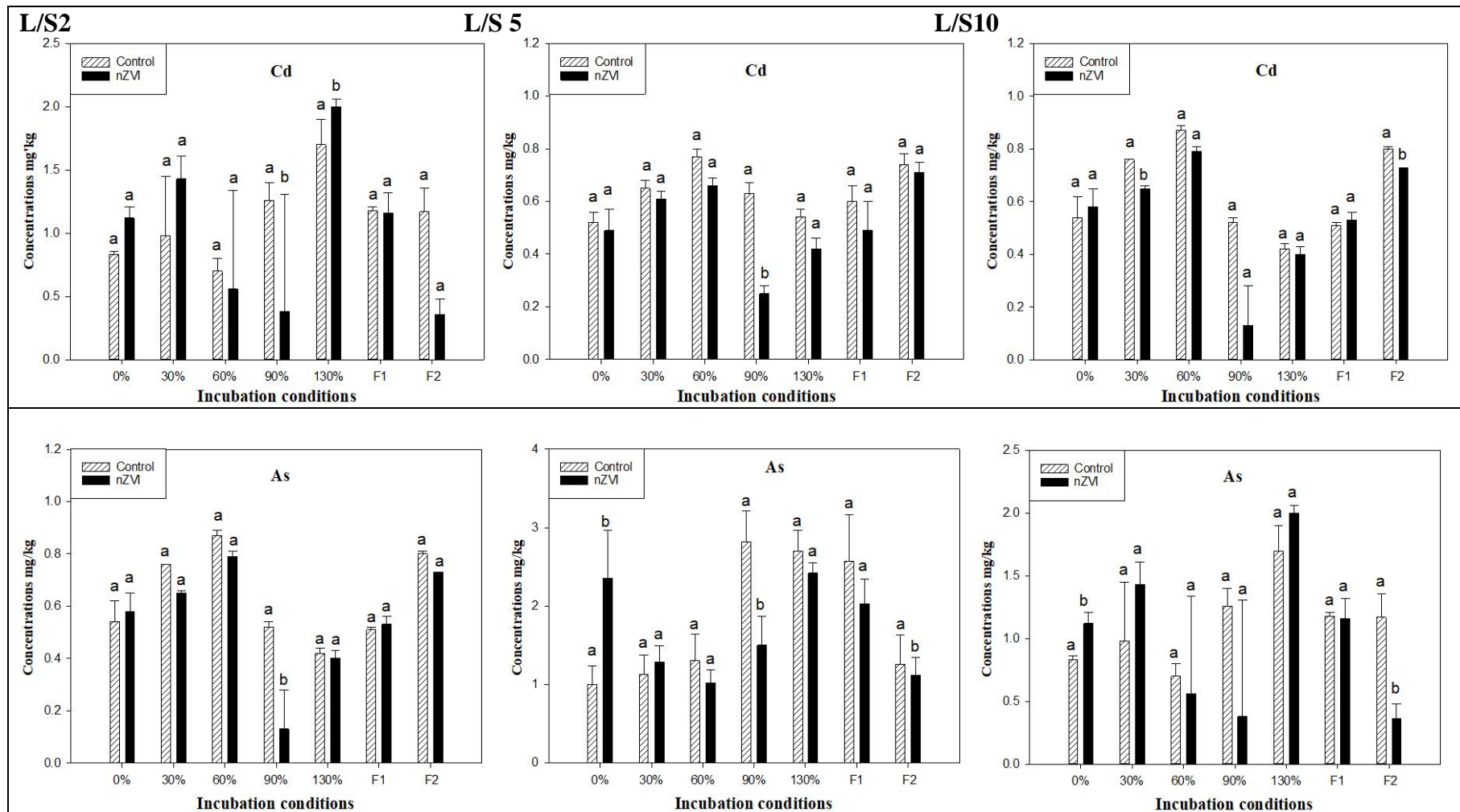
Figure 11. Leaching of arsenic (top row) and cadmium (down row) as a function of incubation conditions. Statistical evaluation was performed separately for each incubation condition. Data with the same letter represent statistically identical values (P < 0.05).

## 4.3 Leaching behaviour of Fe, Mn, DOC and $SO_4^{2-}$

### 4.3.1 Effect of incubation conditions.

The release of major ions (Fe, Mn), DOC and $SO_4^{2-}$ was studied to evaluate their behaviour under the various incubation conditions and L/S (Figures 12 and 13, Appendix 2-4) and influence on metal leaching. A very low amount of Fe was leached for all the different variants of the setup. The highest concentrations of Fe (133.1, 262.05, 203.43 mg/kg) were released at nZVI 130% at L/S 2, 5, and 10 respectively (Appendix 2-4).  Low concentrations of Mn were observed in samples with WHC 60% or less with a sharp increase at WHC 90% (Figure 12). Manganese yielded the highest concentrations (113-180) mg/kg at 90% WHC for the various liquid-to-solid ratios except for L/S 10 where sample nZVI 130% WHC had the highest concentration of 94.06 mg/kg. In the frozen soils, Fe and Mn both leached less concentration for the samples F2 (frozen for 15 days) for the various L/Ss (Figure 12).

Dissolved organic carbon amounts ranged between 72 up to >1000 mg/kg (Figure 13). The highest value of 6566 was detected in the soil sample (90% WHC, control, L/S 10). The concentrations of DOC in leachates were considerably variable with change in the water content of the samples.  Sulphate concentrations displayed different trends for the incubation conditions for the three different L/Ss. For example, it increased marginally with increasing WHC for L/S 5. The sulphates in L/S 2 and 10 did not really show an observable pattern (figure 13).  In frozen soils, DOC and sulphate were lower for the sample F2 which was frozen for 15 days as compared to the 3-months frozen sample F1.

### 4.3.2 Effect of liquid-to-solid ratio

The lowest amount of Fe concentrations was leached at L/S 2 for most of the different moisture content. The leached amount of Fe did not however increase with increasing L/S as concentrations leached in L/S 10 were less than that leached in L/S of 5. Unlike Fe the leaching behaviour with respect to L/S for Mn was highest at L/S of 2 and decreased with an increase to L/S 5 (figure 12). Most of the samples decreased with further increase to L/S 10. Dissolved organic carbon values in terms of L/S, were highest at L/S of 10 for all samples. There is observable decrease with a decrease in L/S as observed in figure 14except for sample (90% WHC) of the nZVI treated

sample, where L/S of 5 (475 mg/kg) had a higher concentration of DOC compared to L/S 10. The concentrations for sulphate showed an increase with higher L/S for the control samples. This trend is not followed by the nZVI treated sample which exhibited an increase from L/S of 2 to 5 but significantly decreased when the L/S was increased to 10 (figure 13).

### 4.3.3   Effect of nZVI on Fe, Mn, DOC and $SO_4^{2-}$

Iron and manganese were observed in most cases to be higher for nZVI-treated samples (Figure 12). Minimum concentration of Fe leached at L/S 2 (6.3 mg/kg, 60% WHC). Low values of Mn (8.3-44 mg/kg) were recorded for most variants of incubation conditions except for samples with 90% and 130% moisture content, which released Mn over 100 mg/kg averagely. Figure 13 illustrates the leaching characteristics of DOC upon the application of nZVI. The control soil contained higher amounts of DOC than the nZVI treated soils. The maximum values of DOC were measured at L/S of 10, ranging from 358 mg/kg (nZVI 90% WHC) to 6566 mg/kg (control 90% WHC). Sulphate ($SO_4^{2-}$) was slightly higher when the soil was treated for L/S 2 and 5 but samples in L/S 10 had their treated samples having lower concentrations as compared to their controls.

**LSR 2**
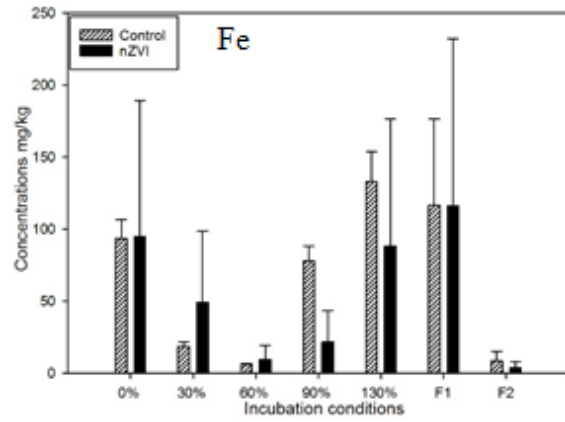
**LSR 5**
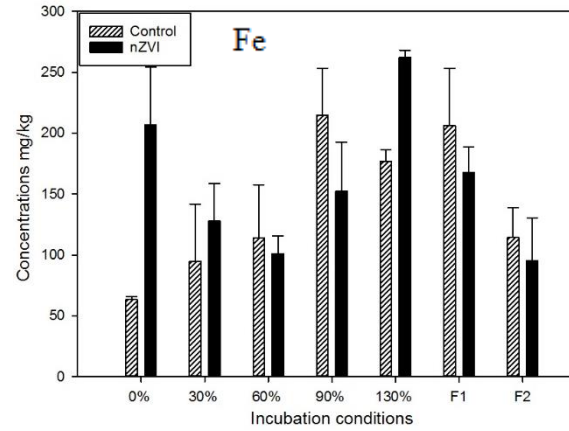
**LSR 10**
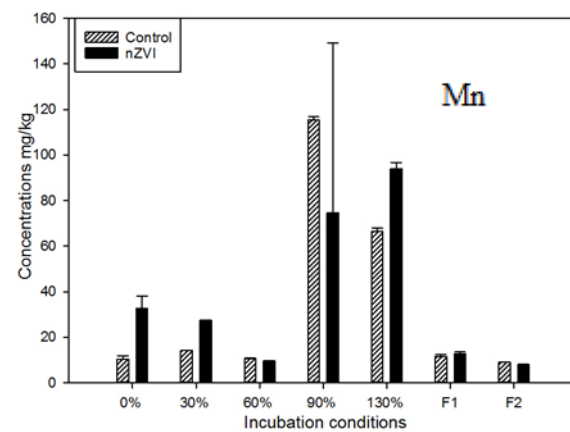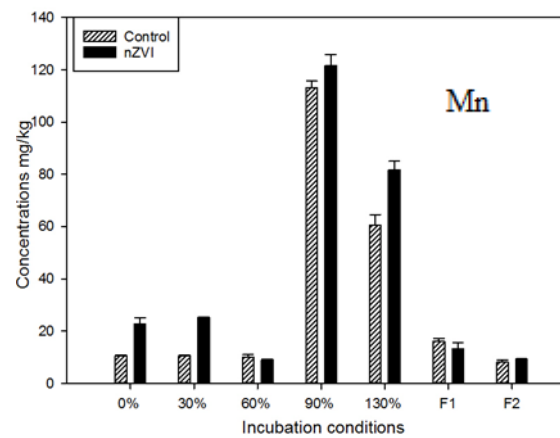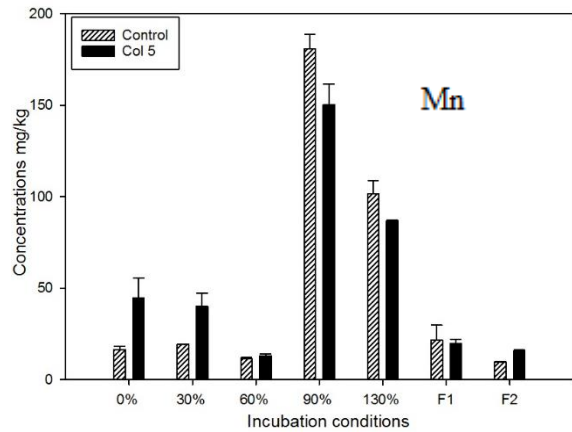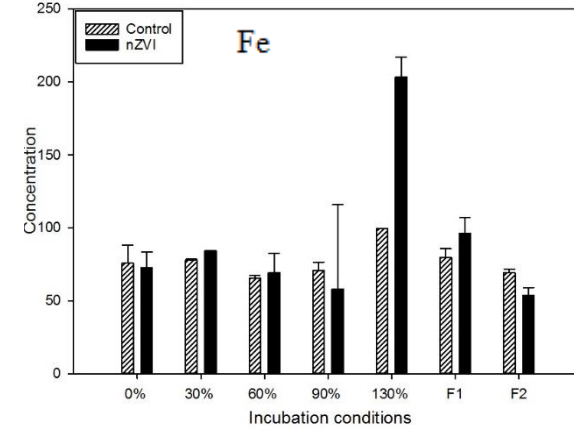


Figure 12. Leaching of Fe (top row) and Mn (down row) as a function of incubation condition.

**L/S 2**          **L/S 5**          **L/S 10**
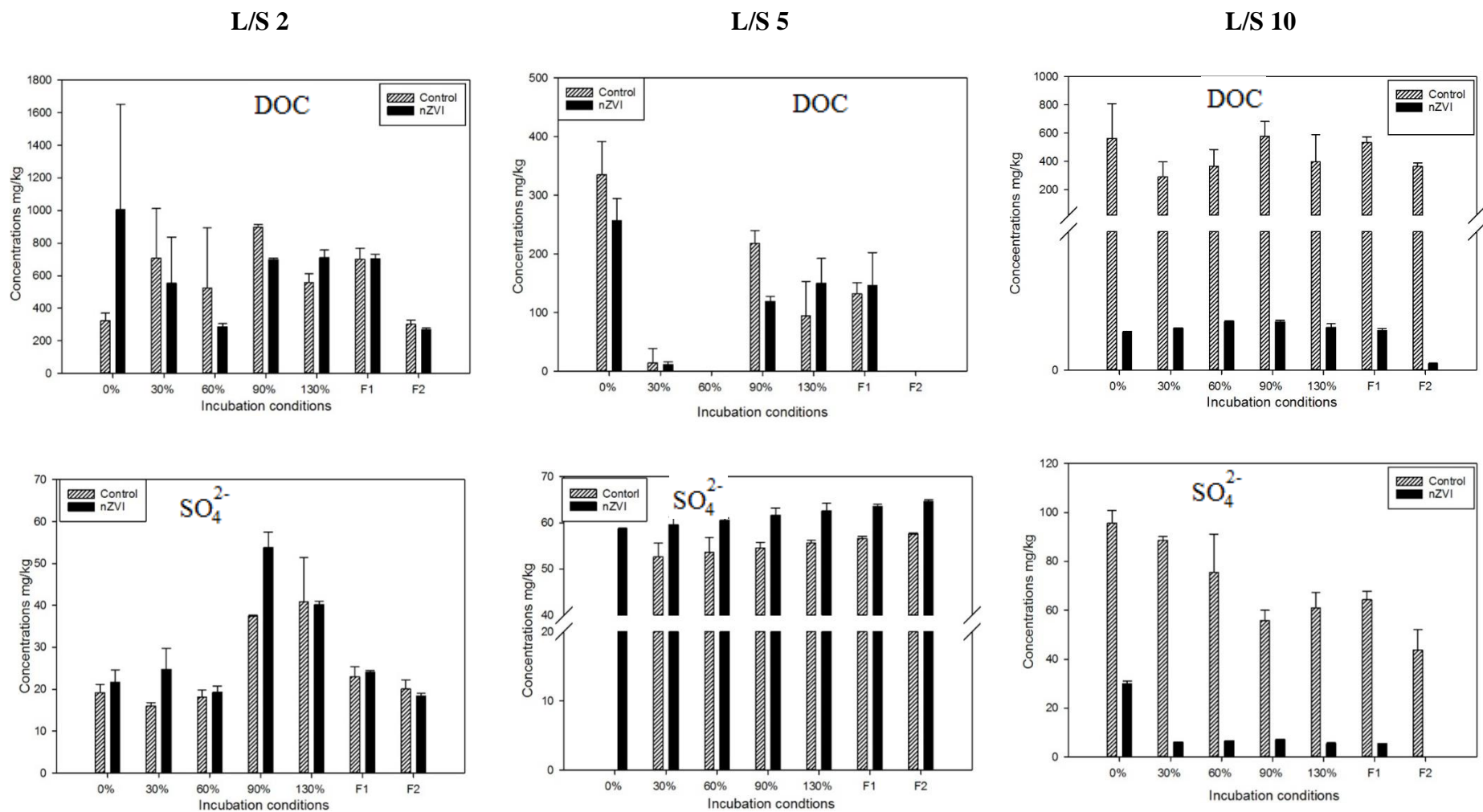


Figure 13. DOC (top row) and Sulphate (down row) as a function of incubation condition.

## 4.4 Solubility of contaminants and saturation phase indices

Saturation indices of selected phases that could probably affect the release of the studied risk metal(loid)s are given in Appendices 5-7. According to the PHREEQC-3 calculations, leachates were undersaturated with respect to Cd and Zn bearing phases, indicating no precipitation under studied conditions (SI <0). From the PHREEQC-3 calculations it is observed that $CO_2$ had an influence of the precipitation of Pb carbonates. Mineral phase influencing Pb precipitation was cerussite ($PbCO_3$) and predicted to form at 90% WHC and 130% WHC for all liquid to solid ratio. Other Pb minerals were only precipitated at L/S 5 and these include plumbogummite ($PbAl_3(PO_4)_2(OH)_5 \cdot H_2O$) and hxypyromorphite ($Pb_5(PO_4)_3OH$) due to the presence of phosphate. Arsenic was predicted to form a ($Ba3AsO4)_2$ complex. There were a high number of mineral phases influencing iron and these were, goethite (FeOOH), hematite ($Fe_2O_3$), maghemite ($Fe_2O_3$), and magnetite ($Fe_3O_4$), all of which had very high saturation indices. A rare form of iron phosphate, strengite ($FePO_4 \cdot 2H_2O$) was formed at L/S 5. The PHREEQC-3-3 calculations, reported no Mn bearing phases, indicating that no precipitation under studied conditions (SI <0).

# 5. DISCUSSION

## 5.1 Effect of incubation conditions on the leachability of contaminants

Periodic changes of the soil moisture regime may affect soil properties, which would consequently affect the release of contaminants (Matranga, 2012). Results from this work have shown that leaching characteristics of metal(loids) are dependent on environmental conditions. Yang et al. (2009) suggest a negative correlation between water content in a soil and redox potential (Eh). Results from this study however followed this suggested trend only when moisture content increased from 90% WHC to flooded condition (>130% WHC) with the flooded sample being the highest reduced. Kashem and Singh (2001) also observed a decrease in Eh when they submerged soil to check the effect of flooding on the soil conditions.

The pH values generally increased slightly with increase in the moisture content. Converse to the Eh and consistent with literature, the highest pH was recorded at the flooded sample (>130% of WHC). This could be attributed to the $H^+$ consumption in reduction reactions, resulting in pH rise in acid soils (Narteh and Sahrawat, 1999). Metal behaviour in the soil samples under the different moisture content can be attributed to changes in Eh and pH (Kashem and Singh, 2001). The results of this work, show low amounts of leached contaminants when there was an increase in pH and a reduced Eh. For example, sample with 90% WHC extracted at L/S 2 had a high pH of 6.9 units and Eh 488 mV, leached only 4.1mg/kg of Zn (figure 10). Work by Vítková et al., (2017) documented similar decrease in leaching concentrations of Zn towards pH 7. Lead values were lowest for 60% WHC for most samples even though the highest pH values were recorded at 90% and 130% WHC setting. This gives credence to the fact that other soil parameters influence metal availability apart from soil pH. In Kashem and Singh, (2001), it is suggested that the Eh, pH changes that occurred may result in increased negative charge on soil particles which fosters higher adsorption of metals and decrease the solubility in especially flooded conditions. It is noteworthy to mention here that, even though flooded condition (> 130% WHC) provided the lowest Eh values, it leached more metals than 90% WHC in many scenarios. Under waterlogged conditions, Fe oxides are dissolved because of the reduction of Fe (Millaleo et al., 2010) and consequently metals become more available.

Low levels of As reported at near neutral pH in this study is contrary to other studies. Smedley and Kinniburgh, (2001) documented As mobilisation at the pH values 6.5–8.5. The low levels of As at near neutral pH could mean As existed as As(v) which is reported by Villalobos et al. (2014) to be sorped better at are lately higher pH value.

## 5.2    Effects of liquid to solid ratio.

The L/S is defined as the volume of extractant in contact with given mass of dry solid sample (Hyks et al., 2009). The L/S was performed to depict different extraction /leaching conditions. Therefore, in this thesis, L/S application is to determine its influence on nZVI contaminant stabilization on metals and Arsenic leaching. An increase in the L/S from 2 to 10, provided different results for individual metals. The elements Zn and Cd had higher leaching concentrations at the lowest L/S of 2, whilst Pb and arsenic leached most at L/S 5.A study of metal leachability from coal combustion residuals by DaSilva et al. (2018) reported similar results. They concluded that this occurrence may be as a result of elements reaching their maximum leaching at low L/S.

In L/S leaching test, the test conditions are meant to approximate chemical equilibrium between the aqueous and solid phases for maximum leaching (Garrabrants et al., 2010). Therefore, the study elements showed different L/S for maximum leaching due to occurrence of different chemical equilibrium between their solid and liquid phases, since in most situations, attaining chemical equilibrium demands longer periods than test durations. This can also be attributed to differences in complexation or chelation with different ligands, thus shifting the equilibrium to the aqueous phase (Kosson et al., 2014).

## 5.3    Assessment of soil stabilisation after treatment with nZVI.

Upon application of the nZVI amendment to the experimental soil, there was significant increase in the pH values as high as 7.2 and a concomitant decrease of Eh, that foster conditions which promote immobilisation process of risk metals. The surge in pH is a result of the further oxidation of already corroded iron by the spontaneous reaction between nZVI and water (Essington, 2004; Gil-Díaz et al., 2014). In anaerobic conditions, this reaction is described as (5) (Ponder et al., 2000):

$$Fe^0_{(s)} + 2H_2O ==== Fe^{2+} + H_{2(g)} + 2OH^-_{(aq)} \qquad\qquad (5)$$
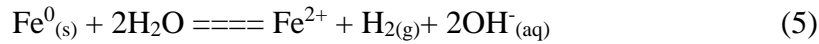
The pH surge also helps abate compounds not reducible by nZVI, as it aids precipitation, sorption and/or incorporation in the structure of the formed iron oxyhydroxides (Klimkova et al., 2011). The pH increments upon addition of nZVI however, will increase to the extent that the soil buffering capacity allows (Gil-Díaz et al., 2014). Many studies show that DOC significantly influences the mobility of risk metals (Weng et al., 2002; Vítková et al., 2017). Lower concentrations of DOC were recorded for nZVI-treated samples as compared to the control. This is in sharp contrast to observations made by Zhao et al. (2012) who reported an increase in the DOC upon addition of nZVI.

The efficiency of the stabilisation process can be assessed by the retention of the risk metalloids (Komárek et al., 2013). There was a considerable decrease of leached amount of metal(loids) upon the addition of nZVI. Zinc leaching was the highest because of the loose binding by solids than other metals (Chaney, 2010). The lowest concentration of Zn was recorded in the nZVI-treated sample with 90% moisture content. This low amount of about 10% of the control value conformed with the high pH and low Eh recorded at that condition. No Cd and Zn potential solubility controlling phase were reported by the PHREEQC-3 calculations. From the phases presented by PHREEQC-3 calculation, the low presence of the studied elements' (Zn, Cd) mineral phases may mean that, these elements were only sorbed onto the secondary Fe (oxyhydr)oxides developed in the soil upon reaction with water. A recent study conducted by Vítková et al. (2017) tends to support this reasoning, as they observed from transmission electron microscopy that Zn was retained under near neutral condition by newly formed Fe oxides. The low levels of Pb recorded upon treatment with nZVI can be as a result of both reduction and adsorption of Pb ions (O'Carroll et al., 2013; Li and Zhang, 2007; Fu et al. 2015 and Wang et al. 2016). Cerussite was predicted by the PHREEQC-3 calculation as the mineral phase influencing Pb precipitation in the soil samples. Similar observations were made by Vítková et al. (2017) as they found that Pb was present in the form of cerussite ($PbCO_3$) or $Pb(OH)_2$. That same study observed retention of Pb by newly formed oxides. According to the PHREEQC-3 calculations, goethite (FeOOH), hematite

($Fe_2O_3$), maghemite ($Fe_2O_3$), and magnetite ($Fe_3O_4$) could be responsible for the retention of contaminants. Low concentrations of As in nZVI-treated soils could result from reduction and precipitation as As is much more positive in terms of redox potential than nZVI (Li et al., 2006). The lower concentrations of As leaching observed in the soil was as a result of the complexation with Ba to form $Ba_3(AsO_4)_2$ complex. Nano zero-valent iron has been proposed as a suitable chemical amendmentment in numerous studies (Kumpiene, 2006; Ramos et al., 2009; O'Carroll et al., 2013; Li et al., 2016; Vítková et al., 2017). Ramos et al. (2009) reported that, nano zero-valent iron causes reduction of less toxic arsenate ($As^{5+}$) to arsenite ($As^{3+}$) a toxic and mobile form of arsenic, which is subsequently adsorbed or co-precipitated at the surface of the nano iron alongside residual $As^{5+}$. Kumpiene et al. (2008) documented that immobilisation of As could be through the adsorption on Fe oxides by replacement of hydroxyl groups with As ion which forms insoluble secondary As bearing minerals.

# 6. CONCLUSION

This work was focused on the efficiency of the use of nano zero-valent iron stabilisation of contaminants in the soil. Leaching of risk metal(loids) was studied as a function of incubation conditions and also liquid to solid ratio. An application of nZVI led to a considerable decrease in the contents of all the monitored contaminants (i.e., Pb, Cd, Zn and As). Based on the results of this work, it is possible to confirm the hypothesis that the leachability of the hazardous metals in the soil depends on the moisture content of the soil. The release of metal(loid)s showed different leaching patterns with an increase in moisture content. Zinc and Cd concentrations increased till 60% WHC and then decreased at 90%. Lead depicted decreasing concentrations with increasing soil moisture content up to 60% WHC. From this experiment, we can conclude that, the influence of moisture content on the leaching behaviour is element specific. Lead tends to be efficiently stabilised at 60% moisture content setting while 90% moisture content is the best condition for the optimal stabilisation of Zn, Cd and As. The addition of nZVI to the soil generally increased pH across the various samples used and decreased the amount of metal(loids) leached in the samples. The results showed a significant effect of pH, Eh, and DOC on the leaching characteristics of the studied elements. The amount of information about nZVI particles transformations, their behaviour in soils, and the mechanisms of capturing different forms of contaminants is still limited. The focus of this thesis fits into the broader context of studying geochemical transformations of nanoiron interactions with risk elements and influence of various environmental conditions on the leachability of metal(loids) from contaminated soils.

# 7. REFERENCE

AlAbed, S. R., Purandare, J., & Allen, D., (2004). Effect of liquid to solid ratio on leaching of metals from mineral processing waste. Presented at 227th American Chemical Society National Meeting, Anaheim, CA, March 28 - April 01, 2004. Abstract.

Ampiah-Bonney, R. J., Tyson, J. F., & Lanza, G. R., (2007). Phytoextraction of arsenic from soil by Leersiaoryzoides, International Journal of Phytoremediation, 9(1), 31–40.

Antoniadis, V., & Alloway, B. J., (2003). Influence of time on the plant availability of Cd, Ni and Zn after sewage sludge has been applied to soils. Agrochimica 47, 81-93.

Astrup, T., Dijkstra, J. J., Comans, R. N. J., van der Sloot, H. A., & Christensen, T. H., (2006). Geochemical modelling of leaching from MSWI air-pollution-control residues, Environmental Science & Technology 40 (11), 3551–3557.

Aydinalp, C., & Cresser, M. S., (2003). The background levels of heavy metals in vertisols under Mediterranean type of climate in the region of Turkey. Journal of Central European Agriculture 4, 289-296.

Boparai, H.K., Meera, J., & O'Carroll, D.M., (2013). Cadmium ($Cd^{2+}$) Removal by Nano Zerovalent Iron: Surface Analysis, Effects of Solution Chemistry and Surface Complexation Modeling. Environmental Science &Pollution Research 20(9), 6210–21.

Bradl, H. B., (2004). Adsorption of heavy metal ions on soils and soil constituents. Colloid and Interface Science 277(1), 1-18.

Cao, X., & Ma., L.Q., (2004). Effects of compost and phosphate on plant arsenic accumulation from soils near pressure-treated wood. Environmental Pollution 132, 435–442.

Cappuyns, V., & Swennen, R., (2008). The application of pH-stat leaching tests to assess the pH dependent release of trace metals from soils, sediments and waste materials. Journal of Hazardous Materials 158, 185-195.

CEN, EN 12457/1 (2002): Characterization of waste leaching compliance test for leaching of granular waste materials and sludges Part 1. CEN, European Committee for Standardization, Brussels.

CEN, EN 12457/3 (2002): Characterization of waste leaching compliance test for leaching of granular waste materials and sludges Part 3. CEN, European Committee for Standardization, Brussels.

Chaney, R. L., (2010). Characteristics and behaviour of individual elements trace elements in soils. Trace Elements. Hooda P.S.(Ed.), Wiley-Blackwell, Chichester, UK.

Cornell, R.M., &Schwertmann, U., (2003). The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses, second ed. Wiley-VCH, Weinheim, Germany.

Dai, J., Becquer, T., Rouiller, J.H., Reversat, G., Reversat, F.B., & Lavelle, P., (2004). Influence of heavy metals on C and N mineralization and microbial biomass in Zn-, Pb-, Cu-, and Cd-contaminated soils. Applied Soil Ecology 25, 99-109.

Da Silva, E.B., Li, S., & De Oliveira, L.M., (2018). Metal leachability from coal combustion residuals under different pHs and liquid/solid ratios Journal of Hazardous Materials 341, 66–74

Degryse F., Smolders E., & Parker D.R., (2009). Partitioning of metals (Cd, Co, Cu, Ni, Pb, Zn) in soils: concepts, methodologies, prediction and applications – a review.European Journal of Soil Science 60, 590-612.

Dermont G., Bergeron M., Mercier G., & Richer-Lafleche M., (2008). Metal-contaminated soils: remediation practices and treatment technologies. Practice Periodical of hazardous, toxic and radioactive waste management 152(1), 188-209.

Du Laing, G., Rinklebe, J., Vandecasteele, B., Meers, E., & Tack, F. M. G., (2009). Heavy metal mobility and availability in estuarine and riverine floodplain soils and sediments: a review. Science of the Total Environment 407, 3972-3985.

Essington, M.E., (2004). Soil and Water Chemistry: an Integrative Approach. CRC Press, Boca Raton, USA.

Ettler V., Knytl V., Komarek M., Della Puppa L., Mihaljevic M., & Sebek O., (2012). Stability of amorphous hydrous manganese oxide in contrasting soils and implications for its use in chemical stabilization of metals/metalloids in contaminated soil environments. Geophysical Research Abstracts Vol. 14, EGU2012-8532,

Evanko, F.R., & Dzombak, D.A., (1997). Remediation of metals contaminated soils and groundwater, Tech. Rep. TE-97- 01, Groundwater Remediation Technologies Analysis Centre, Pittsburg, Pa, USA.

Frumkin, H., & Thun, M.J., (2008). Arsenic. A Cancer Journal for Clinicians, 51(4). http://onlinelibrary.wiley.com/doi/10.3322/canjclin.51.4.254/pdf [2017-10-20].

Fu, R., Yang, Y., Xu, Z., Zhang, X., Guo, X. & Bi, D., (2015). Chemosphere The Removal of Chromium ( VI ) and Lead ( II ) from Groundwater Using Sepiolite-Supported Nanoscale Zero-Valent Iron ( S-NZVI ). Chemosphere 138, 726–34. http://dx.doi.org/10.1016/j.chemosphere.2015.07.051.

Gambrell R.P., Wiesepape J.B., Patrick W. H., & Duff M.C., (1991). The effects of pH, redox, and salinity on metal release from a contaminated sediment: Water, Air, and Soil Pollution, 57-58, 359-367.

Garrabrants A.C., D.S. Kosson, H.A. van der Sloot, F. Sanchez & O. Hjelmar (2010) Background information for the Leaching Environmental Assessment Framework (LEAF) Test Methods, EPA- 600/R-10/170, U.S. Environmental Protection Agency, Air Pollution Prevention and Control Division, December 2010

Gil-Díaz, M., Perez-Sanz, A., Vicente, M.A., & Lobo, M.C., (2014a). Immobilisation of Pb and Zn in soils using stabilised zero-valent iron nanoparticles: effects on soil properties. Clean Soil Air Water 42 (12), 1776-1784.

Gil-Díaz, M., Alonso, J., Rodríguez-Valdes, E., Pinilla, P., & Lobo, M.C., (2014b). Reducing the mobility of arsenic in brownfield soil using stabilised zero-valent iron nanoparticles. J. Environ. Sci. Health A 49 (12), 1361-1369.

Gómez-Pastora, J., Bringas V., & Inmaculada O., (2014). Recent Progress and Future Challenges on the Use of High Performance Magnetic Nano-Adsorbents in Environmental Applications. Chemical Engineering Journal 256, 187–204.

Hooda P.S., (2010). Trace Element in Soils, Wiley-Blackwell, Chichester, UK.

Huber & Prokop (2012). Progress in the management of contaminated sites. EIONET

Workshop on Soil, Ispra, 10- 12 December 2012.

Husson, O., (2013). Redox potential (Eh) and pH as drivers of soil/plants/microorganism system: a transdisciplinary overview pointing to integrative opportunities for agronomy. Plant Soil.362-389.

Hyks J, Astrup T, Christensen T.H., (2009). Long-term leaching from MSWI air pollution-control residues: leaching characterization and modeling. Journal of Hazardous Materials 162(1), 80–91

Joint Research Centre. (2012-04-19). Joint Research Centre: European soil portal – Soil data and information systems. http://eusoils.jrc.ec.europa.eu/library/themes/contamination/ [2016-11-17].

Kashem, M.A., & Singh, B.R., (2000). Metal availability in contaminated soils: I. Effects of flooding and organic matter on changes in Eh, pH and solubility of Cd, Ni and Zn. Nutrient Cycling in Agroecosystems 61, 247-255.

Khalid, S., Shahid, M., Niazi, N. K., Murtaza, B., Bibi, I., & Dumat, C., (2016). A Comparison of Technologies for Remediation of Heavy Metal Contaminated Soils. Journal of Geochemical Exploration. http://dx.doi.org/10.1016/j.gexplo.2016.11.021.

Kim, S. C., (2017). Effect of Chemical Amendments on Remediation of Potentially Toxic Trace Elements (PTEs) and Soil Quality Improvement in Paddy Fields. Environmental Geochemistry and Health 39(2), 345–52. http://link.springer.com/10.1007/s10653-017-9921-x.

Klimkova S., Cernik M., Lacinova L., Filip, J., Jancik, D., & Zboril R., (2011). Zerovalent Iron Nanoparticles in Treatment of Acid Mine Water from in Situ Uranium Leaching, Chemosphere 82, 1178–1184.

Komárek, M., Vanek, A., & Ettler, V., (2013). Chemical stabilization of metals and arsenic in contaminated soils using oxides - a review. Environmental Pollution. 172, 9-22.

Kosson, D., H. van der Sloot, Garrabrants, A., & Seignette P., (2014). Leaching Test Relationships, Laboratory-to-Field Comparisons and Recommendations for Leaching Evaluation using the Leaching Environmental Assessment Framework (LEAF).US Environmental Protection Agency, Cincinnati, OH, EPA/600/R-14/061.

Kumar N., Auffan, M., Gattacceca, J., Rose, J., Olivi, L., Borschneck, D., Kvapil, P., Jublot, M., Kaifas, D., Malleret, L., Doumenq, P. & Bottero, J.Y. (2014). Molecular insights of oxidation process of iron nanoparticles: spectroscopic, magnetic, and microscopic evidence, Environmental Science and Technology. 48 13888–13894.

Kumpiene, J., Lagerkvist, A. & Maurice, C., (2008). Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments - a review. Waste Management 28, 215-225.

Kumpiene J., Ragnvaldsson A., Lovgren D., Tesfalidet S., Gustavsson B., Lattstrom L., Leffler P. & Maurice C., (2009). Impact of water saturation level on arsenic and metal mobility in the Fe-amended soil. Chemosphere 74, 206-215.

Kumpiene, J., Ore, S., Renella, G., Mench, M., Lagerkvist, A. & Maurice, C., (2006). Assessment of zerovalent iron for stabilization of chromium, copper, and arsenic in soil. Environ. Pollution. 144, 62-69.

Lee S-H., Park H., Koo N., Hyun S., Hwang A. (2011). Evaluation of the effectiveness of various amendments on trace metals stabilization by chemical and biological methods. Journal of Hazardous Materials, 188, 44-51.

Liang, B., Xie, Y., Fang, Z. & Tsang, E. P. (2014). Assessment of the transport of polyvinylpyrrolidone-stabilised zero-valent iron nanoparticles in a silica sand medium, Journal of Nanoparticle Research 16(7)

Li X.Q., Elliot W.L., & Zhang W., (2006). Zero-Valent Iron Nanoparticles for Abatement of Environmental Pollutants: Materials and Engineering: Materials and Engineering Aspects Critical Reviews in Solid State and Material Science 31, 111-122.

Li X.Q., & Zhang W.X., (2007). Sequestration of metal cations with zerovalent iron Nanoparticles: a study with High Resolution X-ray Photoelectron Spectroscopy (HR-XPS). Journal of Physical Chemistry.  111(19), 6939 - 6946.

Li, J., Xue, Q., Wang, P., Wang, H., & Zhang T., (2016). Evaluation of leaching characteristics of heavy metals from municipal solid waste incineration fly ash by up-flow percolation column tests. Environmental Earth Science, 75, 714,

Matranga M. (2011). Mobility and Mobilisation of heavy metals and PAHs in partially water repellent urban soils. PhD thesis.

McBride M.B., (1994). Environmental chemistry of soils. Oxford. University Press, New York, NY.

Mueller, N. C., & Bernd N., (2010). Nanoparticles for Remediation: Solving Big Problems with Little Particles. Elements 6(6), 395–400.

Michálková, Z., Komárek, M., Veselská, V. & Číhalová, S., (2016). Selected Fe and Mn (nano)oxides as perspective amendments for the stabilization of as in contaminated soils. Environmental Science Pollution Research 23, 10841-10854.

Michálková, Z., Komárek, M., Vítková M., Rečínská M., & Ettler V., (2016).Stability, transformations and stabilizing potential of an amorphous manganese oxide and its surface-modified form in contaminated soils.Applied Geochemistry 75, 125-136.

Millaleo, R., Reyes-Diaz, M., Ivanov, A.G., Mora, M.L., Alberdi, M., (2010). Manganese as essential and toxic elements for plants: transport, accumulation and resistance mechanisms. Journal of soil science and plant nutrition. 10, 470–481.

Mulligan, C.N., Yong, R.N., & Gibbs, B.F., (2001). Remediation technologies for metal-contaminated soils and groundwater: an evaluation. Engineering Geology 60, 193–207.

NartehL.T., & Sahrawat K.L., (1999). Influence of flooding on electrochemical and chemical properties of West African soils. Geoderma 87, 179–207.

Nurmi J.T., Tratnyek P.G., Sarathy V., Baer D.R., Amonette J.E., Pecher K., Wang C., Linehan J.C., Matson D.W., Penn R.L., & Driessen M., (2005). Characterization and properties of metallic iron nanoparticles: spectroscopy, electrochemistry, and kinetics. Environmental Science and Technology 39 (5), 1221–1230.

Němeček, J., Lhotský, O., & Cajthaml, T., (2014). Nanoscale zero-valent iron application for in situ reduction of hexavalent chromium and its effects on indigenous microorganism populations. Science of the Total Environment 485–486, 739-747.

Nwachukwu, O. I., (2007).  The use of organic materials as amendments in the remediation of soils contaminated by lead, copper and zinc. PhD thesis.

O'Carroll, D., (2013). Nanoscale Zero Valent Iron and Bimetallic Particles for Contaminated Site Remediation. Advances in Water Resources 51: 104–22. http://dx.doi.org/10.1016/j.advwatres.

Parkhurst, D.L., & Appelo, C.A.J., (2013). Description of Input and Examples for PHREEQC Version 3, a Computer Program for Speciation, Batch-reaction, One-dimensional Transport, and Inverse Geochemical Calculations: U.S. Geological Survey Techniques and Methods, Denver, 497pp.

Pierzynski, G.M., Sims J.T., & Vance G.F., (2005). Soils and environmental quality.3rd ed. Boca Raton: radioactive waste management, 188-209.

Ponder, S., Darab, J., & Mallouk, T., (2000). Remediation of Cr(VI) and Pb(II) aqueous solutions using supported, nanoscale zero-valent iron, Environmental Science Technology 34 2564–2569.

Ramos M.A.V., Yan W., Li X.Q., Koel B.E., & Zhang W.X., (2009). Simultaneous oxidation and reduction of arsenic by zero-valent iron nanoparticles: understanding

the significance of the core–shell structure. Journal of Physical Chemistry C; 113, 14591–4.

Schulin, R., Johnson, A., & Frossard, E., (2010). Trace Element- deficient soils.Trace Elements.Hooda P.S. (Ed.), Wiley-Blackwell, Chichester, UK.s

Shiralipour, A., Ma, L., & Cao, R., (2002). Effects of compost on arsenic leachability in soils and arsenic uptake by a fern. Florida Centre for Solid Hazardous Waste Management, State University System of Florida, Gainesville, Florida. Report 02-04.

Smedley, P. L., & Kinniburgh, D. G., (2002). A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry17, 517-568.

Tack, F.M.G (2010). Trace Elements: General soil chemistry, principles and processes. Trace Elements. Hooda P.S.(Ed.), Wiley-Blackwell, Chichester, UK.

Tang J., &Steenari, B.M., (2016). Leaching optimization of municipal solid waste incineration ash for resource recovery: a case study of Cu, Zn, Pb and Cd, Waste Management. 48, 315–322.

UNEP (United Nations Environmental Protection) 2010. Final review of scientific information on cadmium –Version of December 2010

Ur Rehman H., Aziz T., Farooq M., Wakeel A., & Rengel Z., (2012). Zinc nutrition in rice production systems- a review. Plant Soil 361, 203-226.

Usman, A. R. A., Kuzyakov, Y., Lorenz, K. & Stahr, K. (2006). Remediation of a soil contaminated with heavy metals by immobilizing compounds. Journal of Plant Nutrition and Soil Science 69, 205-212.

Vítková, M., Rákosová S., Michálková Z., & Komárek M., (2017). Metal(loid)s Behaviour in Soils Amended with Nano Zero-Valent Iron as a Function of pH and Time. Journal of Environmental Management 186.

Villalobos M., Escobar-Quiroz, I.N., Salazar-Camacho, C., (2014). The influence of particle size and structure on the sorption and oxidation behavior of birnessite: I. Adsorption of As(V) and oxidation of As(III), Geochim. Cosmochim.Acta 125, 564–581.

Wang, W., (2016). Removal of Pb(II) and Zn(II) Using Lime and Nanoscale Zero-Valent Iron (nZVI): A Comparative Study. Chemical Engineering Journal 304, 79–88. http://dx.doi.org/10.1016/j.cej.2016.06.069.

Weng, L., Temminghoff, E.J.M., Lofts, S., Tipping, E., & van Riemsdijk, W.H., (2002). Complexation with dissolved organic matter and solubility control of heavy metalsin a sandy soil. Environmental Science Technology 36, 4804–4810.

WuanaR.A., & Okieimen F.E., (2011). Heavy metals in contaminated soils: A review of sources, chemistry, risks and best available strategies for remediation. International Scholarly ResearchNetwork Ecology, 2011.

Yang, D.Q., & Sacher, E., (2009). Characterization and oxidation of Fe nanoparticles deposited onto highly oriented graphite using X-ray photoelectron spectroscopy, Journal of Physical Chemistry C 114, 6418–6425.

Zeng, F., Ali, S., & Zhang, H., (2011). The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants Environmental Pollution 159, 84-91

Zhou, D.M., Jin, S.Y., Wang, Y.J., Wang, P., Weng, N.Y., & Wang, Y., (2012).Assessing the impact of iron-based nanoparticles on pH, dissolved organic carbon, and nutrient availability in soils. Soil Sediment Contamination Int. J. 21, 101-114.

# APPENDIX

Appendix 1.DOC values for the various liquid to solid ratio.

| WHC | L/S 2 LC | nZVI | L/S 5 LC | nZVI | L/S 10 LC | nZVI |
|------|------|--------|------|------|------|--------|
| 0% | 79 | 215 | 690 | 612 | 6430 | 0 |
| 30% | 155 | 125 | 370 | 367 | 3693 | 885.7 |
| 60% | 119 | 72 | 317 | 252 | 4457 | 754.5 |
| 90% | 194 | 154 | 573 | 475 | 6566 | 358.22 |
| 130% | 126 | 156.03 | 450 | 506 | 4774 | 910.9 |
| F1 | 154 | 155.08 | 488 | 502 | 6152 | 572.7 |
| F2 | 74 | 68.08 | 271 | 273 | 4442 | 3837.5 |

Appendix 2. Concentration values from of the various elements measured (L/S 2)

| | mg/kg Mn | mg/kg Fe | mg/kg Cu | mg/kg Zn | mg/kg Pb | mg/kg Mg | mg/kg Ca | mg/kg K | mg/kg Na | mg/kg As | mg/kg Cd | mg/kg Ba | mg/kg Ti | mg/kg Al | mg/kg Sr | mg/kg Si | mg/kg S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LC 0% | 16.5 | 93.8 | 1.1 | 74.9 | 23.8 | 14.8 | 76.6 | 169.9 | 6.7 | 1.7 | 0.8 | 2.0 | 0.2 | 28.0 | 0.2 | 32.6 | 60.7 |
| LC 30% | 19.3 | 18.7 | 0.4 | 118.6 | 5.3 | 27.2 | 129.3 | 128.2 | 6.2 | 0.5 | 1.2 | 1.9 | 0.1 | 6.1 | 0.5 | 28.9 | 42.9 |
| LC 60% | 11.6 | 6.3 | 0.3 | 145.1 | 2.1 | 32.5 | 159.8 | 131.5 | 6.7 | 0.0 | 1.4 | 2.0 | 0.0 | 2.0 | 0.5 | 30.9 | 41.0 |
| LC 90% | 180.9 | 77.8 | 1.4 | 38.3 | 28.9 | 21.6 | 102.4 | 157.3 | 5.4 | 1.5 | 0.7 | 2.3 | 0.3 | 28.7 | 0.3 | 60.4 | 62.3 |
| LC 130% | 101.5 | 133.1 | 1.4 | 50.4 | 43.0 | 15.7 | 74.4 | 99.6 | 6.0 | 2.6 | 0.7 | 2.0 | 0.3 | 32.8 | 0.2 | 57.3 | 62.5 |
| LC F1 | 21.8 | 116.6 | 1.2 | 75.4 | 32.7 | 14.6 | 72.7 | 158.1 | 5.9 | 1.7 | 0.9 | 2.1 | 0.2 | 33.4 | 0.2 | 36.7 | 69.9 |
| LC F2 | 9.7 | 8.6 | 0.2 | 141.2 | 2.0 | 32.9 | 161.2 | 151.6 | 8.2 | 0.3 | 1.4 | 2.2 | 0.1 | 4.1 | 0.6 | 34.3 | 48.4 |
| nZVI 0% | 44.4 | 94.8 | 1.3 | 84.6 | 24.8 | 21.1 | 114.1 | 104.2 | 8.3 | 1.1 | 0.9 | 1.9 | 0.3 | 29.8 | 0.3 | 40.8 | 74.4 |
| nZVI 30% | 40.1 | 49.3 | 0.6 | 76.5 | 10.9 | 22.0 | 110.1 | 109.1 | 8.6 | 0.6 | 0.8 | 1.5 | 0.2 | 19.0 | 0.3 | 35.8 | 64.9 |
| nZVI 60% | 13.1 | 9.8 | 0.2 | 121.1 | 2.4 | 29.3 | 145.5 | 109.0 | 7.2 | 0.1 | 1.2 | 1.7 | 0.1 | 4.2 | 0.5 | 30.6 | 48.4 |
| nZVI 90% | 150.4 | 21.8 | 0.6 | 4.1 | 3.5 | 20.6 | 86.1 | 150.7 | 7.9 | 0.1 | 0.2 | 1.3 | 0.1 | 4.7 | 0.2 | 68.9 | 28.2 |
| nZVI 130% | 87.0 | 88.4 | 1.0 | 10.7 | 16.4 | 12.9 | 52.8 | 111.8 | 3.9 | 1.1 | 0.2 | 1.4 | 0.3 | 12.3 | 0.2 | 50.6 | 32.7 |
| nZVI F1 | 19.9 | 116.2 | 1.2 | 62.8 | 28.4 | 12.7 | 57.3 | 84.3 | 3.7 | 1.5 | 0.7 | 1.9 | 0.1 | 28.6 | 0.2 | 33.8 | 62.0 |
| nZVI F2 | 15.5 | 4.0 | 0.2 | 131.9 | 1.0 | 33.6 | 173.7 | 282.7 | 8.2 | 0.0 | 1.5 | 2.2 | 0.0 | 1.7 | 0.6 | 31.6 | 45.9 |

Appendix 3. Concentration values from of the various elements measured (L/S 5)

| | mg/kg Mn | mg/kg Fe | mg/kg Cu | mg/kg Zn | mg/kg Pb | mg/kg Mg | mg/kg Ca | mg/kg K | mg/kg Na | mg/kg As | mg/kg Cd | mg/kg Ba | mg/kg Ti | mg/kg Al | mg/kg Si | mg/kg S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LC 0% | 10.60 | 63.19 | 0.83 | 50.89 | 19.11 | 8.23 | 43.41 | 56.39 | 11.37 | 1.00 | 0.52 | 1.60 | 0.09 | 16.19 | 32.88 | 16.48 |
| LC 30% | 10.73 | 94.86 | 0.46 | 62.30 | 11.23 | 16.43 | 64.77 | 70.51 | 12.30 | 1.13 | 0.65 | 1.56 | 1.55 | 89.01 | 133.56 | 15.45 |
| LC 60% | 10.08 | 114.11 | 0.55 | 80.41 | 14.38 | 20.20 | 76.83 | 66.74 | 12.21 | 1.30 | 0.77 | 1.80 | 1.77 | 105.40 | 156.26 | 17.29 |
| LC 90% | 113.09 | 214.77 | 1.45 | 48.24 | 36.40 | 23.59 | 59.63 | 70.09 | 11.86 | 2.82 | 0.63 | 2.49 | 3.54 | 211.71 | 286.44 | 29.59 |
| LC 130% | 60.61 | 176.93 | 1.19 | 44.21 | 35.39 | 15.06 | 44.84 | 55.99 | 14.20 | 2.70 | 0.54 | 2.12 | 2.15 | 137.46 | 185.56 | 22.64 |
| LC F1 | 16.13 | 206.40 | 1.19 | 60.39 | 28.96 | 17.66 | 44.69 | 65.11 | 11.84 | 2.57 | 0.60 | 2.36 | 2.86 | 175.06 | 238.19 | 20.77 |
| LC F2 | 8.12 | 114.21 | 0.48 | 74.40 | 11.94 | 19.65 | 76.63 | 64.89 | 12.67 | 1.26 | 0.74 | 1.67 | 1.95 | 105.73 | 156.23 | 17.19 |
| nZVI 0% | 22.64 | 206.79 | 0.97 | 47.58 | 18.98 | 19.83 | 209.59 | 75.71 | 16.74 | 2.35 | 0.49 | 1.74 | 3.43 | 192.70 | 264.56 | 23.25 |
| nZVI 30% | 25.21 | 127.84 | 0.65 | 58.47 | 17.03 | 18.12 | 68.34 | 70.96 | 12.64 | 1.29 | 0.61 | 1.70 | 1.68 | 105.56 | 155.58 | 16.62 |
| nZVI 60% | 8.94 | 101.04 | 0.45 | 67.53 | 9.82 | 18.83 | 72.56 | 66.92 | 12.50 | 1.02 | 0.66 | 1.50 | 1.57 | 95.66 | 146.87 | 17.21 |
| nZVI 90% | 121.59 | 152.49 | 1.12 | 15.34 | 16.53 | 18.74 | 62.16 | 80.82 | 12.34 | 1.50 | 0.25 | 1.70 | 1.87 | 75.13 | 121.45 | 39.59 |
| nZVI 130% | 81.67 | 262.05 | 1.87 | 29.44 | 42.14 | 13.90 | 44.03 | 70.22 | 13.97 | 2.42 | 0.42 | 2.19 | 1.83 | 91.95 | 121.94 | 27.95 |
| nZVI F1 | 13.33 | 167.58 | 1.02 | 48.84 | 22.03 | 15.00 | 42.22 | 67.66 | 13.49 | 2.03 | 0.49 | 2.02 | 2.31 | 141.57 | 196.14 | 20.17 |
| nZVI F2 | 9.23 | 95.04 | 0.45 | 70.64 | 11.06 | 19.52 | 82.85 | 65.92 | 12.41 | 1.12 | 0.71 | 1.80 | 1.41 | 85.37 | 133.22 | 16.37 |

Appendix 4. Concentration values from of the various elements measured (L/S 10)

| | mg/kg Mn | mg/kg Fe | mg/kg Cu | mg/kg Zn | mg/kg Pb | mg/kg Mg | mg/kg Ca | mg/kg K | mg/kg Na | mg/kg As | mg/kg Cd | mg/kg Ba | mg/kg Si | mg/kg S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LC 0% | 10.46 | 75.65 | 1.17 | 50.95 | 16.00 | 10.02 | 42.34 | 175.63 | 22.05 | 0.83 | 0.54 | 1.87 | 50.18 | 25.21 |
| LC 30% | 14.35 | 77.88 | 0.99 | 75.06 | 17.73 | 14.24 | 65.21 | 91.16 | 22.87 | 0.98 | 0.76 | 2.21 | 44.95 | 23.26 |
| LC 60% | 10.48 | 65.50 | 0.81 | 87.31 | 15.70 | 16.85 | 80.87 | 95.56 | 23.29 | 0.70 | 0.87 | 2.31 | 43.11 | 25.35 |
| LC 70% | 10.58 | 61.53 | 0.89 | 77.48 | 14.99 | 15.57 | 71.98 | 102.89 | 19.27 | 0.62 | 0.75 | 2.16 | 38.39 | 25.77 |
| LC 80% | 89.72 | 83.86 | 1.27 | 35.40 | 27.50 | 11.91 | 45.06 | 78.30 | 20.10 | 1.26 | 0.48 | 2.17 | 48.45 | 34.74 |
| LC 90% | 115.40 | 70.48 | 1.48 | 32.19 | 23.90 | 13.37 | 54.59 | 84.55 | 21.58 | 1.26 | 0.52 | 2.07 | 49.88 | 34.19 |
| LC 130% | 66.51 | 99.22 | 1.36 | 34.31 | 28.88 | 9.32 | 38.38 | 95.99 | 21.30 | 1.70 | 0.42 | 2.03 | 47.07 | 28.33 |
| LC F1 | 11.57 | 79.51 | 1.12 | 46.71 | 18.18 | 8.60 | 37.71 | 101.60 | 20.56 | 1.18 | 0.51 | 1.85 | 42.96 | 25.21 |
| LC F2 | 8.99 | 69.25 | 0.53 | 78.13 | 15.85 | 15.20 | 77.25 | 88.25 | 21.74 | 1.17 | 0.80 | 2.27 | 42.48 | 24.25 |
| nZVI 0% | 32.57 | 72.49 | 1.33 | 52.23 | 15.83 | 13.01 | 59.65 | 222.22 | 24.21 | 1.12 | 0.58 | 1.99 | 40.41 | 23.54 |
| nZVI 30% | 27.41 | 84.16 | 0.93 | 63.28 | 18.01 | 14.88 | 69.90 | 118.47 | 23.87 | 1.43 | 0.65 | 2.14 | 48.48 | 25.92 |
| nZVI 60% | 9.51 | 69.25 | 0.75 | 79.39 | 11.88 | 18.84 | 83.40 | 154.18 | 22.38 | 0.56 | 0.79 | 2.31 | 67.90 | 24.44 |
| nZVI 70% | 13.09 | 70.43 | 0.59 | 58.72 | 11.98 | 14.41 | 69.67 | 100.48 | 22.77 | 0.56 | 0.58 | 2.08 | 42.49 | 25.89 |
| nZVI 80% | 118.69 | 117.25 | 1.00 | 20.53 | 21.33 | 13.76 | 69.88 | 105.34 | 21.32 | 0.96 | 0.31 | 1.85 | 42.50 | 42.23 |
| nZVI 90% | 74.70 | 57.95 | 0.82 | 7.78 | 9.56 | 9.01 | 26.89 | 79.73 | 21.21 | 0.38 | 0.13 | 1.00 | 22.19 | 21.92 |
| nZVI 130% | 94.06 | 203.43 | 2.88 | 25.45 | 37.21 | 13.60 | 42.75 | 93.97 | 24.59 | 2.00 | 0.40 | 2.22 | 45.69 | 30.68 |
| nZVI F1 | 12.60 | 95.90 | 1.21 | 49.54 | 20.70 | 9.08 | 37.27 | 157.10 | 25.72 | 1.16 | 0.53 | 2.16 | 47.77 | 23.81 |
| nZVI F2 | 7.76 | 53.75 | 0.58 | 74.31 | 11.30 | 16.43 | 86.88 | 128.26 | 28.92 | 0.36 | 0.73 | 2.22 | 41.76 | 22.60 |

Appendix 5. Saturated indices for selected phases modelled with PHREEQC-3 program (version 3.0) (L/S 2)

| | | CONTROL | | | | | | | nZVI | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INCUBATION CONDITION | | 0% | 30% | 60% | 90% | 130% | F1 | F2 | 0% | 30% | 60% | 90% | 130% | F1 | F2 |
| PHASE | COMPOSITION | SATURATION INDEX | | | | | | | | | | | | | |
| Adularia | KAlSi3O8 | 1.32 | -0.69 | -1.33 | 2.54 | 2.34 | 1.56 | -1.04 | 1.61 | 0.54 | -1.17 | 0.76 | 1.49 | 1.45 | -1.27 |
| Alunite | KAl3(SO4)2(OH)6 | 9.12 | 6.28 | 4.61 | 7.86 | 8.38 | 9.5 | 5.39 | 9.08 | 8.28 | 5.25 | 4.25 | 5.49 | 9.06 | 3.66 |
| Annite | KFe3AlSi3O10(OH)2 | 0.78 | -5.11 | -7.08 | 3.5 | 3.49 | 1.23 | -5.78 | 2.14 | -0.5 | -4.59 | 0.02 | 4.96 | 5.1 | -4.29 |
| Ba3(AsO4)2 | Ba3(AsO4)2 | 7.38 | 5.21 | - | 10.9 | 10.68 | 7.38 | 4.78 | 7.36 | 5.22 | - | - | 10.96 | 8.17 | - |
| Barite | BaSO4 | 0.43 | 0.31 | 0.34 | 0.74 | 0.69 | 0.5 | 0.38 | 0.44 | 0.37 | 0.26 | 0.69 | 0.61 | 0.54 | 0.34 |
| Basaluminite | Al4(OH)10SO4 | 9.57 | 5.53 | 3.22 | 9.29 | 9.97 | 9.98 | 3.91 | 9.95 | 8.15 | 3.92 | 4.81 | 6.52 | 10.09 | 1.52 |
| Boehmite | AlOOH | 3.3 | 2.17 | 1.58 | 3.62 | 3.72 | 3.38 | 1.69 | 3.44 | 2.83 | 1.7 | 2.6 | 3.05 | 3.5 | 1.16 |
| Cerrusite | PbCO3 | 0.19 | -0.78 | -1.44 | 1.17 | 1.31 | 0.52 | -1.79 | 0.48 | -0.53 | -1.78 | 0.31 | 0.99 | 0.66 | -2.14 |
| CupricFerrite | CuFe2O4 | 14.31 | 10.57 | 9.72 | 16.96 | 17.3 | 14.15 | - | 14.22 | 12.27 | - | 16.41 | 17.91 | 14.6 | - |
| CuprousFerrite | CuFeO2 | 9.32 | 6.68 | 6.27 | 11.07 | 11.14 | 9.09 | - | 9.47 | 8.24 | - | 10.69 | 12.39 | 10.62 | - |
| Diaspore | AlOOH | 5.01 | 3.87 | 3.29 | 5.32 | 5.43 | 5.09 | 3.4 | 5.14 | 4.53 | 3.4 | 4.31 | 4.76 | 5.21 | 2.86 |
| Gibbsite | Al(OH)3 | 3.78 | 2.64 | 2.05 | 4.09 | 4.2 | 3.86 | 2.17 | 3.91 | 3.3 | 2.17 | 3.08 | 3.53 | 3.98 | 1.63 |
| Goethite | FeOOH | 8.81 | 7.61 | 7.17 | 9.51 | 9.67 | 8.88 | 7.21 | 8.87 | 8.24 | 7.25 | 9.14 | 9.75 | 9.01 | 6.88 |
| Halloysite | Al2Si2O5(OH)4 | 3.88 | 1.32 | 0.1 | 4.54 | 4.75 | 4.17 | 0.47 | 4.34 | 2.99 | 0.48 | 1.81 | 2.85 | 4.31 | -0.65 |
| Hematite | Fe2O3 | 19.62 | 17.23 | 16.35 | 21.03 | 21.35 | 19.77 | 16.42 | 19.74 | 18.49 | 16.5 | 20.29 | 21.5 | 20.02 | 15.78 |
| Laumontite | CaAl2Si4O12:4H2O | 2.48 | -0.77 | -1.94 | 5.05 | 4.92 | 2.87 | -1.62 | 3.47 | 1.4 | -1.65 | 2.15 | 3.12 | 3.2 | -2.56 |
| Leonhardite | Ca2Al4Si8O24:7H2O | 12.79 | 6.3 | 3.96 | 17.94 | 17.68 | 13.57 | 4.59 | 14.78 | 10.63 | 4.54 | 12.15 | 14.08 | 14.24 | 2.72 |
| Maghemite | Fe2O3 | 9.23 | 6.84 | 5.95 | 10.64 | 10.96 | 9.37 | 6.03 | 9.35 | 8.1 | 6.11 | 9.9 | 11.11 | 9.63 | 5.38 |
| Magnetite | Fe3O4 | 18.01 | 14.32 | 12.99 | 19.92 | 20.3 | 18.22 | 13.4 | 18.48 | 16.71 | 13.93 | 18.61 | 21.23 | 19.8 | 13.33 |
| Phillipsite | Na0.5K0.5AlSi3O8:H2O | 0.02 | -1.94 | -2.56 | 1.22 | 1.15 | 0.26 | -2.26 | 0.48 | -0.6 | -2.35 | -0.47 | 0.07 | 0.17 | -2.63 |
| Pyrophyllite | Al2Si4O10(OH)2 | 11.97 | 9.11 | 7.86 | 12.66 | 12.87 | 12.39 | 8.37 | 12.61 | 11.15 | 8.38 | 9.23 | 10.4 | 12.42 | 7.21 |
| ZnSiO3 | ZnSiO3 | 1 | 0.44 | 0.5 | 2.4 | 2.31 | 1.04 | 0.37 | 1.31 | 0.63 | 0.31 | 1.67 | 2.17 | 1.31 | 0.51 |

| | | CONTROL | | | | | | | nZVI | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INCUBATION CONDITION | | 0% | 30% | 60% | 90% | 130% | F1 | F2 | 0% | 30% | 60% | 90% | 130% | F1 | F2 |
| PHASE | COMPOSITION | SATURATION INDEX | | | | | | | | | | | | | |
| Adularia | KAlSi3O8 | -0.15 | 2.02 | 2.27 | 5.06 | 4.22 | 3.9 | 2.26 | 4.32 | 2.97 | 2.16 | 3.66 | 3.69 | 3.76 | 2.21 |
| Alunite | KAl3(SO4)2(OH)6 | - | - | - | 5.07 | 5.44 | 7.53 | 5.63 | 7.23 | 5.98 | - | 1.72 | 1.95 | 6.94 | 6.47 |
| Annite | KFe3AlSi3O10(OH)2 | -0.06 | 1.5 | 1.09 | 6.46 | 6.27 | 5.26 | 3.19 | 5.38 | 2.27 | 1.17 | 6.49 | 8.42 | 6.6 | 3.18 |
| Ba3(AsO4)2 | Ba3(AsO4)2 | 6.81 | 5.88 | 6.59 | 11.66 | 11.27 | 8.9 | 6.24 | 8.57 | 7.42 | 5.92 | 11.74 | 12.58 | 8.87 | 6.64 |
| Basaluminite | Al4(OH)10SO4 | - | - | - | 10.31 | 10.08 | 11.44 | 8.96 | 11.5 | 9.91 | - | 6.53 | 6.9 | 11.06 | 9.44 |
| Boehmite | AlOOH | 3.1 | 3.56 | 3.63 | 4.51 | 4.33 | 4.32 | 3.63 | 4.44 | 4.01 | 3.6 | 3.76 | 3.85 | 4.32 | 3.68 |
| Cerrusite | PbCO3 | -0.59 | -2.53 | - | 0.74 | 0.45 | -0.5 | - | -0.26 | -1.94 | - | 0.56 | 1.02 | - | -0.39 |
| CupricFerrite | CuFe2O4 | 14.09 | 14.28 | 14.48 | 18.74 | 18.63 | 16.28 | 14.16 | 16.36 | 15.43 | 14.22 | 19.47 | 20.24 | 16.21 | 14.11 |
| CuprousFerrite | CuFeO2 | 9.69 | 9.68 | 9.5 | 12.1 | 12.37 | 10.85 | 10.08 | 10.64 | 9.9 | 9.38 | 13.16 | 14.1 | 11.29 | 10.01 |
| Diaspore | AlOOH | 4.8 | 5.26 | 5.33 | 6.21 | 6.03 | 6.03 | 5.34 | 6.14 | 5.71 | 5.3 | 5.46 | 5.55 | 6.02 | 5.38 |
| Gibbsite | Al(OH)3 | 3.57 | 4.03 | 4.1 | 4.98 | 4.8 | 4.8 | 4.11 | 4.91 | 4.48 | 4.07 | 4.23 | 4.32 | 4.79 | 4.15 |
| Goethite | FeOOH | 8.62 | 8.62 | 8.7 | 9.95 | 9.87 | 9.34 | 8.6 | 9.44 | 9.05 | 8.66 | 10.03 | 10.27 | 9.33 | 8.61 |
| Halloysite | Al2Si2O5(OH)4 | 2.94 | 5.08 | 5.36 | 7.65 | 6.9 | 7.11 | 5.37 | 7.44 | 6.12 | 5.24 | 5.4 | 5.59 | 6.93 | 5.32 |
| Hematite | Fe2O3 | 19.24 | 19.24 | 19.4 | 21.91 | 21.75 | 20.69 | 19.2 | 20.89 | 20.12 | 19.33 | 22.07 | 22.54 | 20.67 | 19.23 |
| Hxypyromorphite | Pb5(PO4)3OH | 11.23 | 7.08 | 9.92 | 17.72 | 18.11 | 14.36 | 9.02 | 13.51 | 12.25 | 17.42 | 19.69 | 13.49 | 10.07 | -8.93 |
| Laumontite | CaAl2Si4O12:4H2O | 0.78 | 3.88 | 4.34 | 9.22 | 7.99 | 7 | 4.36 | 8.29 | 5.64 | 4.19 | 7.05 | 7.08 | 6.87 | 4.39 |
| Leonhardite | Ca2Al4Si8O24:7H2O | 9.39 | 15.59 | 16.51 | 26.28 | 23.82 | 21.84 | 16.55 | 24.42 | 19.12 | 16.22 | 21.94 | 22 | 21.57 | 16.62 |
| Maghemite | Fe2O3 | 8.85 | 8.85 | 9.01 | 11.52 | 11.36 | 10.3 | 8.81 | 10.5 | 9.72 | 8.93 | 11.68 | 12.15 | 10.28 | 8.84 |
| Magnetite | Fe3O4 | 17.84 | 17.63 | 17.57 | 20.94 | 21 | 19.71 | 18.08 | 19.81 | 18.45 | 17.56 | 21.58 | 22.68 | 20.18 | 18.12 |
| Pb3(PO4)2 | Pb3(PO4)2 | 7.81 | 5.27 | 7.12 | 11.5 | 11.73 | 9.71 | 6.54 | 9.15 | 8.44 | - | 11.17 | 12.55 | 9.1 | 7.19 |
| Phillipsite | Na0.5K0.5AlSi3O8:H2O | -1.08 | 1.06 | 1.31 | 4.09 | 3.33 | 2.95 | 1.32 | 3.4 | 2.01 | 1.21 | 2.67 | 2.76 | 2.83 | 1.26 |
| Plumbogummite | PbAl3(PO4)2(OH)5:H2O | 10.51 | 13.86 | 14.28 | 17.09 | 15.97 | 16.4 | 14.28 | 16.81 | 15.03 | 14.1 | 14.1 | 14.28 | 16.04 | 14.1 |
| Pyrophyllite | Al2Si4O10(OH)2 | 10.51 | 13.86 | 14.28 | 17.09 | 15.97 | 16.4 | 14.28 | 16.81 | 15.03 | 14.1 | 14.1 | 14.28 | 16.04 | 14.1 |
| Strengite | FePO4:2H2O | 5.93 | 5.67 | 6.49 | 6.24 | 6.17 | 6.79 | 6.21 | 6.64 | 6.5 | - | 5.58 | 5.93 | 6.34 | 6.31 |
| ZnSiO3 | ZnSiO3 | 0.61 | 0.87 | 1.05 | 3.28 | 3.07 | 1.9 | 1.02 | 2.03 | 1.51 | 0.96 | 3.22 | 3.51 | 1.95 | 1.12 |

Appendix 7 Saturated indices for selected phases modelled with PHREEQC-3 program (version 3.0) (L/S 10)

| | | CONTROL | | | | | | | nZVI | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INCUBATION CONDITION | | 0% | 30% | 60% | 90% | 130% | F1 | F2 | 0% | 30% | 60% | 90% | 130% | F1 | F2 |
| PHASE | COMPOSITION | SATURATION INDEX | | | | | | | | | | | | | |
| Adularia | KAlSi3O8 | -0.64 | -1.12 | -1.49 | 0.47 | 0.54 | -0.33 | -0.69 | 0.03 | -0.13 | 0.79 | 0.21 | 0.31 | 0.4 | -1.46 |
| Alunite | KAl3(SO4)2(OH)6 | 6.91 | 6.53 | 6.29 | 5.07 | 4.14 | 6.55 | 4.69 | 8.04 | 6.63 | 7.28 | 4.1 | 5.23 | 6.71 | - |
| Ba3(AsO4)2 | Ba3(AsO4)2 | 5.3 | 5.3 | 4.89 | 9 | 10.31 | 6.84 | 6.5 | 7.04 | 6.84 | 7.23 | 9.42 | 9.29 | 7.63 | - |
| Basaluminite | Al4(OH)10SO4 | 7.58 | 7.39 | 6.74 | 7.41 | 6.56 | 8.18 | 6.92 | 8.77 | 8.18 | 9.02 | 6.25 | 7.5 | 8.57 | - |
| Boehmite | AlOOH | 2.87 | 2.81 | 2.59 | 3.31 | 3.21 | 3.22 | 3.05 | 3.24 | 3.22 | 3.46 | 3.06 | 3.3 | 3.42 | 2.52 |
| Cerrusite | PbCO3 | -0.25 | -0.33 | -0.46 | 0.79 | 0.92 | 0.29 | 0.06 | 0.14 | 0.06 | -0.08 | 0.57 | 0.84 | 0.29 | -0.68 |
| CupricFerrite | CuFe2O4 | 12.28 | 12.64 | 11.99 | 15.87 | 16.94 | 13.87 | 13.52 | 14.99 | 14.8 | 15.05 | 16.27 | 16.51 | 15.81 | 11.85 |
| CuprousFerrite | CuFeO2 | 7.34 | 7.55 | 7.2 | 9.82 | 10.52 | 8.16 | 7.86 | 9.42 | 9.35 | 9.7 | 11.3 | 10.67 | 10.43 | 7.35 |
| Diaspore | AlOOH | 4.58 | 4.52 | 4.29 | 5.01 | 4.91 | 4.92 | 4.76 | 4.95 | 4.92 | 5.17 | 4.77 | 5.01 | 5.12 | 4.22 |
| Gibbsite | Al(OH)3 | 3.34 | 3.29 | 3.06 | 3.78 | 3.68 | 3.69 | 3.53 | 3.72 | 3.69 | 3.94 | 3.54 | 3.78 | 3.89 | 2.99 |
| Goethite | FeOOH | 8.26 | 8.31 | 8.11 | 9.17 | 9.45 | 8.73 | 8.58 | 8.79 | 8.77 | 8.77 | 9.29 | 9.56 | 9.01 | 8.02 |
| Halloysite | Al2Si2O5(OH)4 | 2.25 | 2.05 | 1.55 | 3.12 | 2.87 | 2.81 | 2.47 | 2.81 | 2.91 | 3.7 | 2.55 | 3.04 | 3.31 | 1.4 |
| Hematite | Fe2O3 | 18.53 | 18.64 | 18.22 | 20.35 | 20.9 | 19.47 | 19.16 | 19.58 | 19.55 | 19.56 | 20.58 | 21.13 | 20.02 | 18.05 |
| Laumontite | CaAl2Si4O12:4H2O | -0.64 | -0.75 | -1.39 | 2.32 | 2.26 | 0.54 | 0.29 | 0.83 | 0.99 | 2.37 | 1.94 | 1.88 | 1.52 | -1.53 |
| Leonhardite | Ca2Al4Si8O24:7H2O | 6.55 | 6.34 | 5.06 | 12.48 | 12.35 | 8.91 | 8.42 | 9.49 | 9.82 | 12.57 | 11.72 | 11.59 | 10.89 | 4.78 |
| Maghemite | Fe2O3 | 8.14 | 8.24 | 7.82 | 9.95 | 10.51 | 9.08 | 8.77 | 9.19 | 9.16 | 9.16 | 10.19 | 10.73 | 9.63 | 7.66 |
| Magnetite | Fe3O4 | 15.87 | 15.92 | 15.4 | 18.39 | 19.12 | 16.98 | 16.41 | 17.35 | 17.4 | 17.51 | 19.95 | 20.16 | 18.4 | 15.35 |
| Pyrophyllite | Al2Si4O10(OH)2 | 9.57 | 9.28 | 8.75 | 10.45 | 10.14 | 10 | 9.64 | 9.93 | 10.19 | 11.29 | 9.78 | 10.29 | 10.59 | 8.57 |
| ZnSiO3 | ZnSiO3 | -0.02 | 0.11 | -0.05 | 1.66 | 2.06 | 0.65 | 0.68 | 0.84 | 0.85 | 1.3 | 1.76 | 1.4 | 1.15 | -0.12 |

Appendix 8 - Abstract of International Conference on the Biogeochemistry of Trace Elements (ICOBTE)2017 in Zurich, Switzerland.

## Different incubation conditions for nano zero-valent application in contaminated soils

Martina Vítková[a], K. G. Gordor[a], A. Cortial[a] and M. Komárek[a]

*a Department of Environmental Geosciences, Faculty of Environmental Sciences, Czech University of Life Sciences Prague, Czech Republic*

*vitkovam@fzp.czu.cz*

Zero-valent iron (ZVI) and its nanoscale form (nZVI) are widely used amendments for groundwater and soil remediation. Based on the properties of both Fe oxides and metallic Fe, the treatment with (nano) ZVI particles involves co-precipitation, adsorption and/or reduction of contaminants. The transformation products may vary under different environmental conditions and in the presence of particular metal(loid)s. When nZVI is applied into soils, the interactions strongly depends on several key factors including the soil pH-Eh conditions, the chemical and mineralogical compositions, water holding capacity (WHC) and the presence of dissolved organic matter. Therefore, wide range of factors need to be taken into account when assessing the use of nZVI under given conditions and the efficiency of the stabilization process.

In this context, the applicability of nZVI in two contrasting soils was investigated under different incubation and extraction conditions, (i) as a function of moisture content, simulating various environmental conditions (i.e., dry and wet seasons, flooding, etc.) and (ii) as a function of liquid-to-solid (L/S) ratio, simulating the aging of nZVI particles. Thus, the main objectives of this study were (i) to assess the effect of soil water content on the changes in redox potential and the behavior of metals/metalloids in nZVI-treated soils, (ii) to assess the L/S ratio-dependent interactions between nZVI and metals/metalloids and (iii) to assess the efficiency of nZVI on contaminant stabilization.

An aliquot of each soil sample was carefully mixed with active nZVI (1 wt.%) and placed in a pot. Control soil samples without amendment were prepared simultaneously. With respect to corresponding WHC, the pots were maintained at 0%, 30%, 60%, 90% and 120% of WHC for 3 months. After this incubation period, the samples were dried and subjected to a set of laboratory experiments including the determination of basic physico-chemical parameters and extractions in demineralized water.

In general, the addition of nZVI increased the soil pH and the flooded sample showed more reducing conditions. Moreover, changes in the available fractions of the target risk elements (As, Pb, and Zn) were observed as a function of moisture content. The behavior of metals showed correlation with changes in pH and the content of organic carbon. Finally, the stabilization efficiency of nZVI was mainly pronounced for As, representing the crucial redox-sensitive element in our study.

The presented experimental approach allows to investigate the behavior of different inorganic contaminants in various environmental scenarios and to assess the applicability of nZVI under given conditions. Enhanced metal(loid)-nZVI interactions related to high soil water content indicated the importance of redox changes on the mobility of metals/metalloids. Although the immobilization efficiency of nZVI depends on several factors, it proved to be an efficient amendment for As-contaminated soils.