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Remediation of metal contaminated soils – evaluation of long-term effects of zero-valent iron amendments

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Abstract

The efficiency of contaminant stabilization in soil treated with zero-valent iron (ZVI) should be evaluated in long-term experiments, as stabilization techniques do not decrease total metal concentration. With time, properties of soil can change and iron hydroxides can crystalize, what can lead to a release of contaminants. This study evaluates the influence of ZVI on arsenic, copper, cadmium and nickel solubility in contaminated soils after 16 and 6 years after applying the treatment. The soils were treated with 1% iron grit (Reppel and Louis Fargues) and 2% iron grit (Biogeco). Louis Fargues soil was additionally treated with sewage sludge and sewage sludge with addition of 1% iron grit. Batch equilibrium experiments were performed to investigate solubility of metals in a wide pH-range (3-9). Observed solubility was evaluated using the geochemical equilibrium program Visual MINTEQ (Cu and As). Batch experiments showed that ZVI addition did not have an influence on cadmium and nickel solubility, whereas the solubility of arsenic decreased significantly (approximately a factor of ten). Influence on copper was pH dependent – at ambient pH (ca. 6.5) the solubility was significantly reduced. In contrast, the solubility at lower pH remained the same in control and ZVI-treated soils. This behaviour could be mimicked with Visual MINTEQ, strengthening the validity of these data. This study suggest that ZVI addition can be a suitable remediation method for As and Cu, also in a long-term-perspective. For Cu pH needs to be kept at about 7, since binding strength of Cu by ferric (hydr)oxides decreases with decreasing pH.

Keywords: zero-valent iron, stabilization, trace elements, soil contamination, remediation

Popular science summary

Nowadays more and more people focus on healthy life-style, including food. But do we know what salad, wheat, rice or spinach may contain? Plants are taking up water with all the necessary microelements from soil. However, not only microelements are found in soil water. Soil water can contain also toxic pollutants, such as trace elements. Uptake of contaminated water leads to intoxication of plants. When such plants are eaten by humans it may have negative effects on our health. Most adverse effects that trace elements might have on humans are cancer, cardiovascular problems, liver and kidney damage and anaemia.

Are there any solutions to prevent the uptake of contaminants and reduce the risk related to trace element contamination? Yes, there are!

Today, soil remediation, instead of soil disposal, is a widely used solution to decrease bioavailability of contaminants (including trace elements) in soil. One of the technologies is stabilization of trace elements. It can be done in different ways. Phytostabilization is stabilization of trace elements in root zone of a plant, while chemical stabilization use different chemicals e.g. lime or iron grit.

Researchers are investigating influence of iron grit on stabilization of trace elements in soil. Addition of iron to soil might cause trace elements to be sorbed to the surface of the iron particles. This is because the iron grit, i.e. small particles of metallic iron, is being transformed to iron hydroxides in the soils. It is the iron hydroxides that is sorbing the metals. Hence, the metals are stabilized and cannot leach to groundwater and cannot be taken up by plants. Previous experiments using iron grit are promising. However, knowledge about the long-term effects of such stabilization is needed.

Soils from different parts of Europe contaminated with i) arsenic, ii) copper and iii) cadmium and nickel were treated with iron grit. After 16 years soils contaminated with arsenic and cadmium and nickel were collected. Soil contaminated with copper was collected after 6 years of implementing iron grit. Afterwards investigation of solubility of trace elements in each soil was conducted.

Results showed that after 16 years arsenic is still very well stabilized by iron. Another experiment showed that copper is also stabilized after 6 years of application of iron grit. However, stabilization of copper depends on the pH of soil. In acidic soil there is no influence of iron addition. In higher pH values (above 6) copper is stabilized by iron very well. In case of cadmium and nickel there was no influence of iron addition on stabilization these two elements.

In order to reduce risk related with soil contamination remediation with iron grit amendment can be an option. Especially for arsenic stabilization in South-East Asia, where concentration of this trace element is very high in soils and groundwater. In that area many people have been suffering because of arsenic pollution. However, iron grit is only working in well drained soils, because arsenic needs to be present as arsenate to work. Addition of iron grit to soil contaminated with copper can also be recommended. However, soil properties have to be monitored. Monitoring of soil pH is necessary to prevent the release of copper to groundwater. There was no influence on stabilization of cadmium and nickel in long-term perspective. However, other research showed that iron grit treatment in short-term perspective for these metals is efficient. Therefore iron addition to soil can be temporary solution, before other remediation strategies can be implemented.

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1. Introduction

Soil – the top layer of Earth’s crust – is an important environmental constituent. It has an important role for ecosystems. For instance, it is habitat for organisms and it influences water management. For humans, soil is also important – it influences human well-being as well as economy. Moreover, soil is a base for food production.

Soil is defined as non-renewable resource, which means that it cannot be restored on a time scale in which its consumption rate will be sustained (SERI, 2011). Recently, soil has become one of the concerns of the European Union. EU has defined several threats to soil, such as: acidification, erosion or pollution.

For a long time soil has been polluted with different contaminants: organic and inorganic. Inorganic contaminants are commonly trace elements; i.e. metals (e.g. nickel, copper, cadmium) and metalloids (arsenic). Trace elements in too high concentration have a negative influence on soil organisms, plants and animals which consume intoxicated plants. Mobility of metals can be high in certain environments and, therefore, metals can be taken up by plants. This process can lead to decreased yield or poisoning of animals, as well as humans, eating the plants.

Over-exploitation and contamination of soil can lead to a situation in which soil ceases to fulfill its functions. Therefore, soil should be protected so that it can maintain its important functions.

To remediate soils contaminated with trace elements, various disposal strategies might be used. However, this kind of solution does not treat the contaminants in soil. Therefore, solutions, which treat the contaminants (immobilize or extract), are proposed. Remediation of trace element contaminated soils might be difficult, as, in contrast to organic pollutants, trace elements do not degrade. One of the remediation strategies is soil stabilization of trace elements. Stabilization involves adding different amendments to soils, which adsorb, co-precipitate or in other ways bind trace elements. Due to these processes the mobility of contaminants decreases and hence, the contaminants are not available for plant uptake and do not leach to groundwater. What has to be taken into account is, that this stabilization method does not decrease total trace element concentration (Kumpiene et al., 2006). Moreover, when in-situ stabilization methods are applied, several important aspects have to be taken into consideration. For example, whether maintenance is needed, whether the method is effective or what are the costs (Mench et al., 2006). To answer these questions long-term studies are needed.

Research presented in this thesis concerns the long-term influence of ZVI addition on trace element solubility in soil samples from three contaminated sites in Europe. These soils were contaminated with the following: arsenic (Reppel soil), nickel and cadmium (Louis Fargues soil), and copper (Biogeco soil). Reppel and Louis Fargues experiments started in 1997 and Biogeco experiment was started in 2006. Behavior of these trace elements was investigated in control soils and soils treated with ZVI. Batch leaching experiments were performed and the results were evaluated using the Visual MINTEQ – geochemical computer software.

2. Aim and objectives

Zero-valent iron is an amendment used to stabilize trace elements in soils. However, with time iron can lose its properties and previously stabilized trace elements can leach to deeper soil layers or even groundwater.

The aim of this research is to investigate the influence of zero-valent iron amendments on solubility of trace elements (cadmium, copper, nickel and arsenic) in soils in a long-term perspective.

To investigate the influence of zero-valent iron on trace element solubility a batch leaching experiment was conducted covering a wide pH range. The experiment was conducted on soils, which were amended with zero-valent iron 16 and 6 years ago. Additionally, the geochemical model Visual MINTEQ was used to evaluate laboratory results.

3. Literature review

3.1. Soil and its functions

Soil is the top layer of Earth's crust. It consists of mineral particles, water, air, organic matter, as well as living organisms. Soil plays an important role in ecosystems – it is a habitat for living organisms, serves as a gene pool and it is the second biggest carbon sink, with a potential to slow down the climate change. Furthermore, soil is a platform for human activities, such as food and fiber production (EEA, 2010).

The main functions of soil, according to European Environmental Agency (2010) are the following:

- Soil is the main global food supplier – 99% of food for humans comes from production based on land.
- Soil has an ability to purify water supplies through filtration processes. Also, its water storing capacity is an important component in flood regulation. Moreover, soil is able to neutralize some pollutants, either by transforming them to less harmful particles, or by accumulation and adsorption of toxic particles.
- Soil is the habitat for millions of organisms, such as: bacteria, fungi, protozoa, nematodes etc. These organisms are important for fundamental processes in soils such as nutrient cycling processes, degradation of pollutants, and stabilization of soil structure and regulation of plant communities.
- As it was already mentioned, soil plays an important role in regulating biological and chemical cycles (e.g. nitrogen, carbon cycles), which are crucial to life sustainability.
- Soil preserves our cultural heritage, as it holds evidences of past human life and historic remains. The latter are thus protected from damage and depletion. Hence, soil should be recognized as a valuable element in the protection of cultural heritage.
- Soil is the base for construction of infrastructure, such as: buildings and roads. Moreover, soil contributes different raw materials, which are needed for daily use, e.g. clay for pottery.

3.2. Soil threats

Soil is a non-renewable resource and its over-exploitation leads to degradation and irreversible loss of this valuable good. Estimations show that the loss rate of fertile soils in Europe is between 8 and 10 km² per day, due to urbanization and industrialization (Blum, 2008). It is recognized that human activities are the main causes of soil degradation. Soil degradation makes soil unable to maintain ecosystem services. This leads to food deficiency, decline in yield, increase in commodity prices, desertification, as well as destruction of ecosystems (EEA, 2010). The main threats to soils, recognized by the European Union, caused by industrial activities and changes in land use are the following:

- Loss of organic carbon,
- Erosion,
- Soil compaction,
- Soil sealing,
- Soil acidification,
- Soil salinization,

- Desertification,
- Landslides,
- Loss of biodiversity,
- Soil contamination.

3.3. Soil contamination with trace elements

Trace elements naturally appear in low concentrations in soils or plants. Some of them are relevant for growth and development of organisms (humans, animals, plants). The natural concentration of trace elements in soils can differ from site to site and can reach high levels (Pierzynski et al., 2005). As an illustration, table 1 presents natural and geochemically anomalous concentrations of trace elements.

According to the definition of Joint Research Center (2012), soil contamination occurs when the concentration of contaminant (e.g. certain trace element) is above a level, at which one or more soil functions declines or are lost. Contamination of soil by trace elements is a large problem mainly in industrialized countries. More than 200 years of industrialization have made soil contamination a wide-spread problem in Europe (EEA, 2010). The main sources of trace elements in soils are the following: atmospheric deposition, mining, fossil fuel combustion, irrigation, waste incineration, use of fertilizers and agrochemicals, as well as industrial activities such as wood impregnation. Moreover, natural processes, such as volcano eruptions, forest fires and chemical composition of parent material, can lead to pollution of soil (Wuana and Okieimen, 2011).

Contamination with metals and metalloids is a serious threat to environment and human health. Heavy metals and metalloids found most frequently in soils are: arsenic, chromium, lead, zinc, nickel, cadmium, copper and mercury (Dermont et al., 2008). In these study main focus is on arsenic, copper, cadmium and nickel. These elements are briefly described in the following paragraphs.

Table 1. Trace elements concentrations in soils at normal and geochemically anomalous levels (Pierzynski et. al, 2005)

Element	'Normal' range[mg/kg]	Metal-rich range [mg/kg]
Arsenic (As)	<5 to 40	Up to 2 500
Cadmium (Cd)	<1 to 2	Up to 30
Copper (Cu)	2 to 60	Up to 2 000
Molybdenum (Mo)	<1 to 5	10 to100
Nickel (Ni)	2 to 100	Up to 8 000
Lead (Pb)	10 to 150	10 000 or more
Selenium (Se)	<1 to 2	Up to 500
Zinc (Zn)	25 to 200	10 000 or more

One of the ways to categorize soil trace metals is by using their expected chemical form in soil and soil solution. Chemicals can be divided into three sorptive groups (Thompson and Goyne, 2012):

- Anionic sorptives, which are negatively charged (e.g. oxyanions such as AsO_4^{3-})
- Cationic sorptives, which are positively charged (e.g. cations Cd^{2+})
- Uncharged organic sorptives (e.g. benzene)

Arsenic

Arsenic is a metalloid, which occurs in many minerals. It can be found in copper, lead, zinc, silver and gold ores. As may have several oxidation states (-III, 0, III and V). It is present in the soil and soil solution as oxyanion, which means that As is combined with oxygen into negatively charged molecule (such as: AsO_4^{3-} or AsO_3^{3-}) (Wuana and Okieimen, 2011). However, it can be present as well with other inorganic compounds, such as iron and sulfur (Frumkin and Thun, 2008). As toxicity depends on its chemical form. Pentavalent forms of As, which are dominant in aerobic conditions (e.g. arsenate AsO_4^{3-}) are less toxic than trivalent compounds (e.g. arsenite).

As is one of the elements of greatest concern especially in South and Southeast Asia. As, which naturally occurs in rocks and sediments in Himalaya region, enters groundwater by biogeochemical and hydrologic processes. Population exposed to increased levels of As in this area reached more than 100 million. Studies showed that in these areas mortality is doubled, due to liver, bladder and lung cancers as well as cardiovascular diseases (Fendorf et al., 2010). Moreover, arsenic can inhibit children mental development .

At aerobic conditions and low pH values arsenate co-precipitates with or adsorbs to iron hydroxides. Co-precipitates are immobile; however, their mobility grows when pH increases (Wuana and Okieimen, 2011). While anoxic conditions appear arsenate is being reduced to arsenite, which can be easily transported to the groundwater (Kumpiene et al., 2009). Additionally, reduction of Fe(III), in anaerobic conditions, can lead to further release of arsenic due to loss of adsorbing surfaces (Islam et al., 2004)

Cadmium

Cadmium is one of the trace elements, which are a great concern for the environment, due to its toxicity to animals and humans. Acute poisonings with Cd are rare. More common are chronic poisonings, as Cd, which is ingested with food, accumulates in human organs, mainly in kidney, liver and reproductive organs. Contamination of environment with Cd has increased rapidly in recent years. In contrast to Pb, Cu and Zn, Cd started to be used widely in 20th century. Cd enters the environment via different pathways, such as: industrial wastes from electroplating, manufacturing of plastics, mining, paint pigments, batteries containing Cd. Cd also has many applications in households, vehicles, agricultural implements, tools (industrial and hand) and many more. Cd pollution in Taiwan has changed that valuable farmland into non-arable land. Therefore techniques, which will allow remediate cadmium contaminated soils, are needed (Kirkham 2006).

Cd in solution occurs mainly as a divalent ion (Cd (II)) (Wuana and Okeimen, 2011). Cd is fairly mobile in soils and, therefore, it is more available to plants, than, for example, copper.

Copper

Copper is one of the most frequently used metals in the world. Cu is an essential element for humans, animals and plants. However, soil contaminated with Cu can impose direct and indirect threats. Direct threats include, for instance, reduced crop growth and yield. Indirect threats include poisoning due to ingestion of contaminated food. In high doses, Cu can cause anemia, liver and kidney damage or stomach irritation.

Research shows that in soils Cu binds strongly to organic matter, and only a small fraction of ionic Cu can be found in solution. In soil solution Cu is present as ionic copper Cu(II) (Wuana and Okeimen, 2011). However if the pH of soil is acidic Cu is mobilized and can be uptaken by plants and influence crop yield (Wuana and Okeimen, 2011).

Nickel

In natural environments nickel occurs in low levels. In low doses, it is an essential element for animals. However, when the dose is too high it can cause various kinds of cancer. Sources of Ni contamination mainly include metal planting industries, fossil fuel combustion, nickel mining and electroplating. Ni is released to the environment by power plants and waste incinerators and, after a long time, it is deposited on the ground. In low pH values Ni occurs as free ions Ni(II) and in alkaline environment Ni forms precipitate – Ni(OH)₂, which is stable compound. Majority of released and deposited Ni is immobilized, as it adsorbs to sediments and soil particles. However, as other cationic trace elements (copper and cadmium) nickel is mobile in acidic pH values and can leach to groundwater (Wuana and Okeimen, 2011).

3.4. Bioavailability of trace elements and risk assessment

Risk is the probability of injury, loss or damage. This broad definition includes different situations such as: financial losses or human/animal health effects after exposure to contaminants. In determining risk for human health related with soil contamination important is pathway: soil – plant – human and the most critical step is soil – plant transfer of trace elements.

It is necessary to remediate contaminated soils in order to create favorable conditions for plant growth. However, it is important not to remediate areas, which are not highly contaminated. Additionally, the cleanup levels are not unified and may be overprotective or underprotective (Pierzynski et al., 2005), due to economy, policy and inappropriate risk assessment.

Risk assessment is a scientific base for regulations or determining cleanup levels. Most of the European countries have introduced regulatory guidelines and safety concentrations for soil contaminants including trace elements. Guideline values are set in order to protect:

- People living on the contaminated site
- Soil environment
- Ground and surface water

Table 2 presents estimated general guideline values for contaminated land in Poland, Sweden and Austria. For Swedish guideline values, there is differentiation for sensitive and non-sensitive land use. Values for sensitive land use concern concentrations of trace elements to protect humans from the exposure via consumption of vegetables grown on the site. Guidelines for non-sensitive land use are values which should not be exceeded in order to protect soil biota.

Often risk assessment is related to total concentrations of trace elements in soil (Lee et al., 2011). However these values not necessarily indicate risk. Therefore, integration of bioavailability of metals and metalloids concept into risk assessment can significantly improve its precision (Dijkstra et al., 2009). According to the definition in ISO 11075:2005 the bioavailability shows “the degree to which chemicals which are in the soil may be adsorbed or metabolized by humans or ecological receptors”

(Brack, 2011). In another words, bioavailable fraction of contaminants is a fraction of total concentration of trace elements, which can become available for uptake by organisms in a certain time span. According to Degryse et al. (2009) uptake of trace elements by plants is related to solubility of trace elements in soil. There are different methods which are used to predict the concentration of contaminants in plants for example short-term bioassays.

Summarizing, information about bioavailability can help to design more cost-effective assessment of land and remediation strategy. Additionally, this information can be efficient tool in risk assessment or it can help in decision making (Pelfrêne et al., 2012).

Table 2. Guideline values for trace elements in soils

Trace element	Sweden ¹		Austria ²	Poland ³
	Sensitive landuse [mg/kg]	Non sensitive landuse [mg/kg]	Agricultural use[mg/kg]	Agricultural use (soil depth 0-30 cm) [mg/kg]
Arsenic	10	25	20	20
Cadmium	0.5	15	1 (0.5*)	4
Copper	80	200	100	150
Chromium (total)	80	150	100	150
Mercury	0.25	2.5	1	2
Molybdenum	40	100	5	10
Nickel	40	120	60	100
Vanadium	100	200	50	N/A
Zinc	250	500	300	300

*valid for slightly acid soils

3.5. Behaviour of trace elements

As it was stated in previous chapter, in order to improve risk assessment introduction of concept of bioavailability is recommended. Behaviour of the element in soil, such as leachability, bioavailability, risk for human health and remediation strategies depend on chemical species, which are determined by soil chemistry. Trace elements can be present in soils in several forms, so called species (Dermont et al., 2008). Bioavailability and mobility of species is dependent mainly on solid solution partitioning and solution speciation (Groenenberg et al., 2012). According to Degryse et al. (2009) main elements responsible for determination of bioavailability are free metal ions. And the mechanisms which determine solid-solution partitioning of trace elements in soils are various sorption processes involving reactive surfaces (Dijkstra et al., 2009).

There are three main and possible mechanisms responsible for controlling the solubility. These are as following:

- Mineral solubility
- Ion exchange
- Surface complexation (chemisorptions)

¹Riktvärden för förorenad Mark Modellbeskrivning och vägledning, 2009

²6th Report on the State of the Environment in Austria – 6. Soil, 2002

³Standardy jakości gleby oraz standardy jakości ziemi, 2002

Mineral solubility

The distribution of substances (inorganic) in solid-solution phases is influenced by mineral dissolution (e.g. $\text{CaCO}_3 - \text{Ca}^{2+}$; $\text{Al}(\text{OH})_3 - \text{Al}^{3+}$) or precipitation (e.g. insoluble sulfide salts with Hg^{2+} , Cu^{2+} or Cd^{2+}) processes. It concerns elements present in moderate or high concentrations in soil solution. In order to determine the process responsible for controlling mineral solubility (mineral dissolution or precipitation) knowledge about chemical properties of soil (mainly ion activities) and the intrinsic stability of minerals is required (Essington, 2004).

Electro static adsorption (Ion exchange)

Cation exchange is an adsorption process in which involved is exchange of an adsorbate (from the soil surface) by an adsorptive. This process is distinguished from other adsorption processes due to the nature of interactions (Essington, 2004). As the most heavy metals (with some exceptions) occur as cations in soil solution, their adsorption depends on the density of negative charges on the surfaces of the soil colloids. The surface negative charge is balanced by equal quantity of cations to maintain electroneutrality (Alloway et al., 1995). The interactions between exchangeable ions are electrostatic bonds, which are weak. Cation exchange is a reversible process. Moreover, cations present in soil solution can precipitate. These cations either form outer-sphere complexes or stay in the diffuse layer of the solid-solution phase (Essington, 2004)

Surface complexation (chemisorption)

The ion activity in solution is controlled by sorption reaction, rather than precipitation. (Welp and Brümmer, 1999). The reactive surfaces (solid-phase materials) to which trace elements can bind are silicate clays, metal (oxy)hydroxides (mainly, iron, manganese and aluminum) as well as soil organic matter (SOM). Clay minerals are negatively charged and therefore they bind only positively charged species. Metal (oxy)hydroxides are variably charged depending on pH. In acidic environment (oxy)hydroxides bind mainly anionic elements, whereas in alkaline pH values they bind more easily cationic elements (Thompson and Goyene 2012). In soil organic matter there are many different reactive groups: most predominant being the carboxyl and hydroxyl groups, giving a net negative surface charge of SOM in natural environments (Thompson and Goyene, 2012).

Research made in Canada by Sauvé et al. (2003) and Ge and Hendershot (2005) state that heavy metals have high affinity to bind to organic matter. Especially cadmium shows tendency to accumulate in organic matter in forest soils (Sauvé et al., 2003). Ge and Hendershot (2005) stated that in boreal regions organic matter is primary sorbent for trace elements and due to its reactive character it can sorb well metal cations.

To determine the sorptive fate important are sign and magnitude of electrical charge of sorptive and sorbent. As it was stated before anions will bind to positively charged sorbents and cations will bind to negatively charged surfaces. In case of metal (oxy)hydroxides and SOM main element, which is influencing magnitude and sign of sorptive and sorbent, is pH. For example with increasing pH functional groups of metal (oxy)hydroxides and SOM are deprotonating, which leads to increase of negative charge on the adsorbent surface causing cation adsorption and anion desorption (Thompson and Goyene, 2012).

3.6. Soil remediation

Remediation processes are methods for treating a contaminated media in the environment in a way that they are contained, removed or degraded. Remedial actions should be taken when risk assessment indicates high and unacceptable level of risk. Moreover, if there is evidence of environmental and human harm or if the limits for contaminants in food, water and soil are exceeded, remedial actions should be taken.

Contamination of soils and groundwater with trace elements is a major concern for human health, environment and urban development (Dermont et al., 2008; Lee et al., 2011). Remediation of metals and metalloids in soils might be more difficult than remediation of organic pollutants. There are several reasons for that. The distribution (vertical/horizontal) of heavy metals on site is very often heterogeneous. Furthermore, heavy metals are non-degradable and cannot be destroyed. Moreover, the physical and chemical aspects of metals in the soil matrix differ, as trace elements are discharged to the soil in different physicochemical forms, such as salts, ions, particles. (Dermont et al., 2008).

Furthermore, metals and metalloids can be present with organic pollutants, which influence metal mobility in soil, which can cause problems for remediation of metals. In these instances organic pollutants should be removed first (Dermont et al., 2008).

3.7. Remediation strategies

Containment/Disposal

Containment/disposal technologies are still most commonly used. Methods such as isolation (in situ containment) or off-site disposal (relocation) are used in order to prevent leaching of the trace elements to the groundwater. Containment technology can also be used when the mobility of metals and metalloids must be temporarily reduced until the proper remediation measurement can be applied (Dermont et al., 2008).

Monitored Natural Attenuation (MNA)

This is a natural attenuation process, which is regularly monitored. Primarily it is applied for the remediation of soils polluted with organic contaminants, for the metals it is regarded as a “passive treatment”. This technique is appropriate for metals where a change of valence state reduces toxicity and mobility (e.g. oxidation of As(III) to As(V)). MNA is usually insufficient for remediation of trace elements in soils, as it is a very slow process, and it needs to be assisted by engineering actions. This technique can be used after the proper remedial treatment (Dermont et al., 2008).

Immobilization and extraction

Soil washing or extraction processes are based on separation of metals from soil and hence, reducing their concentration. The aim is to decontaminate the soil completely and ideally to recover and reuse the metals. However, due to the lack of economic viability and proper technologies, metal recovery is not practiced today. In some cases, metal extraction can be difficult (strong soil-metal binding) and, therefore, this method is used only to reduce the concentration of metals to acceptable levels (Dermont et al., 2008).

The aim of immobilization techniques is to stabilize metals – reduce leaching and/or create the forms of metals which are less soluble, toxic or bioavailable. If the fractions of trace elements are less available, the toxicological and/or environmental risk decreases as well as functionality of soil can be kept (Komárek et al., 2013). In situ stabilization techniques can be divided into three subcategories: biological stabilization, phytostabilization and chemical stabilization. The principle of biological stabilization is to use biosolids amendments or microorganisms to form less toxic and less soluble metal forms. Phytostabilization is based on using plants in order to immobilize metals. Chemical stabilization is still in the research and development state. The principle of this method is to use chemical amendments, such as iron (hydr)oxides, zero-valent iron (ZVI), phosphates, lime, fly ashes or aluminosilicates, in order to stabilize metals (Dermont et al., 2008).

Each contaminant has different properties; therefore, the chosen amendment should not cause complications, such as pH fluctuations. Changes in pH can lead to mobilization of trace elements. One of the amendments which does not change (or causes minor changes) pH is ZVI (Fe^0) (Kumpiene et al., 2006).

Benefits from stabilization techniques are improvement of soil properties (physical, chemical and biological), no by-products and not expensive. The relevantly low price of stabilization techniques causes that they are suitable for remediation of land, which has low value (Lee et al., 2011)

3.8. Zero-valent iron (ZVI) remediation

Soil oxides, such as hydroxides or oxyhydroxides, occur naturally in soils. These are products of weathering and appear in soil as e.g. discrete crystals or coatings on other particles (Sparks, 2003).

Traditional methods as containment or disposal are not suitable (or even not effective) if large areas are contaminated; therefore, there is increase in development of alternative remediation technologies (Cundy et al., 2008, Lee et al., 2011).

Sorption properties of metal oxides, especially iron, is well studied. It has been shown that iron oxides can be a good stabilization amendment, especially in soils and waters contaminated with arsenic (Komárek et al., 2013). Application of precursors of iron oxides (such as iron grit or iron sulphates) should decrease bioavailability and bioaccessability of metals and metalloids and hence, decrease risk of environmental contamination, leaching to groundwater and uptake by plants (Komárek et al., 2013). Moreover, ZVI is able to stabilize several contaminants, as iron oxide surfaces can adsorb cations, as well as anions. Additionally, ZVI oxidation state does not change pH significantly (Kumpiene et al., 2006).

Iron-based technologies can be divided into two groups, depending on the property of iron which is involved in the remediation process: reductive technologies and sorptive/stabilization technologies. Reductive technologies use the electron from iron to convert the contaminants into form, which is less toxic or less mobile. Iron as an electron donor (oxidation Fe^{2+} to Fe^{3+}) influences contaminant mobility, sorption and breakdown (Cundy et al., 2008).

Hydrous ferric oxides (HFO) are considered to be effective adsorbents for different contaminants, due to a high reactive specific surface area. However, with time HFO crystalize to other forms, such as hematite or goethite. The surface area of these minerals is reduced and, therefore, they are less effective as sorbents. Chemically driven reactions, like an increase in acidity can cause breakdown

and solubilisation of iron and, hence, release of contaminants (Cundy et al., 2008). Therefore the long-term studies should be performed (Komárek et al., 2013).

According to Cundy et al. (2008) the use of ZVI amendments shows promising results in periods up to 6 years. Previous research showed that addition of ZVI to soil is significantly decreasing leaching of different trace elements (Kumpiene, 2006), as well as supporting plant growth.

3.9. Geochemical modelling

In order to assess the risk related to soil contamination different models, which describe processes in dissolved and solid phase, are used (Dijkstra et al., 2009). Geochemical models include the essential retention and release reactions of trace elements, such as ion exchange, adsorption/desorption, precipitation/dissolution and other mechanisms (Magdi Selim, 2011).

As it was already mentioned leaching and bioavailability of trace elements depends on solid-solution partitioning. There are two main approaches which help to describe speciation of trace elements in soil. First one is empirical “partition-relations”. This approach is based on relations between trace elements and soil properties such as pH and SOM. In this approach model coefficients are obtained from the soil data and solution extracts by linear regression analysis. The second approach are so-called “multisurface models”. They describe processes between soil solution and reactive surface (Groenenberg et al., 2012).

In soils occur different sorbents which can bind trace elements. Therefore, simulation of concentration of heavy metals and metalloids in mechanistically based models is complicated. Sorbents which are responsible for metal binding are organic matter, oxides and clay minerals. There are few approaches to model metal binding to soil components. One way is to use component additivity (CA) approach. The principle of this method is to treat each sorbing soil components (oxides, clay, OM) separately in different “submodels”. Results of each “submodel” are summed and the result is the net metal sorption in the sample. Another approach is to identify and focus on the most important sorbing component. However, such an approach will not be valid for all kind of soil (Gustafsson et al., 2003).

One frequently used software is the Visual MINTEQ. It is free software, which can be downloaded from: <http://www2.lwr.kth.se/English/OurSoftware/vminteq/>. Visual MINTEQ can be used to calculate metal speciation, solubility equilibriums, as well as sorption by different kind of surfaces (Gustafsson, 2010).

4. Materials and methods

4.1. Soil samples

Louis Fargues (France)

Louis Fargues is agricultural soil contaminated mainly with Ni and Cd. The experiment started in 1997. The soil was treated in 3 different ways. To some plots only 1% ZVI was added. Other plots were treated with sewage sludge (B100) and with sewage sludge together with 1% ZVI (B100+1% ZVI). Some plots were not treated and used as a control (Jurate Kumpiene, personal communication, March 27, 2013).

Reppel (Belgium)

This soil originates from a village in Belgium, where from 1910 to 1965 was an As (III) refinery. There were no laws and regulations regarding the treatment and disposal of wastes. In consequence, the surrounding area was contaminated with Zn and As products, which caused the creation of phytotoxic soil. Even adjacent agricultural fields have an increased concentration of As and were slightly phytotoxic. The Reppel experiment was set in 1997 (Mench et al., 2006). Part of the site was treated with 1% iron grit and the other part was not treated (control). The lysimeter - mesocosmes are still managed and cultivated with *Pteris Vittata*.

Biogeco P7 (France)

Biogeco soil sample comes from south-western France, where copper sulphate and chromated copper arsenate (CCA) were used to protect wood against insects and fungi. Copper sulphate was in use between 1913 and 1980. Since 1980 CCA has been in use. Cu is the main soil contaminant and its concentration varies from 65 to 2 600 mg Cu/kg of soil in sample Biogeco P7 (Mench and Bess, 2009). Despite the use of CCA, As and Cr have not accumulated in topsoil. Around 6 ha of the area is abandoned, with some plots of natural vegetation dominated by poplars and willows. Another two hectares are still in industrial use with wood preservative treatment, recycling of treated wood, as well as frame production. In 2006 field plots with dimensions 1 m x 2 m were established. Some plots were treated with 1% iron grit and after two weeks 1% iron grit was added. Therefore, the total concentration of iron grit is 2%. The other plots were not treated with iron grit and formed the control group (Mench and Bess, 2009).

4.2. Soil characterization and analyses

Carbon analyses

Total carbon, inorganic carbon and organic carbon in soils were analyzed on the Leco Analyzer at SLU on air-dried soil samples.

HNO₃ extraction

In order to obtain information about the “geochemical active” concentration of cationic trace elements an extraction with 0.1 M HNO₃ was conducted (Gustafsson et al., 2003). To 1 gram of soil 30 mL of 0.1 M HNO₃ was added. The samples were shaken for 16 hours. Afterwards they were

centrifuged for 20 minutes at 3000 rpm and filtrated with syringe filter (0.2 μm). The samples were sent to ALS Laboratory in Luleå for analyses using ICP-MS.

Oxalate extraction

Iron and aluminum hydrous oxides are important components of almost all soils. They have large specific areas and therefore they are highly reactive. There are three main ways to extract iron and aluminum oxides (Parfitt and Childs, 1988). In this study oxalate/oxalic acid extraction was conducted in order to obtain information about “geochemical active” concentration of iron and aluminum, together with its sorbed As.

1 gram of soil was transferred to 250 ml polyethylene bottle. Soil was mixed with 100 mL 0.2 M oxalate solution (pH 3) and was placed on the end-over-end shaker. The solution was equilibrated for 4 hours in darkness. Afterwards 30 mL of the suspension was transferred to centrifuge tube and centrifuged for 15 minutes at 4000 rpm. Next, supernatant was carefully transferred to 20 mL polyethylene vial. 2.53 grams of solution was filtrated by using plastic syringe filter (0.2 μm) into a polyethylene vial and 10 mL of deionized water was added in order to get five-fold dilution. The samples were sent to ALS Laboratory in Luleå for analyses using ICP-MS.

4.3. Batch leaching experiment

To determine the buffering capacity of the soil samples a pilot laboratory experiment was conducted. 1 gram of soil was transferred to test tubes after which 10 mL of solutions (L/S 10) were added in proportions presented in table 3.

Samples were shaken on an end-over-end shaker for 48 hours. Next, the samples were centrifuged for 15 minutes at 3000 rpm. pH was measured on clear solutions. The results are presented in Appendix 1. Results of pH measurements were plotted versus added acid in order to find appropriate additions of acid or base to cover the pH range 4.0 to 8.0.

Table 3. Ratios of NaNO_3 , NaOH and HNO_3 added in pilot experiment

Number of treatment	Volume of added 10mM NaNO_3 [mL]	Volume of added 10 mM HNO_3 [mL]	Volume of added 100 mM NaOH [mL]	Volume of added 100 mM NaNO_3 [mL]	Volume of added water [mL]
1	10	0	-	-	-
2	8	2	-	-	-
3	6	4	-	-	-
4	4	6	-	-	-
5	2	8	-	-	-
6	0	10	-	-	-
7	-	-	0.2	1	8.8
8	-	-	0.4	1	8.6
9	-	-	0.6	1	8.4
10	-	-	0.8	1	8.2
11	-	-	1	1	8

In the main experiment 3 grams of soil was added to 30 mL of solution (L/S 10) and different amounts of acid or base were added to cover a pH-range of about 4.0 – 8.0. Suspensions were prepared in two replicates. The prepared suspensions were shaken on end-over-end shaker for 5 days. Additionally, Biogeco suspension with 30 mL 10 mM NaNO₃ solutions were shaken for 2 and 30 days. Afterwards, samples were centrifuged for 20 minutes at 3000 rpm. 5 mL of supernatant was transferred to non-acid washed tubes to measure pH. In order to avoid contamination between transfers, the used pipette was cleaned with 1% HNO₃ and double rinsed with ultra-pure water. Another 5 mL of supernatant was filtrated with Supor® Acrodisc® syringe filter (0.2µm) into acid washed polyethylene vials in order to measure dissolved organic carbon and UV absorption (254 nm). Dissolved organic carbon, pH, and UV absorption were measured at SLU. Dissolved organic carbon was measured on TOC 5000 Total Organic Carbon Analyzer Shimadzu, pH was measured on combined glass electrode pH M210 Standard pH-meter from Meter Lab™ and UV adsorption was measured on UV/VIS Spectrometer Jasco V-530. The remaining supernatant was filtrated with 0.2 µm syringe filter into acid washed polyethylene vials and acidified with 1% HNO₃. The prepared samples were sent to ALS laboratory in Luleå to measure concentration of trace elements using ICP-MS with an ICP-SFMS Thermo-Scientific instrument.

4.4. Geochemical modelling

In order to make a quantitative and qualitative evaluation of the experimental data a geochemical model, Visual MINTEQ was used (Apul et al., 2005). Modeling was applied on the Biogeco (Cu) and Reppel (As) soils. For surface complexation HFO sorption constants were used from Dzombak and Morel (1990). For organic complexation Stockholm Humic Model (SHM) was used. Version of Visual MINTEQ generic database used for all constants is 3.0. Values of parameters and assumptions for modeling are presented in table 4. Data which were entered to Visual MINTEQ, such as background analytes, sorbate and sorbent concentrations (obtained in pH leaching tests and extractions) are presented in Appendix 5. Before modeling calibration of the model might be done (Gustafsson et al., 2003). However, in this case no model calibration was conducted since modeling was considered to be tentative.

Table 4. Values of parameters and assumptions used in Visual MINTEQ

Parameter	Value	Remarks
Temperature	20°C	
Dissolved Organic Matter (DOM)	Ratio of active DOM to DOC = 2	100% of active DOM are Fulvic acids
Activity of Al³⁺	logK _s = 8.29	Activity controlled by Al(OH) ₃
Activity of Fe³⁺	logK _s = 2.69	Activity controlled by ferryhydririte (aged)
CO₂ pressure	3.8*10 ⁻⁴	In equilibrium with open system
Geochemically active concentration of Ca²⁺	32.8 mg/l in Biogeco UNT 38.7 mg/l in Biogeco + 2%Fe 158 mg/l in Reppel UNT 165 mg/l in Reppel + 1% Fe	0.1 M HNO ₃ extractable, recalculated to valid L/S ratio
Geochemically active concentration of K⁺	3.91 mg/l in Biogeco UNT 5.22mg/l in Biogeco + 2%Fe 7.82 mg/l in Reppel UNT 6.71 mg/l in Reppel + 1% Fe	0.1 M HNO ₃ extractable, recalculated to valid L/S ratio
Geochemically active fraction of Mg²⁺	3.69 mg/lin Biogeco UNT 4.77 mg/l in Biogeco + 2%Fe 32.3 mg/l in Reppel UNT 38.1 mg/l in Reppel + 1% Fe	0.1 M HNO ₃ extractable, recalculated to valid L/S ratio
Geochemically active fraction of Cu²⁺	35700 µg/l in Biogeco UNT 64650 µg/lin Biogeco + 2%Fe	0.1 M HNO ₃ extractable, recalculated to valid L/S ratio
Geochemically active fraction of As⁵⁺	9060 µg/l in Reppel UNT 10450 µg/l in Reppel + 1% Fe	Oxalate extractable, recalculated to valid L/S ratio
Concentration of active organic matter	1.14 g/Lin Biogeco UNT 0.60 g/L in Biogeco + 2%Fe 1.24g/L in Reppel UNT 0.96 g/L in Reppel + 1% Fe	0.5*concentration of organic carbon
Fulvic acid content (FA)	0.57 g/L in Biogeco UNT 0.30 g/L in Biogeco + 2%Fe 0.62 g/L in Reppel UNT 0.48 g/L in Reppel + 1% Fe	50% of active organic matter concentration
Humic acid content (HA)	0.57 g/L in Biogeco UNT 0.30 g/L in Biogeco + 2%Fe 0.62 g/L in Reppel UNT 0.48 g/L in Reppel + 1% Fe	50% of active organic matter concentration
HFO concentration	0.17g/L in Biogeco UNT 2.53/L in Biogeco + 2%Fe 0.22 g/L in Reppel UNT 0.70 g/L in Reppel + 1% Fe	Iron concentration obtained in the oxalate extraction, recalculated to HFO concentration
Surface area of HFO	600 m ² /g	

5. Results

Table 5. Properties of soils

Soil	pH	Organic carbon [%]	Inorganic Carbon [%]	Fe*** [mg/kg soil]	Al*** [mg/kg of soil]	Ca**** [mg/kg of soil]	Mg**** [mg/kg of soil]	K**** [mg/kg of soil]
Louis Fargues UNT*	6.25	0.99	0.01	322	101	703	27.5	30.9
Louis Fargues + 1%Fe	6.47	0.63	0.00	1200	86,5	721	25.9	29.1
Louis Fargues + B100**	7.55	0.94	0.00	1060	188	2700	73.6	35.6
Louis Fargues + B100 +1% Fe	7.91	0.60	0.01	1600	143	2450	64.8	32.0
Reppel UNT*	7.79	1.24	0.02	1390	1076	1580	322	78.1
Reppel + 1% Fe	7.95	0.97	0.00	4410	1075	1650	381	67.1
Biogeco UNT*	6.00	1.14	0.02	1080	677	3280	36.9	39.2
Biogeco + 2% Fe	6.47	0.59	0.24	15800	500	387	47.7	52.2

*UNT – untreated

** B100 – with addition of sewage sludge

***oxalate extractable

****0.1 M HNO₃ extractable

5.1. Louis Fargues soil

Soil properties

Louis Fargues soil was contaminated with cadmium and nickel. Measured pH in untreated soil was 6.2. Addition of sewage sludge caused that the soil became more alkaline – the pH was 7.5 (Table 5). In untreated soil the organic carbon content was around 1% (Table 5) and slightly lower in the ZVI treatment (0.63%). In plots where sewage sludge has been added the concentration of organic C content was similar as in non-amended plots. Concentrations of iron aluminum, magnesium, calcium and potassium are presented in Table 6.

Sewage sludge addition had influence on total extractable amount of Ca²⁺ and Mg²⁺. On contrary to ZVI, which did not have any influence on these elements. The most noticeable influence of sewage sludge was on Ca, which was about two and half times higher in sewage treated soil. For potassium there was no apparent difference between sewage sludge treated and not treated soil (Table 5).

Sewage sludge addition also appears to have influenced oxalate extractable iron and aluminum concentrations – in soils treated with sewage sludge both iron and aluminum concentrations were higher. The ZVI addition caused a marked additional increase in oxalate extractable iron (Table 5 and Table 6).

The concentration of Cd in the Louis Fargues soil was 7 mg/kg (Table 6), which exceeded the Swedish value for sensitive land use and the Polish and Austrian values, which are 0.5, 1 and 4 mg/kg of soil

respectively. What is important, these soil quality criteria regard to total trace element concentration. In the Table 6 are presented values of “geochemically active” concentrations, therefore the total concentrations of trace elements can be higher. The Ni concentration in the control soil was lower than these limit values. Sewage sludge additions caused an increase in 0.1 M HNO₃ extractable Cd and Ni. Apparently the sludge was contaminated with these elements. This was possibly also true with the iron grit, indicated by the slightly higher Cd and Ni concentrations in the ZVI treatments compared the controls.

Table 6. Concentration of iron, aluminum, cadmium and nickel in Louis Fargues soil.

Soil	Iron concentration *[mg/kg soil]	Aluminum concentration *[mg/kg soil]	Total extractable cadmium** [mg/kg soil]	Total extractable nickel** [mg/kg soil]
Louis Fargues UNT	322	101	6.97	10.0
Louis Fargues + 1% Fe	1200	86.4	11.1	17.6
Louis Fargues + B100	1000	188	77.6	102
Louis Fargues + B100 +1% Fe	1600	143	75.0	92.3

*oxalate extractable, recalculated to L/S in batch experiment

** 0.1 M HNO₃ extractable recalculated to L/S in batch experiment

Results of batch leaching experiment

Cd and Ni have about the same pH dependency in this soil (Table 7, Figures 1 and 2). Solubility decreased with increasing pH with a minimum at 6.5-7.5. At higher pH values the Cd and Ni solubility increased again. This increase in solubility is probably explained by the increase in DOC in solutions at pH >7 (Figure 3). Below pH 7 DOC concentrations were low (<10 mg/l). Addition of ZVI did not have any major influence on concentration of DOC in the soil solution.

In soil amended with ZVI, the concentration of dissolved Cd and Ni was higher than in untreated soil (Figures 1 and 2). Cd and Ni behave in the same way also in sewage sludge treated soil. The concentration of dissolved Cd and Ni was highest in this treatment (Figures 1 and 2, Table 7).

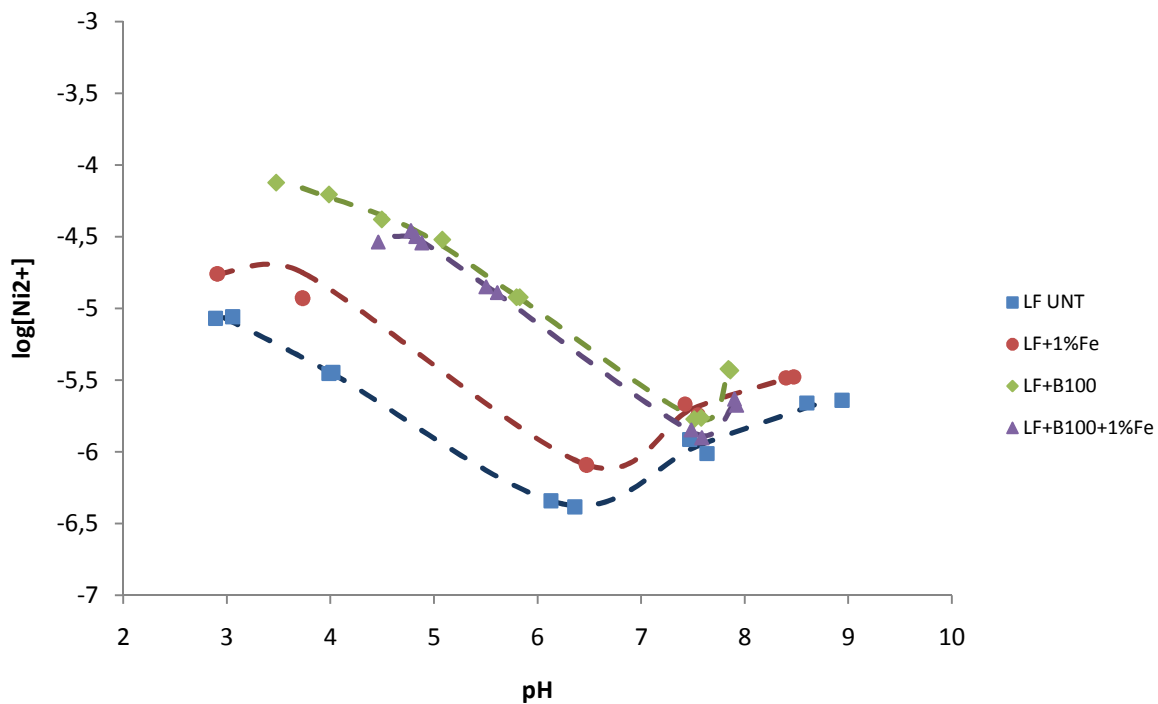


Figure 1. Nickel solubility diagram in Louis Fargues soil

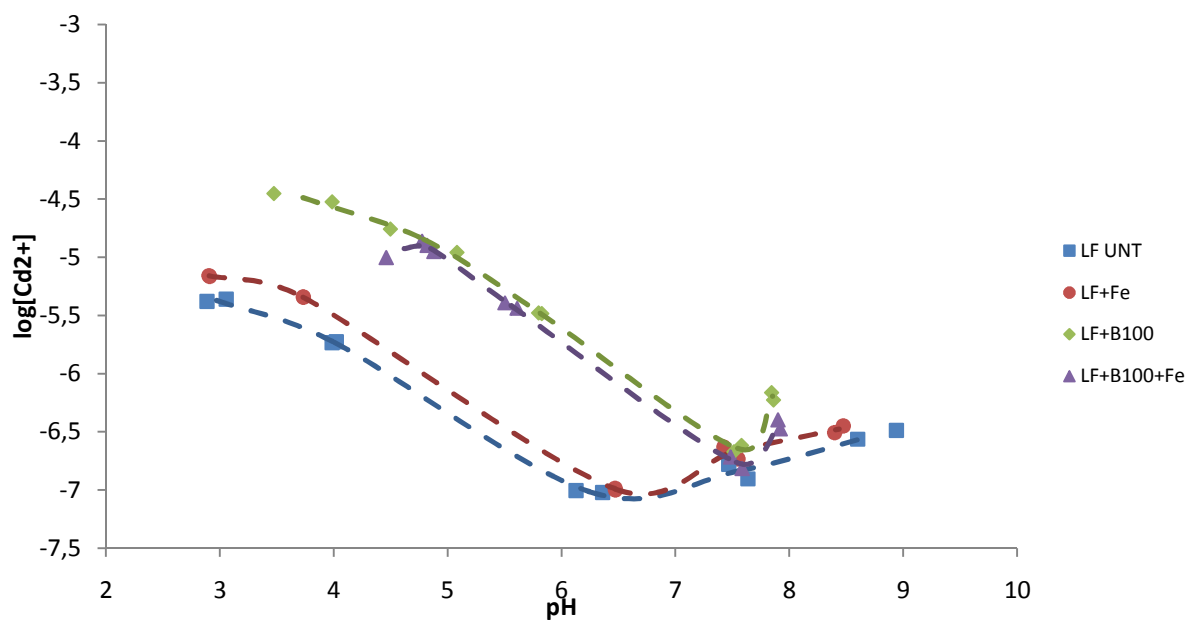


Figure 2. Cadmium solubility diagram in Louis Fargues soil

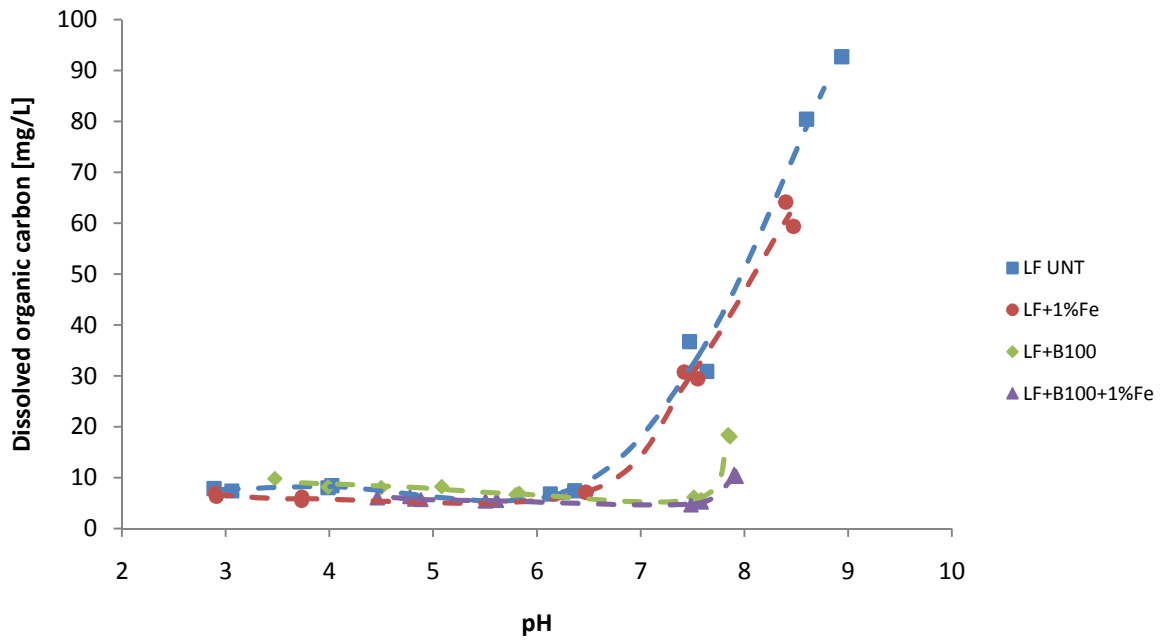


Figure 3. Dissolved organic carbon concentration in Louis Fargues soil

Because the concentration of “geochemically active” Cd and Ni (as determined by 0.1 M HNO₃) varied between control and treated soils, the data were recalculated to the percentage of sorbed Cd and Ni (Figures 4 and 5). Percent values of adsorbed Cd and Ni were calculated from the equation below:

$$\%_{\text{sorbed}} = 100 - \left(\frac{\text{amount of dissolved cations}}{\text{amount of 0.1M HNO}_3 \text{ extractable cations}} * 100 \right)$$

As shown in Figures 4 and 5, the percentage of bound cadmium and nickel increased when pH increases. However, as become evident in these plots, the differences between treatments were rather small. This is particularly true for Cd (Figure 5). For Ni in plots with no sewage sludge amendments, sorption is slightly lower in ZVI treated plots compared to non-ZVI treated plots at pH < 6 (Figure 4).

Table 7. Louis Fargues – results obtained in acid-base titration experiment

Soil	Repetition	pH	DOC [mg/L]	Total extractable Cd* [µg/L]	Dissolved Cd [µg/L]	Total extractable Ni* [µg/L]	Dissolved Ni [µg/L]
Louis Fargues	1	2.89	7.83	697	470	1000	499
UNT	2	3.06	7.41	697	491	1000	512
Louis Fargues	1	3.99	8.04	697	207	1000	207
UNT	2	4.02	8.37	697	211	1000	210
Louis Fargues	1	6.13	6.74	697	11.1	1000	26.7
UNT	2	6.36	7.37	697	10.7	1000	24.2
Louis Fargues	1	7.64	30.8	697	14.1	1000	57.3
UNT	2	7.47	36.7	697	18.7	1000	71.8
Louis Fargues	1	8.94	92.6	697	36.5	1000	134
UNT	2	8.60	80.4	697	30.9	1000	129
Louis Fargues+1% Fe	1	2.91	6.34	1110	771	1750	1020
	2	2.90	6.97	1110	787	1750	1020
Louis Fargues+1% Fe	1	3.73	5.52	1110	512	1750	699
	2	3.73	6.11	1110	509	1750	687
Louis Fargues+1% Fe	1	6.47	7.17	1110	11.6	1750	47.7
	2	6.47	7.07	1110	11.3	1750	47.4
Louis Fargues+1% Fe	1	7.55	29.4	1110	20.8	1750	106
	2	7.42	30.7	1110	26.3	1750	126
Louis Fargues+1% Fe	1	8.47	59.3	1110	40.0	1750	195
	2	8.40	64.0	1110	34.9	1750	192
Louis Fargues + B100	1	3.48	9.77	7750	3970	10200	4420
	2	3.99	8.14	7750	3370	10200	3660
Louis Fargues + B100	1	5.08	8.19	7750	1240	10200	1770
	2	4.50	8.00	7750	1970	10200	2450
Louis Fargues + B100	1	5.83	6.88	7750	369	10200	702
	2	5.80	6.67	7750	374	10200	701
Louis Fargues + B100	1	7.51	6.16	7750	24.0	10200	99
	2	7.58	5.65	7750	27.2	10200	101
Louis Fargues + B100	1	7.86	18.0	7750	67.0	10200	216
	2	7.84	18.4	7750	77.3	10200	222
Louis Fargues +B100+1% Fe	1	4.78	6.23	9060	1550	10680	2040
	2	4.46	5.98	9060	1120	10680	1700
Louis Fargues +B100+1% Fe	1	4.82	5.71	9060	1420	10680	1860
	2	4.88	5.65	9060	1260	10680	1680
Louis Fargues +B100+1% Fe	1	5.50	5.36	9060	456	10680	828
	2	5.61	5.50	9060	410	10680	755
Louis Fargues +B100+1% Fe	1	7.49	4.59	9060	21.6	10680	83.3
	2	7.59	5.20	9060	17.2	10680	73.4
Louis Fargues +B100+1% Fe	1	7.90	10.5	9060	45.0	10680	137
	2	7.92	10.2	9060	37.6	10680	124

*0.1 M HNO₃ extractable, recalculated to L/S ratio in batch experiment

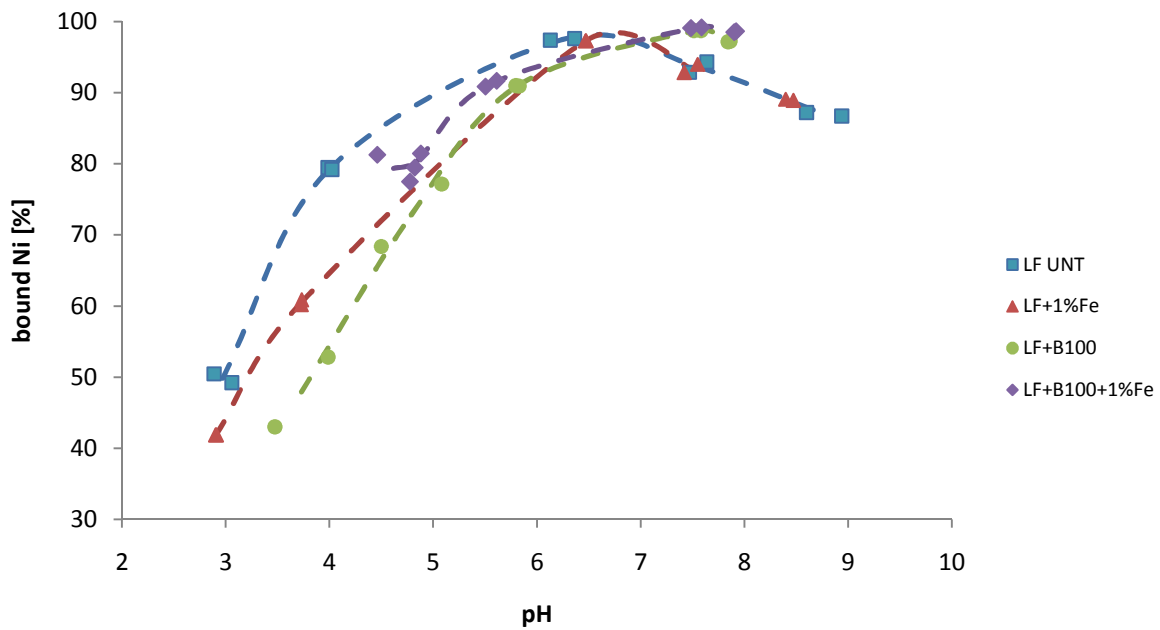


Figure 4. Influence of pH on binding Ni in different soil treatments

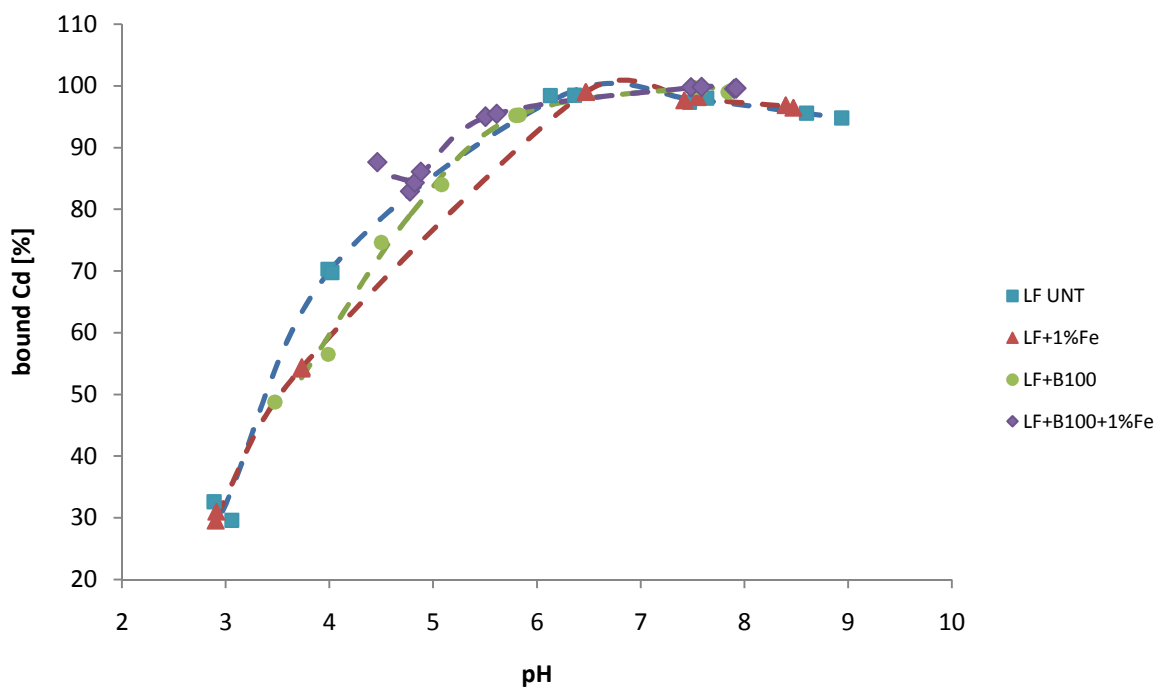


Figure 5. Influence of pH on binding Cd in different soil treatments

5.2. Reppel soil

Soil properties

Reppel soil was highly contaminated with arsenic. In Reppel experiment the only treatment was ZVI amendment. This soil is strongly alkaline– its pH is highly above 7.0 (Table 5). Moreover this soil contains very high concentration of calcium – almost 2500 mg/kg of soil in untreated soil and 1500 mg/kg of soil in ZVI treated soil (Table 5). Organic carbon content is, as in case of previous soil (Louis Fargues), lower in iron treated soil than in untreated soil (0.97% and 1.24%, respectively). As it can be noticed, ZVI appears to have an influence on organic carbon concentration in soil. Another properties of soil, such as Fe, Al, Mg and K concentrations are presented in Table 5. Addition of ZVI has not changed the concentration of aluminium in the soil. Arsenic concentration was significantly higher than the recommended values for agricultural use (Table 2). In ZVI treated soil concentration of oxalate extractable arsenic was similar to that in the control soil (Table 8).

Table 8. Concentration of iron, aluminium and arsenic in Reppel soil

Soil	Iron concentration* [mg/kg soil]	Aluminum concentration* [mg/kg soil]	Arsenic concentration* [mg/kg soil]
Reppel UNT	1390	1076	90.6
Reppel + 1% Fe	4415	1075	104

*oxalate extractable

Results of batch leaching experiment

The concentration of As in the solution was also pH dependent (Table 9, Figure 6). However, the influence of pH was not as strong as for the cations in Biogeco and Louis Fargues soils. In contrast to cations, the concentration of dissolved arsenate increases with increasing pH, which is to be expected from anion sorption to HFO. The pH dependency was most pronounced in the ZVI treated soil. The addition of iron grit to the Reppel soil had a marked positive effect on the binding of As; the concentration of As was about one order of magnitude lower in the ZVI treated soil, the effect being stronger at pH < 6 (Table 9).

Table 9. Reppel soil – results obtained in acid-base titration experiment.

Soil	Repetition	pH	DOC [ppm]	Total extractable As [mg/L]*	Total dissolved As [mg/L]	% bound
Reppel UNT 1	1	4.81	11.7	9060	0.71	99,9
	2	4.66	10.9	9060	0.54	99,9
Reppel UNT 2	1	5.10	11.5	9060	0.47	99,9
	2	5.18	10.6	9060	0.45	99,9
Reppel UNT 3	1	6.13	11.4	9060	0.31	99,9
	2	6.17	12.2	9060	0.35	99,9
Reppel UNT 4	1	7.76	15.5	9060	0.31	99,9
	2	7.81	15.4	9060	0.29	99,9
Reppel UNT 5	1	8.02	20.9	9060	0.42	99,9
	2	8.07	21.2	9060	0.40	99,9
Reppel+ 1% Fe 1	1	5.16	5.90	10450	0.03	99,9
	2	4.87	5.60	10450	0.03	99,9
Reppel+ 1% Fe 2	1	5.57	5.74	10450	0.02	99,9
	2	5.49	6.26	10450	0.03	99,9
Reppel+ 1% Fe 3	1	6.24	6.31	10450	0.02	99,9
	2	6.00	7.45	10450	0.05	99,9
Reppel+ 1% Fe 4	1	6.93	9.72	10450	0.07	99,9
	2	6.88	10.1	10450	0.06	99,9
Reppel+ 1% Fe 5	1	7.95	13.6	10450	0.16	99,9
	2	7.94	13.3	10450	0.15	99,9

*oxalate extractable, recalculated to L/S ratio in batch experiment

Results of modelling with Visual MINTEQ

Results of modelling with Visual MINTEQ confirm the general behaviour of ZVI addition; the As concentration in solutions decreases (Figure6). Furthermore, in results from Visual MINTEQ, it can be seen that with increasing pH more arsenate is dissolved in soil solution, although this effect was more pronounced with the model. However, results from Visual MINTEQ showed a much stronger sorption of As than observed in the laboratory experiment.

According to results from Visual MINTEQ, 100% of arsenate binds to iron oxides. At low pH the FeAsO_4^{-2} form is dominant, but with increasing pH, concentration of this form slightly decreased and the FeOHAsO_4^{-3} increases.

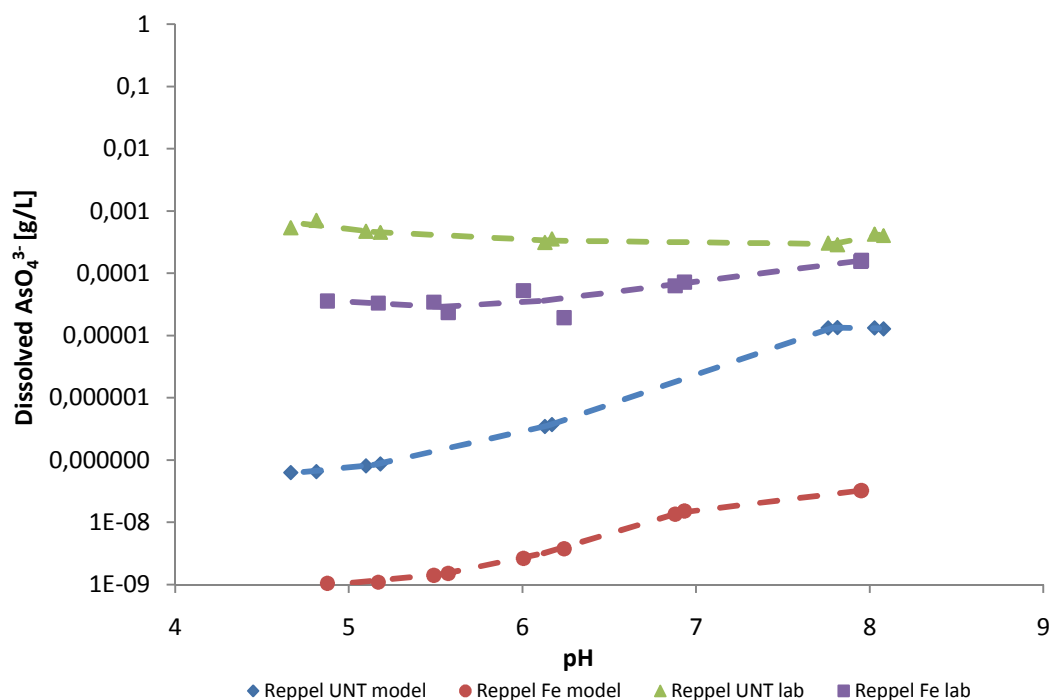


Figure 6. Comparison of results of dissolved arsenate concentration obtained in laboratory and Visual MINTEQ

5.3. Biogeco soil

Soil properties

Biogeco soil is highly contaminated with copper. Concentration of 0.1 M HNO₃ extractable copper is higher in ZVI treated soil than in untreated soil. Iron concentration had significantly increased (approximately 15 times) after addition of 2% ZVI (Table 10). Concentration of aluminium is similar in not treated and ZVI treated soil (Table 10). Organic carbon content in ZVI treated Biogeco soil is only half of that in control soil (Table 5).

Table 10. Iron, aluminum and copper concentration in Biogeco soil

Soil	Iron concentration* [mg/kg soil]	Aluminum concentration* [mg/kg soil]	Copper concentration* [mg/kg soil]
Biogeco UNT	1080	677	357
Biogeco + 2% Fe	15800	500	646

*0.1 M HNO₃ extractable, recalculated to L/S in batch experiment

Results of batch leaching and kinetic experiments

Dissolved copper concentration decreases with increasing pH (Figure 9 and Table 11). For untreated soil the lowest dissolved copper concentration is at pH 6 and for ZVI treated soil the pH value is slightly higher – approximately 6.5. At pH lower than 6 the solubility in ZVI treated and control soils is similar, whereas in the pH range 6-8, the solubility is lower in the ZVI treated soil.

As in case of nickel and cadmium, at high pH values (above pH 8) the concentration of copper in the solution is increasing, which can be caused by increase in dissolved organic carbon content in the soil solution (Figure 8).

Table 11. Biogeco soil - results obtained in acid-base titration experiment

Soil	Repetition	pH	DOC [ppm]	Total extractable Cu [mg/L]*	Total dissolved Cu [mg/L]	% bound
Biogeco UNT 1	1	3.32	5.37	35.7	26.8	24.9
	2	3.25	5.56	35.7	21.2	40.6
Biogeco UNT 2	1	4.09	3.06	35.7	13.1	63.3
	2	3.85	3.07	35.7	10.8	69.7
Biogeco UNT 3	1	6.02	5.55	35.7	0.36	98.9
	2	5.99	6.17	35.7	0.29	99.1
Biogeco UNT 4	1	8.03	44.6	35.7	1.06	97.0
	2	8.04	42.8	35.7	1.56	95.6
Biogeco UNT 5	1	9.07	96.6	35.7	3.17	91.1
	2	8.88	91.3	35.7	2.90	91.8
Biogeco+2% Fe 1	1	3.01	3.73	64.7	47.2	26.9
	2	2.94	3.28	64.7	49.2	23.8
Biogeco+2% Fe 2	1	3.93	2.98	64.7	40.1	37.9
	2	4.00	3.51	64.7	31.1	51.8
Biogeco+2% Fe 3	1	6.57	3.07	64.7	0.09	99.8
	2	6.60	2.23	64.7	0.09	99.8
Biogeco+2% Fe 4	1	8.05	19.7	64.7	0.92	98.5
	2	8.12	25.8	64.7	0.71	98.8
Biogeco+2% Fe 5	1	8.49	26.9	64.7	1.21	98.1
	2	8.39	21.0	64.7	1.09	98.3

*0.1 M HNO₃ extractable, recalculated to L/S ratio in batch experiment

For Biogeco soil an additional kinetic experiment was performed. As mentioned above, 30 mL of NaNO₃ was added to 3gram of soil and afterwards the solution was equilibrated for 2, 5 and 30 days, respectively. Results of different equilibration times are presented in Figure 7.

Time of equilibration has an influence on dissolution of copper in the soil solution. Copper concentration in the soil solution had slightly increased between 2nd and 5th day of shaking. This could be caused by a kinetically constrained release of copper. Between 5th and 30th day of shaking the concentration of copper in the soil solution had slightly decreased. Due to long shaking there could be an increase in surface area of sorbing soil components, which could be followed by increase of Cu sorption. DOC and pH remained constant with time.

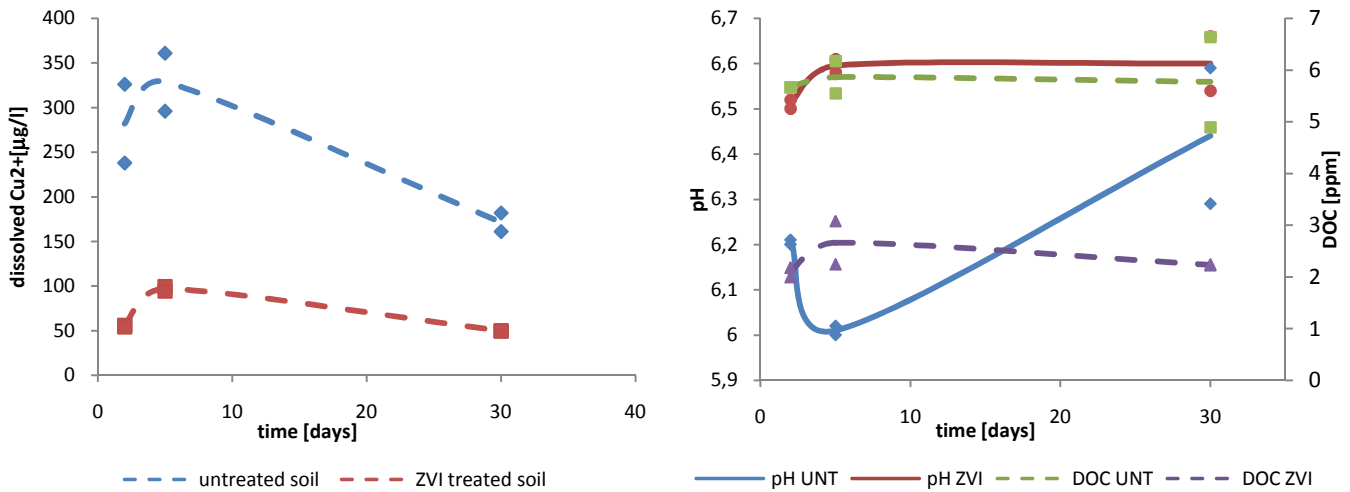


Figure 7. Results of kinetic experiment for Biogeco soil

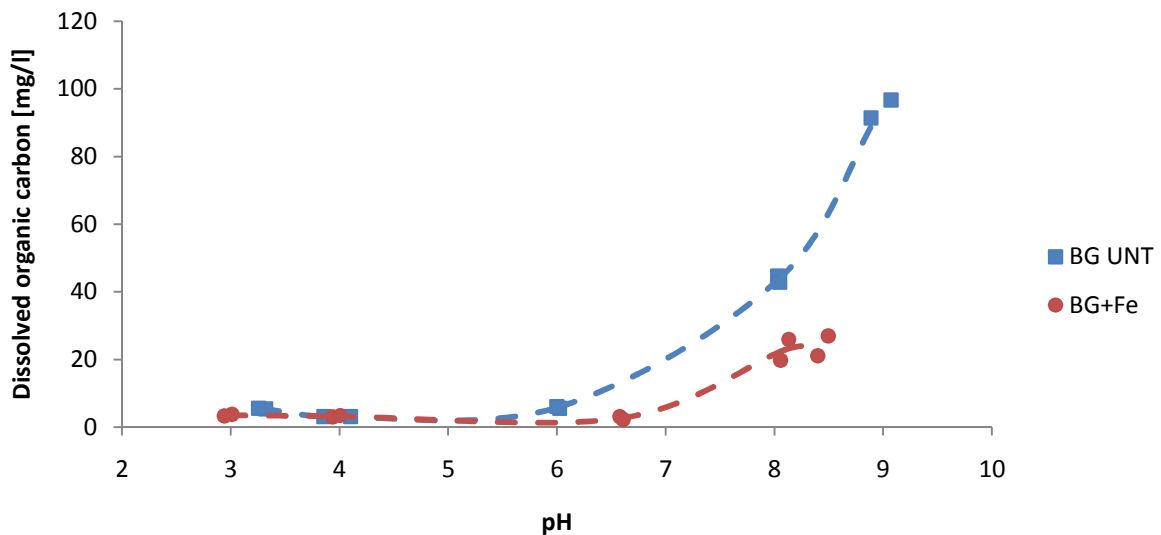


Figure 8. Dissolved organic carbon concentration in Biogeco soil

Results of modelling in Visual MINTEQ

The comparison of modelled solubility of Cu and results obtained in the laboratory shows the same pH dependency (Figure 9). The model results are remarkably similar to the experimental results, considering the fact that no optimizations of either input data or binding parameters were made.

Species distribution charts obtained with Visual MINTEQ (Figures 10 and 11) show that in both untreated and ZVI treated soils, dissolved copper cations (Cu^{2+}) concentration decreases with increasing pH.

The model suggests that there is a shift in speciation following ZVI addition (Figure 10 and 11). In control soil organic complexes are dominating in whole pH range, whereas in the ZVI treated soil binding to Fe (hydr)oxides dominates at pH ca. 6 and higher. This shift in speciation is in accordance

with the observed enhanced sorption in the ZVI treated soil (Figure 9). In untreated soil in very acidic environment, the dominant forms are: dissolved copper ions and organic complexes with copper. In the range of pH 4 – pH 5, the concentration of organic complexes is dominant and concentration of dissolved free copper ions (Cu^{2+}) decreases. In pH 7-8 still the most dominant are forms of copper bound to humic acids However, with increasing pH, forms of copper bound to iron oxides also appears.

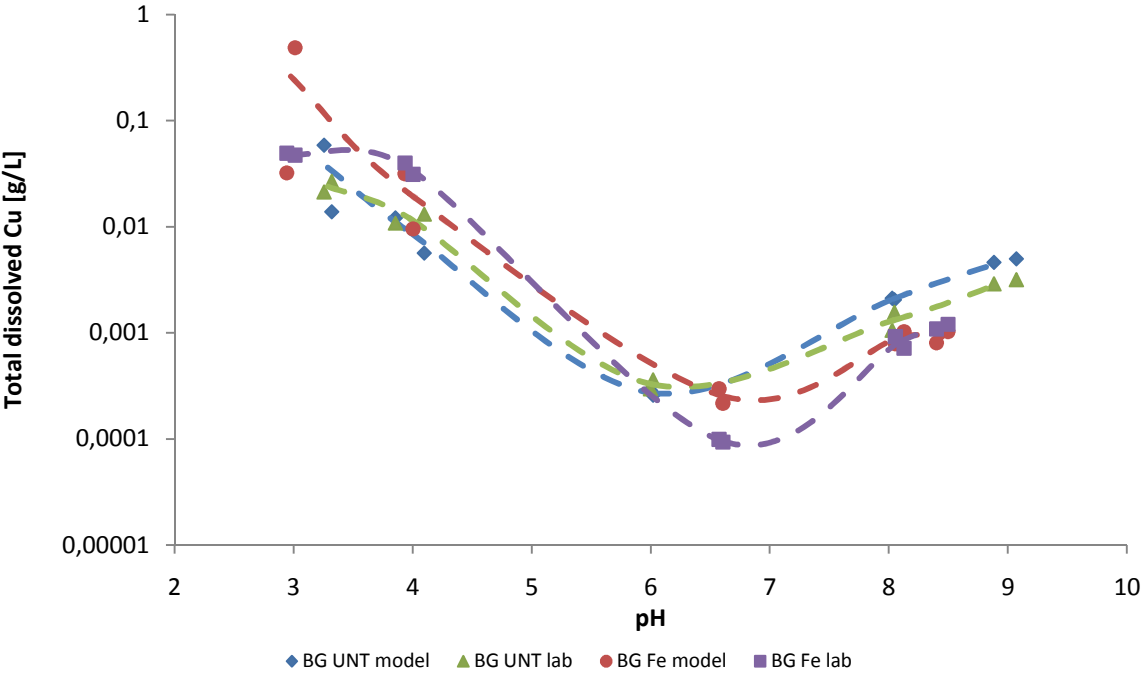


Figure 9. Comparison of results of dissolved copper concentration obtained in laboratory and Visual MINTEQ

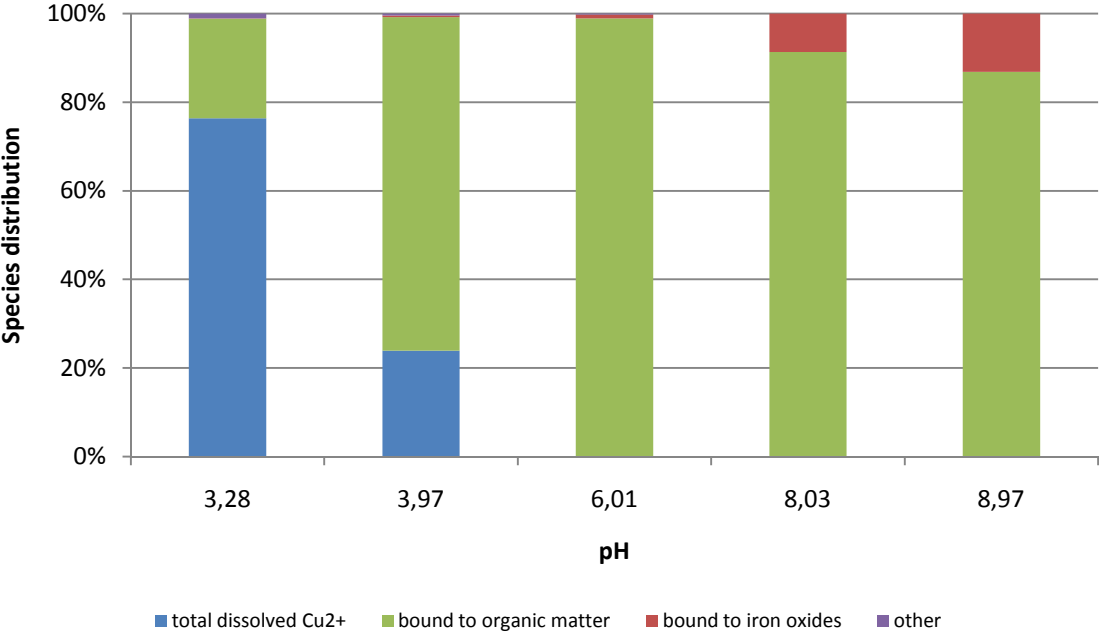


Figure 10. Species distribution in untreated Biogeco soil

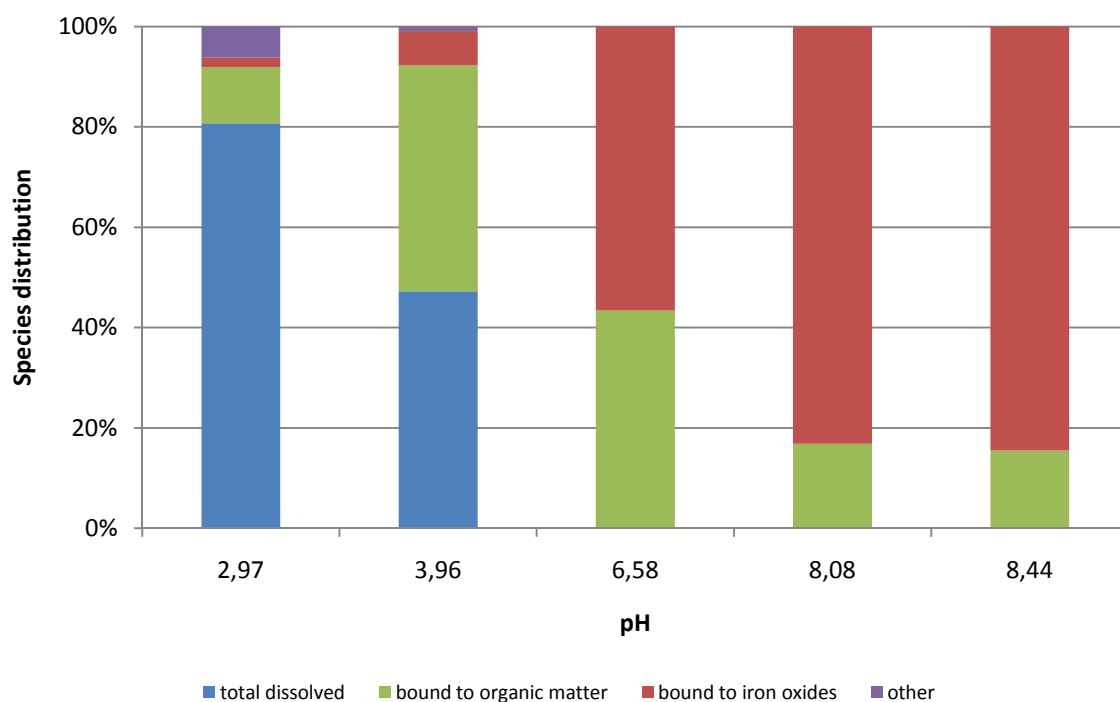


Figure 11. Species distribution in ZVI treated Biogeco soil

6. Discussion

Leaching of trace elements

Solubility of trace elements is strongly pH dependent. According to study conducted by Dijkstra et al. (2004) concentration of cationic trace elements can decrease even 2 orders of magnitude between acidic and neutral pH. Here it was found that with increasing pH the concentration of cations is decreasing. However with increase of pH from neutral to alkaline the concentration of cations is increasing again, as the dissolved organic matter concentration is increasing as well. According to Bloomfield (1981), in the presence of FA and HA, cations can be remobilized from solid phases.

The addition of zero-valent iron had generally increased 0.1 M HNO₃ extractable concentration of all trace elements. One possible explanations that iron grit used for remediation also contains contaminants. For instance iron grit used for remediation of Biogeco soil contains: metallic iron (97%), manganese (0.8%), chromium (0.3%), copper (0.1%) as well as some fractions of nickel and aluminum (Mench et al., 2000). Another possible explanation is spatial heterogeneity i.e. that soil samples taken from the ZVI treated plots contained more contaminants than samples taken from non-treated plots.

Influence of ZVI on cadmium and nickel stabilization

Watanabe et al. (2009) had conducted a study, regarding Cd uptake by rice plants in ZVI treated soils. He stated that ZVI application had decreased concentration of soluble Cd in the soil solution. His research is in opposition to the results obtained in this research, where no influence of ZVI on cCd mobility was noticed. In natural conditions Cd has high affinity to bind to organic matter, it is weakly bind to HFO and can be easily mobilized. However, in the research conducted by Watanabe 5 grams

of iron was added to 100 g of soil, which gave approximately 5% content of ZVI. In Louis Fargues only 1% of iron was added. This could be reason, why ZVI had such an influence on Cd immobilization in Watanabe research. Lee et al. (2011) also reports significant decrease in Cd concentration in soil solution after addition of ZVI amendments (2% of ZVI w/w). Moreover, in his research was shown that there was significant shift of cadmium bound to Fe-Mn oxides.

With time HFO crystallizes to forms which are more ordered (e.g. hematite or goethite). The reactive surface area of these elements is reduced and their role as a sorbent is disturbed (Cudy et al., 2008). For example the reactive surface of HFO is 600 m²/g and the specific surface area of goethite is 150 m²/g (Smedley and Kinniburgh, 2002). Also pH can influence the release of contaminants bound to iron oxides. Decrease of pH can cause solubilisation of iron phase, which leads to release of contaminants (Cundy et al., 2008).

Another possible explanation of lack of influence of ZVI on Cd stabilization is that Cd forms stable soluble complexes with dissolved organic matter (Ashworth and Alloway, 2004). Especially in soils treated with sewage sludge the influence of DOC could be stronger, as the decomposition of sludge organic matter leads to an increase of DOC. This is followed by reduction of Cd adsorption onto soil surfaces (Antoniadis and Alloway, 2002).

The influence of ZVI amendment on stabilization of Ni was similar as on stabilization of Cd. As in case of Cd is the iron addition did not have an influence on decreasing the mobility of Ni. On the contrary, even more cations were dissolved in soil treated with iron grit, than in the untreated soil. Ni has also higher affinity to organic matter than to iron oxides and therefore the effect of ZVI amendments might be expected to be fairly small.

Addition of sewage sludge had increased the 0.1 M HNO₃ extractable concentration of Cd and Ni in soil solution. Sewage sludge contains cadmium and other trace elements. Therefore application of sewage sludge may increase the concentration of these elements. Additionally, processes in sewage sludge, such as nitrification or microbial production of CO₂ might cause a decrease in pH and hence increase of leaching of trace elements (Kirkham, 2006). Studies on long-term application of sewage sludge (Granato et al., 2004) showed decrease (50%) in cadmium concentration in leaves and grains of corn (*Zea mays*), however the concentration of cadmium in soil did not change.

Influence of ZVI on arsenic stabilization

Arsenic is present in soil solution mainly in the form of oxyanion – AsO₄³⁻ (arsenate). Therefore, its behavior in soil is different from the other investigated trace elements which are cations.

Results of this research showed that ZVI addition is significantly decreasing the concentration of As in soil solution, even after 16 years after application of ZVI. Cundy et al. (2008) states that arsenate, as well as arsenite, has high affinity to bind to iron oxides, even when it occurs in low concentrations in soils. This strong affinity of As to amorphous iron oxides is used for removal of arsenic from drinking water - even up to 90% of As can be removed from drinking water due to ZVI additions. Moreover Kumpiene et al. (2009) also obtained similar results. In her study addition of 1% iron grit had significantly reduced mobility of arsenic.

Research conducted in this study showed that changes in pH have little influence on arsenic concentration in soil solution. Researchers stated that, when arsenate is bound to iron oxides, its desorption is difficult. Study conducted by Mench et al. (2006) confirms this statement. He stated that the arsenate and arsenite are strongly bound to iron oxides and strong pH variations are not changing the concentration of elements in soil solution. Similar results were obtained Apul et al. (2005). The amount of leached arsenate was similar in whole pH range.

ZVI addition has significant influence on decreasing the mobility of arsenic. However, Kumpiene et al. (2009) reported that ZVI can change the speciation of arsenic from As (V) to As (III), which is more toxic to plants. It occurs mainly in anaerobic conditions (e.g. high water saturation) in the presence of organic matter. Therefore, the conditions in soil have to be controlled in order to avoid reduction of arsenate. To some extent reduction of arsenate can also be caused by microorganisms (Kumpiene et al., 2009).

Influence of ZVI on copper stabilization

Cu presents different behavior in comparison to Cd and Ni. As in the case of Ni and Cd, in acid environments slightly more Cu ions are released to the solution in ZVI treated soil. The situation changes at pH 6, where Cu ions start to be adsorbed stronger by the ZVI treated soil. Modeling of Cu solubility with Visual MINTEQ suggested that most Cu was bound to iron oxides in the ZVI amended soil, explaining the lower solubility at pH >5.5. Similar results were obtained by Kumpiene et al. (2011), which showed that iron grit stabilizes copper very well. Addition of 2% iron grit caused increase in stabilization of copper by iron oxyhydroxides, which was confirmed by EXAFS.

Cu ions have high affinity to bind to organic matter (Degryse et al., 2009). In untreated Biogeco soil, Cu was present mainly either as free Cu^{2+} ion (pH<3.5) or in organic complexes (pH>3.5), as indicated by the Visual MINTEQ modeling. At very high pH – above 8.5 Cu was bound to iron oxides also in this soil. According to Stevenson and Fitch (1981), humic and fulvic acids can bind between 48-160 mg Cu per gram of humic acid, which is equal to the content of acidic functional groups in organic matter.

In the research conducted by Mench and Bes (2009) it was presented that plot 7 (P7) of Biogeco soil is highly phytotoxic. Moreover, presence of Cu in the soil had decreased lettuce leaf yield and inhibited radish growth. However, Zhao et al. (2006) finds that the total concentration of Cu in soil is not directly related to toxicity, but depends on its speciation. Kumpiene et al. (2011) conducted research in 2006 on the same soil. After 2 years after application of ZVI, the concentration of extractable Cu decreased and on plots treated with ZVI all plant species germinated (*Agrostis Castellana Boiss. & Reut.*, *Agrostis Gigantea Roth.*, *Dactylis Glomerata L.*, *Holcus Lanatus L.*, *Populus Nigra L.*, *Salix Caprea L.* and *Salix viminalis L.*). Whereas on untreated plot germinated only *A. Castellana*, which is metal-tolerant plant (Kumpiene et al., 2011).

7. Conclusions

Stabilization of soil with ZVI amendments had different effects on different trace elements.

For Cd and Ni there was no influence of ZVI addition to soil. In Biogeco soil, the influence of ZVI addition on Cu immobilization could be seen in pH values higher than 5.5. The highest Cu stabilization was in pH range 6-8. Therefore in order to keep the positive influence of ZVI on Cu stabilization other measurements should be taken, especially for soils which pH is lower than 6. One of the solutions can be liming. Results for arsenate are different than results for cations. An addition of iron had a great influence on binding this oxyanion. The solubility of As had decreased by one order of magnitude. However the treatment was most efficient pH below 6.

Because stability of trace elements depend on many factors, such as pH, organic matter content or time, the effectiveness of remediation must be monitored. Mobile and bioavailable fractions of contaminants should be regularly measured. Stabilization of contaminants with ZVI might be followed by biological stabilization, phytostabilization and the chemical conditions (e.g. leaching) at the site should be monitored.

As a final conclusion it can be stated that addition of zero-valent iron amendments is effective for stabilization of As and Cu in soils. Even after 16 years arsenate is well bound to iron oxides. For copper ZVI stabilization was proved to have an effect, even after 6 years. However changes in soil pH should be monitored, as decrease in pH can increase leaching of copper.

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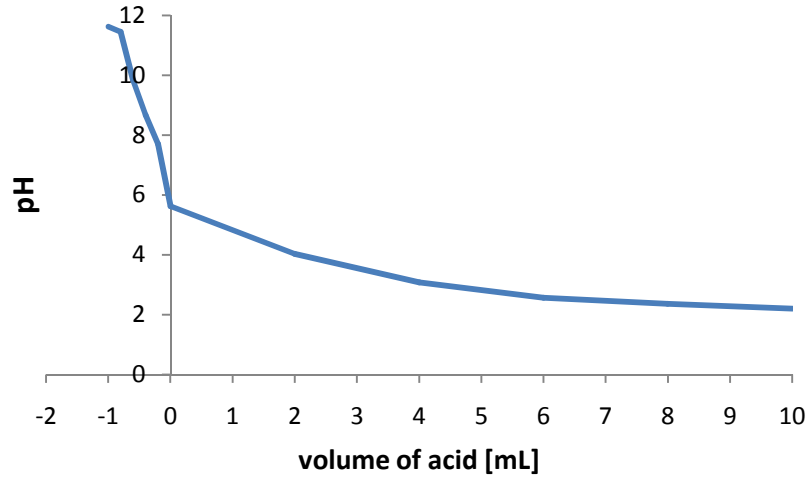
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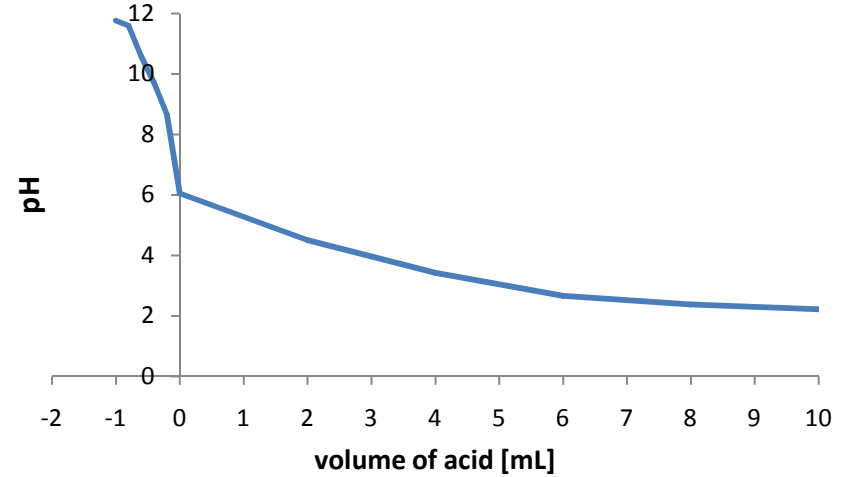
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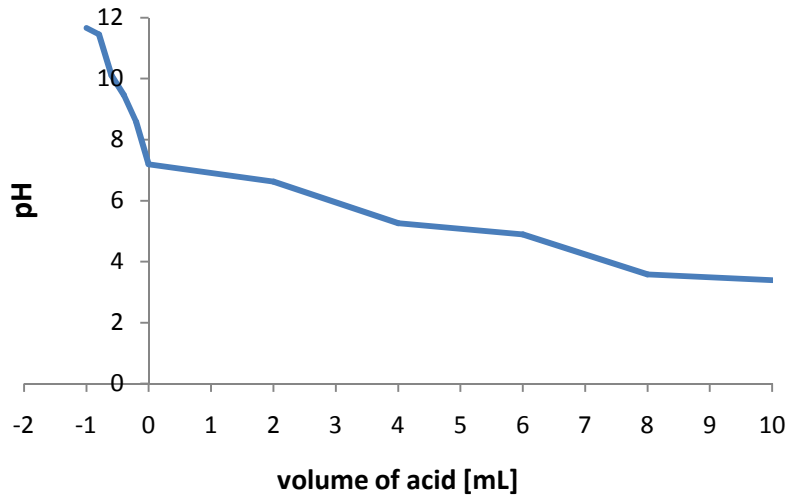
Appendix 1. Results of 1st acid-base titration



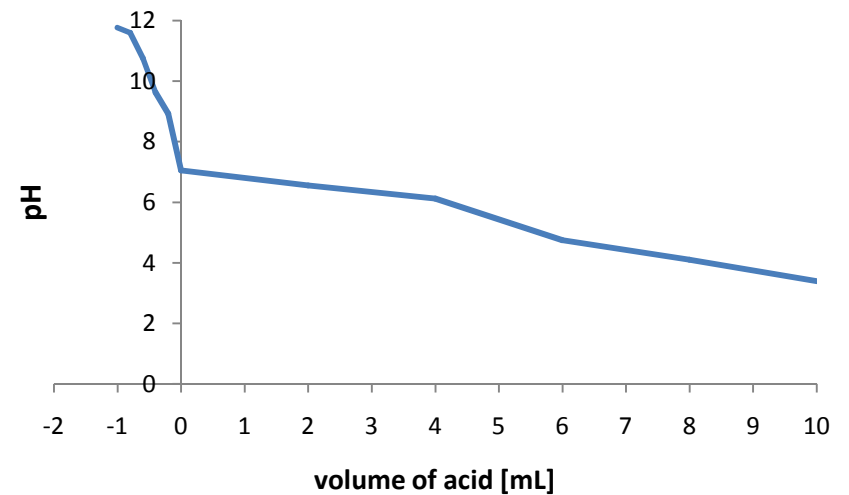
Acid– base titration in Louis Fargues UNT soil



Acid-base titration in Louis Fargues + 1%Fe soil

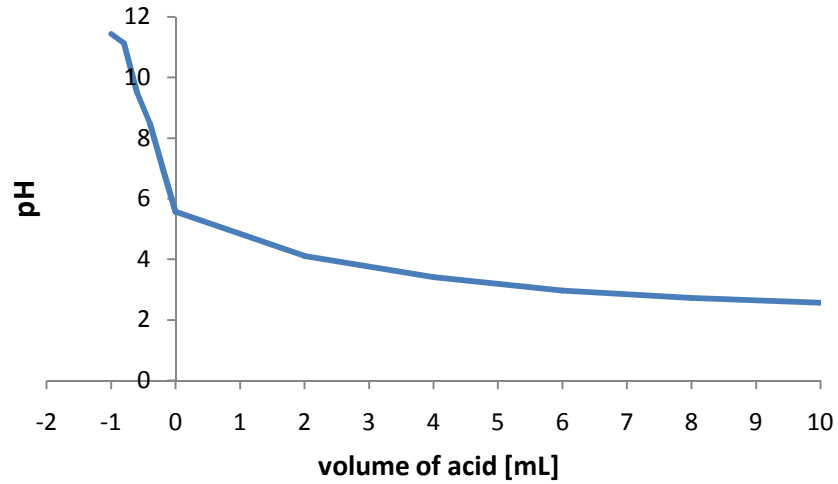


Acid – base titration in Louis Fargues +B100 soil

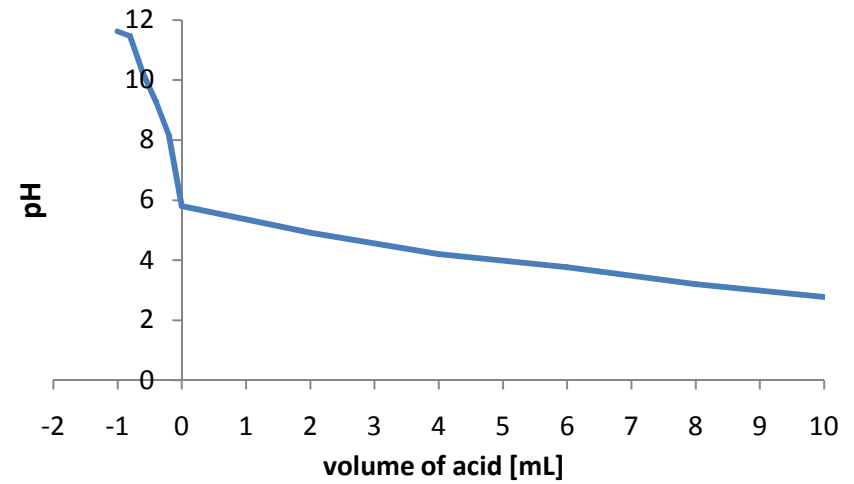


Acid – base titration in Louis Fargues + B100+1% Fe soil

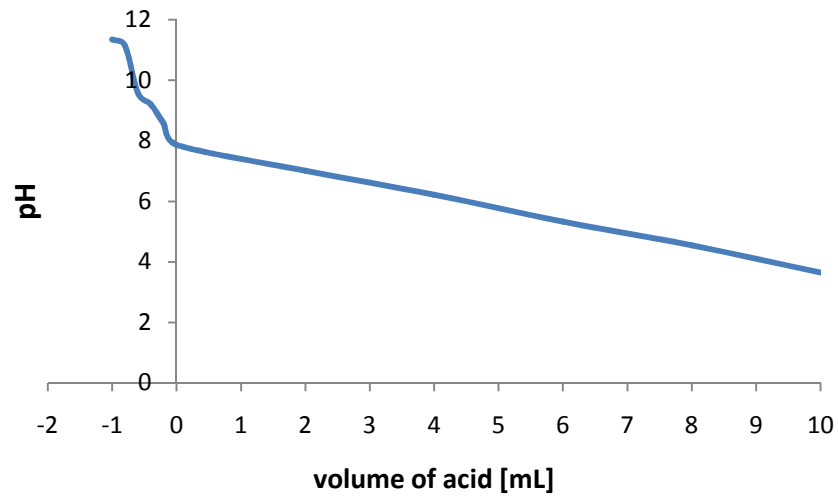
Appendix 1. Results of 1st acid-base titration



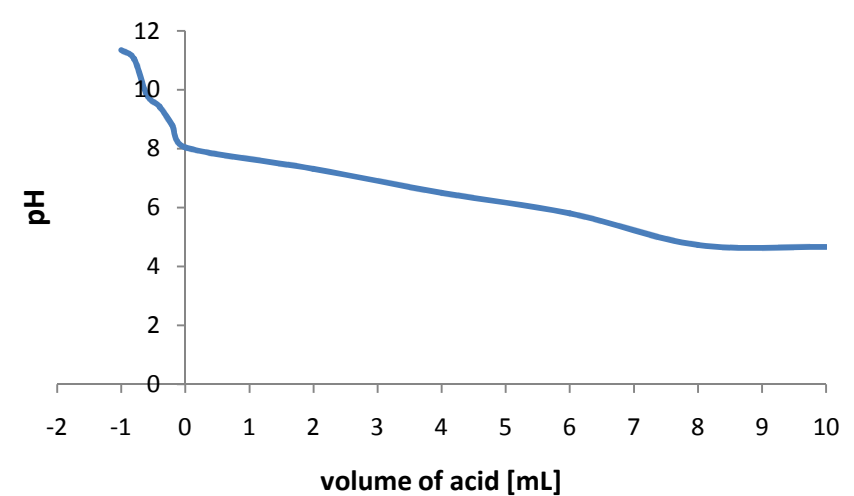
Acid – base titration in Biogeco UNT soil



Acid – base titration in Biogeco + 1%Fe soil



Acid – base titration in Reppel UNT soil



Acid – base titration in Reppel+1% Fe soil

Appendix 2. Volumes of acid and base for 2nd acid-base titration

Soil	pH value to which solution is adjusted	Volume of added solutions [mL]				
		10 mM NaNO ₃	10 mM HNO ₃	100 mM NaOH	100 mM NaNO ₃	water
Biogeco UNT (2 days shaking)	5.57	30.0	-	-	-	-
Biogeco+2% Fe (2 days shaking)	5.80	30.0	-	-	-	-
Louis Fargues UNT	3.00	17.3	12.7	-	-	-
	4.00	23.6	6.40	-	-	-
	5.62	30.0	0	-	-	-
	7.00	-	-	0.39	3.00	26.6
	8.00	-	-	0.78	3.00	26.2
Louis Fargues+1% Fe	3.00	14.6	15.4	-	-	-
	4.00	21.6	8.40	-	-	-
	6.05	30.0	0	-	-	-
	7.00	-	-	0.33	3.00	26.6
	8.00	-	-	0.60	3.00	26.4
Biogeco UNT	3.00	12.8	17.2	-	-	-
	4.00	23.2	6.80	-	-	-
	5.57	30.0	0	-	-	-
	7.00	-	-	0.60	3.00	26.4
	8.00	-	-	0.90	3.00	26.1
Biogeco+2% Fe	3.00	3.40	26.6	-	-	-
	4.00	15.4	14.6	-	-	-
	5.80	30.0	0	-	-	-
	7.00	-	-	0.45	3.00	25.5
	8.00	-	-	0.54	3.00	26.4
Reppel UNT	4.70	6.30	23.7	-	-	-
	5.00	9.60	20.4	-	-	-
	6.00	16.5	13.5	-	-	-
	7.87	30.0	0	-	-	-
	8.00	-	-	0.24	3.00	26.7
Reppel+ 1% Fe	4.70	3.00	27.0	-	-	-
	5.00	7.80	22.2	-	-	-
	6.00	13.5	16.5	-	-	-
	7.00	21.9	8.04	-	-	-
	8.04	30.0	0	-	-	-
Louis Fargues + B100	4.00	2.70	27.3	-	-	-
	5.00	9.00	21.0	-	-	-
	6.00	17.2	12.7	-	-	-
	7.55	30.0	0	-	-	-
	8.00	-	-	0.30	3.00	26.7
Louis Fargues+B100+1% Fe	4.00	11.7	18.3	-	-	-
	5.00	15.0	15.0	-	-	-
	6.00	20.4	9.60	-	-	-
	7.05	30.0	0	-	-	-
	8.00	-	-	0.15	3.00	26.8
Biogeco UNT (30 days of shaking)	5.57	30	0	-	-	-
Biogeco+ 2% Fe (30 days of shaking)	5.80	30	0	-	-	-

Appendix 3. Results of pH, TC, IC and DOC

Soil	pH value to which solution is adjusted	Repetition	pH measuerd	TC [ppm]	IC [ppm]	DOC [ppm]	ABS [254nm]	Soil	pH value to which solution is adjusted	Repetition	pH measuerd	TC [ppm]	IC [ppm]	DOC [ppm]	ABS [254nm]	
Biogeco UNT (2 days shaking)	5.57	1	6.21	6.89	1.23	5.67	0.25	Louis Fargues+1% Fe	8.00	1	8.47	67.4	8.09	59.3	3.16	
	5.57	2	6.20	6.10	0.89	5.67	0.24		8.00	2	8.40	72.4	8.38	64.0	3.48	
Biogeco+2% Fe (2 days shaking)	5.80	1	6.52	3.10	0.93	2.17	0.08	Biogeco UNT	3.00	1	3.32	5.64	0.27	5.37	0.16	
	5.80	2	6.49	2.94	0.99	2.00	0.08		3.00	2	3.26	5.89	0.33	5.56	0.17	
Louis Fargues UNT	3.00	1	2.89	8.32	0.49	7.83	0.31		4.00	1	4.10	3.31	0.25	3.06	0.10	
	3.00	2	3.06	7.88	0.47	7.41	0.31		4.00	2	3.86	3.37	0.24	3.07	0.11	
	4.00	1	3.99	8.63	0.59	8.04	0.36		5.57	1	6.02	6.05	0.50	5.55	0.23	
	4.00	2	4.02	8.88	0.51	8.37	0.39		5.57	2	5.99	6.69	0.52	6.17	0.24	
	5.62	1	6.13	7.63	0.88	6.74	0.31		7.00	1	8.03	47.6	3.05	44.6	2.36	
	5.62	2	6.36	8.31	0.94	7.37	0.34		7.00	2	8.05	47.4	4.58	42.8	2.22	
	7.00	1	7.64	36.6	5.83	30.8	1.61		8.00	1	9.07	99.5	2.84	96.6	4.64	
	7.00	2	7.47	42.8	6.16	36.7	1.91		8.00	2	8.89	95.2	3.93	91.3	4.65	
	8.00	1	8.94	100	7.53	92.6	4.48		Biogeco+2% Fe	3.00	1	3.01	4.01	0.28	3.73	0.34
	8.00	2	8.60	89.1	8.74	80.4	3.99			3.00	2	2.94	3.56	0.27	3.28	0.33
Louis Fargues+1% Fe	3.00	1	2.91	6.69	0.35	6.34	0.18		4.00	1	3.94	3.29	0.31	2.98	0.08	
	3.00	2	2.90	7.39	0.42	6.97	0.18		4.00	2	4.01	3.81	0.29	3.51	0.07	
	4.00	1	3.73	6.02	0.49	5.52	0.19		5.80	1	6.58	4.16	1.09	3.07	0.09	
	4.00	2	3.73	6.55	0.44	6.11	0.21		5.80	2	6.61	3.02	0.78	2.23	0.10	
	6.05	1	6.47	8.68	1.51	7.17	0.36	7.00	1	8.06	23.0	3.34	19.7	1.47		
	6.05	2	6.47	8.90	1.83	7.07	0.34	7.00	2	8.13	30.1	4.25	25.8	1.52		
	7.00	1	7.55	36.4	7.06	29.4	1.65	8.00	1	8.50	30.3	3.41	26.9	1.75		
	7.00	2	7.42	38.0	7.33	30.7	1.78	8.00	2	8.40	24.4	3.37	21.0	1.47		

Soil	pH value to which solution is adjusted	Repetition	pH measuerd	TC [ppm]	IC [ppm]	DOC [ppm]	ABS [254nm]	Soil	pH value to which solution is adjusted	Repetition	pH measuerd	TC [ppm]	IC [ppm]	DOC [ppm]	ABS [254nm]
Reppel UNT	4.70	1	4.81	12.8	1.00	11.7	0.43	Louis Fargues + B100	4.00	1	3.47	11.7	1.96	9.77	0.35
	4.70	2	4.66	11.7	0.85	10.9	0.38		4.00	2	3.98	10.3	2.20	8.14	0.34
	5.00	1	5.10	13.2	1.69	11.5	0.44		5.00	1	5.08	9.73	1.55	8.18	0.33
	5.00	2	5.18	12.1	1.56	10.6	0.43		5.00	2	4.49	9.71	1.71	8.00	0.32
	6.00	1	6.13	14.7	3.82	11.4	0.51		6.00	1	5.82	9.56	2.77	6.88	0.29
	6.00	2	6.17	15.2	2.96	12.2	0.53		6.00	2	5.79	9.44	2.78	6.66	0.29
	7.87	1	7.76	27.1	11.6	15.5	0.74		7.55	1	7.51	14.5	8.36	6.15	0.34
	7.87	2	7.81	27.4	12.0	15.4	0.75		7.55	2	7.58	13.6	8.02	5.65	0.31
	8.00	1	8.02	35.0	14.1	20.9	1.05		8.00	1	7.86	24.6	6.60	18.0	0.90
	8.00	2	8.07	35.5	14.3	21.2	1.09		8.00	2	7.84	25.2	6.83	18.4	0.93
Reppel+Fe	4.70	1	5.16	7.07	1.16	5.90	0.19	Louis Fargues +B100+1%Fe	4.00	2	4.77	8.34	2.11	6.22	0.25
	4.70	2	4.87	6.60	0.99	5.60	0.18		4.00	3	4.46	6.90	0.92	5.97	0.23
	5.00	1	5.57	7.84	2.10	5.74	0.19		5.00	1	4.82	7.62	1.91	5.70	0.22
	5.00	2	5.49	8.05	1.97	6.26	0.22		5.00	2	4.88	7.61	1.96	5.64	0.22
	6.00	1	6.24	9.53	3.22	6.31	0.24		6.00	1	5.50	7.14	1.79	5.35	0.22
	6.00	2	6.00	9.98	2.53	7.45	0.30		6.00	2	5.61	6.06	0.50	5.50	0.22
	7.00	1	6.93	17.4	7.71	9.72	0.47		7.05	1	7.48	10.2	5.64	4.59	0.23
	7.00	2	6.88	17.7	7.54	10.1	0.44		7.05	2	7.58	11.3	6.17	5.19	0.23
	8.00	1	7.95	25.1	11.4	13.6	0.74		8.00	1	7.90	16.2	5.68	10.5	0.59
	8.00	2	7.94	24.8	11.5	13.3	0.68		8.00	2	7.92	16.1	5.96	10.2	0.56
Biogeco UNT (30 days of shaking)	5.57	1	6.29	6.97	2.07	4.89	0.24								
	5.57	2	6.59	17.2	10.6	6.64	0.32								
Biogeco+ 2% Fe (30 days of shaking)	5.80	1	6.54	6.19	3.97	2.22	0.08								
	5.80	2	6.65	6.05	3.81	2.23	0.08								

Appendix 4. Concentration of total, inorganic, organic carbon and recalculation of fulvic and humic acids

Soil	Tot-C %	Inorg-C %	Org-C %	Organic matter [%]	Organic matter [g/1g soil]	Active organic matter (FA+HA) [g/1g soil]	FA+HA [g/L]	FA* [g/L]	HA [g/L]
Reppel UNT	1.25	0.02	1.24	2.48	0.03	0,01	1,24	0,62	0,62
Reppel + 1% Fe	0.97	0.00	0.97	1.95	0.02	0,01	0,98	0,49	0,49
Biogeco + 2% Fe	0.83	0.24	0.59	1.18	0.01	0,01	0,59	0,30	0,30
Biogeco UNT	1.16	0.02	1.14	2.28	0.02	0,01	1,14	0,57	0,57
Louis Farques UNT	1.01	0.02	0.99	1.99	0.02	0,01	1,00	0,50	0,50
Louis Farques + 1% Fe	0.63	0.00	0.63	1.26	0.01	0,01	0,63	0,32	0,32
Louis Farques +B100	0.94	0.00	0.94	1.88	0.02	0,01	0,94	0,47	0,47
Louis Farques B100 + 1% Fe	0.61	0.01	0.60	1.21	0.01	0,01	0,60	0,30	0,30

*assumed that 50% of FA+HA is FA

Appendix 5. Data for Visual MINTEQ

Soil	Repetition	pH	DOC ppm	Ca* mg/l	Fe** mg/l	K* mg/l	Mg* mg/l	Al** µg/l	Cu* µg/l	HFO*** g/L	FA g/L	HA g/L	Na ⁺ Mm	NO ₃ ⁻ mM
Biogeco UNT 1	1	3.32	5.37	32.8	108	3.91	3.69	67700	35700	0.17	0.57	0.57	10	4.27
	2	3.25	5.56	32.8	108	3.91	3.69	67700	35700	0.17	0.57	0.57	10	4.27
Biogeco UNT 2	1	4.09	3.06	32.8	108	3.91	3.69	67700	35700	0.17	0.57	0.57	10	7.73
	2	3.85	3.07	32.8	108	3.91	3.69	67700	35700	0.17	0.57	0.57	10	7.73
Biogeco UNT 3	1	6.02	5.55	32.8	108	3.91	3.69	67700	35700	0.17	0.57	0.57	10	10
	2	5.99	6.17	32.8	108	3.91	3.69	67700	35700	0.17	0.57	0.57	10	10
Biogeco UNT 4	1	8.03	44.6	32.8	108	3.91	3.69	67700	35700	0.17	0.57	0.57	10	12
	2	8.04	42.8	32.8	108	3.91	3.69	67700	35700	0.17	0.57	0.57	10	12
Biogeco UNT 5	1	9.07	96.6	32.8	108	3.91	3.69	67700	35700	0.17	0.57	0.57	10	13
	2	8.88	91.3	32.8	108	3.91	3.69	67700	35700	0.17	0.57	0.57	10	13
Biogeco+2% Fe 1	1	3.01	3.73	38.7	1580	5.22	4.77	50050	64650	2.53	0.29	0.29	10	4.27
	2	2.94	3.28	38.7	1580	5.22	4.77	50050	64650	2.53	0.29	0.29	10	4.27
Biogeco+2% Fe 2	1	3.93	2.98	38.7	1580	5.22	4.77	50050	64650	2.53	0.29	0.29	10	7.73
	2	4.00	3.51	38.7	1580	5.22	4.77	50050	64650	2.53	0.29	0.29	10	7.73
Biogeco+2% Fe 3	1	6.57	3.07	38.7	1580	5.22	4.77	50050	64650	2.53	0.29	0.29	10	10
	2	6.60	2.23	38.7	1580	5.22	4.77	50050	64650	2.53	0.29	0.29	10	10
Biogeco+2% Fe 4	1	8.05	19.7	38.7	1580	5.22	4.77	50050	64650	2.53	0.29	0.29	10	12
	2	8.12	25.8	38.7	1580	5.22	4.77	50050	64650	2.53	0.29	0.29	10	12
Biogeco+2% Fe 5	1	8.49	26.9	38.7	1580	5.22	4.77	50050	64650	2.53	0.29	0.29	10	13
	2	8.39	21.0	38.7	1580	5.22	4.77	50050	64650	2.53	0.29	0.29	10	13

*Geochemically active cations (0.1 M HNO₃ extractable)

** Oxalate extractable iron and aluminium

*** Iron oxyhydroxides, recalculated from oxalate extractable iron concentration

Soil	Repetition	pH	DOC ppm	Ca* mg/l	Fe mg/l	K* mg/l	Mg* mg/l	Al** µg/l	As** µg/l	HFO*** g/L	FA g/L	HA g/L	NO ₃ ⁻ mM	Na ⁺ mM
Reppel UNT 1	1	4.81	11.7	158	139	7.81	32.2	107600	9060	0.22	0.62	0.62	10	2.1
	2	4.66	10.1	158	139	7.81	32.2	107600	9060	0.22	0.62	0.62	10	2.1
Reppel UNT 2	1	5.10	11.5	158	139	7.81	32.2	107600	9060	0.22	0.62	0.62	10	3.2
	2	5.18	10.6	158	139	7.81	32.2	107600	9060	0.22	0.62	0.62	10	3.2
Reppel UNT 3	1	6.13	11.4	158	139	7.81	32.2	107600	9060	0.22	0.62	0.62	10	5.5
	2	6.17	12.2	158	139	7.81	32.2	107600	9060	0.22	0.62	0.62	10	5.5
Reppel UNT 4	1	7.76	15.5	158	139	7.81	32.2	107600	9060	0.22	0.62	0.62	10	10
	2	7.81	15.4	158	139	7.81	32.2	107600	9060	0.22	0.62	0.62	10	10
Reppel UNT 5	1	8.02	20.9	158	139	7.81	32.2	107600	9060	0.22	0.62	0.62	10	10.8
	2	8.07	21.2	158	139	7.81	32.2	107600	9060	0.22	0.62	0.62	10	10.8
Reppel+ 1%Fe 1	1	5.16	5.90	165	441	6.70	38.1	107500	10450	0.70	0.49	0.49	10	1
	2	4.87	5.60	165	441	6.70	38.1	107500	10450	0.70	0.49	0.49	10	1
Reppel +1%Fe 2	1	5.57	5.74	165	441	6.70	38.1	107500	10450	0.70	0.49	0.49	10	2.6
	2	5.49	6.26	165	441	6.70	38.1	107500	10450	0.70	0.49	0.49	10	2.6
Reppel+1% Fe 3	1	6.24	6.31	165	441	6.70	38.1	107500	10450	0.70	0.49	0.49	10	4.5
	2	6.00	7.45	165	441	6.70	38.1	107500	10450	0.70	0.49	0.49	10	4.5
Reppel+1% Fe 4	1	6.93	9.72	165	441	6.70	38.1	107500	10450	0.70	0.49	0.49	10	7.32
	2	6.88	10.1	165	441	6.70	38.1	107500	10450	0.70	0.49	0.49	10	7.32
Reppel+1% Fe 5	1	7.95	13.6	165	441	6.70	38.1	107500	10450	0.70	0.49	0.49	10	10
	2	7.94	13.3	165	441	6.70	38.1	107500	10450	0.70	0.49	0.49	10	10

*Geochemically active cations (0.1 M HNO₃ extractable)

** Oxalate extractable iron and aluminium

*** Iron oxyhydroxides, recalculated from oxalate extractable iron concentration

