

Assessment of Arsenic Stability in Iron Amended Soil by Laboratory and Field Experiments

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ABSTRACT

The aim of this study was to assess the effectiveness of chemical stabilization technique on arsenic (As) contaminated soil amended with metallic or zerovalent iron (Fe^0) and combination of Fe^0 and peat by laboratory and pilot scale field experiments. The used iron amendments were spent blasting sand (BS), a by-product from a steel industry containing 98.3% of Fe^0 , and its combination with peat.

A pilot scale landfill cover was built at Brännkläppen landfill in Northern Sweden. The untreated and treated As-contaminated soils were used as a 2 m thick vegetation/protection layer of the landfill top cover.

The main exposure pathways concerning risks to human health and the environment were studied by analysing leachates from field, soil pore water, As fractionation in soil, phytotoxicity and bioaccessibility. Using the bioaccessibility results, a bioavailability of As to humans was calculated.

The results showed that the stabilization of As-contaminated soil with a combination of Fe^0 and peat significantly reduced the As concentration in soil pore water, uptake by plants and improved the main morphological parameters of plants. The soil treatment also reduced the bioaccessibility and the bioavailability of As indicating the reduced risks to human health.

Nevertheless, the soil treatment using Fe and peat only works under oxidizing soil conditions. Leachates collected in field below the 2 m layer showed an increased As concentration in the water percolating through the treated soil profiles over time, when compared to the leachate collected under the untreated soil.

These results point out an importance of maintaining oxidizing conditions in the soil treated with Fe amendments in order to retain the positive impact of the soil treatment on As immobilization in soil. Soil layer containing the stabilized soil should be used only in the very top layer of the landfill cover.

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1 INTRODUCTION

The number of potentially contaminated sites in Europe is estimated at 2.5 million, while there are around 342 000 sites in which the contamination has been verified and it is already confirmed that they represent a risk to human, water and ecosystem (Panagos et al., 2013). 35% of the sites are contaminated with heavy metals and metalloids (Panagos et al., 2013).

A rank of hazardous substances was drawn up by Johnson and DeRosa (1995), based on three criteria: frequency of occurrence of a substance at contaminated sites, the substance's toxicity, and the potential for human exposure. Arsenic is at the second place of that list. Moreover, World Health Organization (WHO) also declared As among the elements of major concern for human health, due to its acute toxicity. Thus, As contaminated soil have been extensively studied considering that the remediation priority should be given to the pollutants on the basis of their toxicity, environmental persistence, mobility, and bioaccumulation (WHO, 2000).

There are several techniques to clean up the polluted area, but the most extensively applied is excavation and landfilling. This method is attractive for small and highly contaminated industrial sites, but it becomes prohibitively costly, non-sustainable and irrational for remediation of large or moderately contaminated areas. The method also requires the availability of large land areas to confine the excavated masses. It is apparent that there is a need for the development of more cost efficient and *in situ* applicable alternatives that would enable the treatment of more contaminated sites within the limited budget of the society.

One of the suitable alternatives might be a chemical stabilization technique, that aims at rendering the metal(loid) less available and thus decreasing the risks associated with their leaching, ecotoxicity, plant uptake and human exposure. The contaminant concentration will be the same after the remediation, but it is in less toxic and more inert forms (Komárek et al., 2013). The main principle of this technique is that the contaminated soil is blended with the selected stabilizing material or their combination, which can be done both *in situ* and *ex situ*. If the suitable amendments are industrial by-products, this technique can become a cost-effective treatment. If the soil is treated on site, the method can also be considered as less disruptive to the soil ecosystem than conventional excavation technologies (Peng et al., 2009).

Although several amendments have been studied to remediate As contaminated soils in order to reduce As mobility and toxicity, iron minerals and iron-containing industrial by-products show a great potential for *in situ* remediation (Miretzky and Cirelli, 2010). Due to their strong binding capacities, Fe oxides have been extensively evaluated as potential stabilization amendments in soils contaminated with metals and As. Application of Fe oxides, either directly or indirectly through the application of their precursors (e.g., iron grit or Fe sulfates) is supposed to decrease mobile, bioavailable and bioaccessible fractions of As (Komárek et al., 2013). In particular several studies showed high efficiency for As immobilization applying zerovalent iron (Fe^0). Oxidation of Fe^0 does not lead to a strong fluctuation of pH in soil that could remobilize contaminants and lower the soil quality (Boisson et al., 1999; Mench et al., 2006; Lidelöw et al., 2007; Maurice et al., 2007; Kumpiene et al., 2008). The application rate for Fe^0 ameliorant usually range from 0.5% to 5% by dry weight, but applying 2% to 5% do not usually improve the contaminant retention (Mench et al., 2000). Nevertheless, Kumpiene et al.

(2013) demonstrated by laboratory experiments that the effectiveness of the stabilization is verified only in the upper soil layer, where oxidizing condition prevail.

In this study the efficiency of As stabilization using Fe^0 and its combination with peat are investigated in field. Peat helps to supports the plant growth in sandy soil and improves the soil texture, and is expected to maintain a high redox potential along the soil layer (Kumpiene et al., 2013). Since the mobility, solubility and toxicity of As is strongly influenced by its oxidation state (Masscheleyn et al., 1991) and binding strength in soil, a chemical fractionation using sequential extraction was performed to evaluate distribution of As between various soil fractions and better understand the changes in As binding caused by soil treatment.

A pilot scale landfill cover was built at Brännkläppen landfill in Northern Sweden. Leachate percolating through a 2 m thick layer of treated and untreated soil was collected in field to evaluate the solubility of As along the soil profile.

The main exposure pathways concerning the risks for human health and the environment were studied by analyzing As solubility, phytotoxicity and bioaccessibility in the untreated and treated soil.

2 SCOPE OF THE THESIS

The aim of this study was to assess the effectiveness of chemical stabilization technique in As contaminated soil amended with Fe^0 and combination of Fe^0 and peat by laboratory and pilot scale field experiments. The following questions cover the scope of the thesis:

- how stabilization with chosen ameliorants affect As solubility and mobility in soil layer used as a landfill top cover;
- how the soil treatment affect As bioaccessibility to humans and availability to plants.

The literature review of the subject is given in Appendix 1.

2.1 Delimitation

The evaluation of the pilot scale field experiment was implemented during one summer and only represents short-term observations. To be able to conclude whether the studied soil remediation method is efficient or not in a long-term, follow up studies are necessary.

3 MATERIALS AND METHODS

3.1 Soil and amendments

The soil used in the field experiment originated from a former industrial site at Solgårdarna, Boden municipality in Northern Sweden. The site was used for timber treatment with chromated copper arsenate (CCA) chemical, which caused the soil was contamination mainly with As. About 800 t of soil was excavated from the site and transported to Brännkläppen waste management facility in Boden.

Two different types of amendments were applied: 1) spent blasting sand (BS) from SSAB, Luleå, containing 98.3% of Fe⁰ and some impurities; 2) peat, obtained from Geogen production AB, Arjeplog.

The total amount of soil (800 t) was homogenized and divided in three parts, the first was kept untreated (ca. 267 t), while the remaining quantity was amended with 1% of Fe⁰ (by weight). A half of this volume (one third of the overall amount) was further mixed with 5% of peat (by weight). The soil was mixed with a scoop tractor.

The untreated and treated soil was used to form a vegetation/protection layer on the top of the experimental landfill cover during the autumn 2012. Ca 15 kg of untreated soil and the same mass of treated soil were brought to the Environmental laboratory at Luleå University of Technology for additional tests.

Figure 1 illustrates the schematic drawing of the field experiment. The heap consists of a 2 m thick top layer of untreated and stabilized As contaminated soil, a drainage layer and a liner. In this work only the top layer was studied. The heap is divided into three parts, the first one is untreated soil, the second one contains soil amended with Fe⁰ and the last one is soil mixed with a combination of Fe⁰ and peat. 1 m² glass fiber lysimeters were placed below the soil layer, three for each type of soil, and were used to collect leachate.

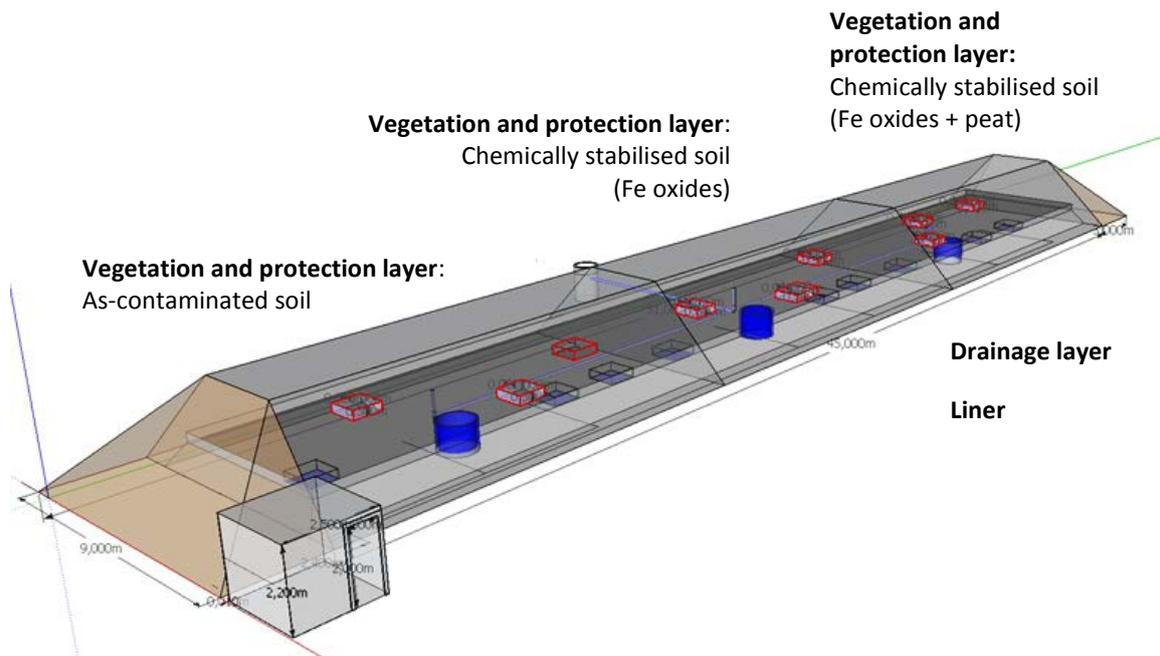


Figure 1. Sketch of the pilot field experiment in Brännkläppen. The top layer consists of untreated and amended soil as indicate in the drawing. The lysimeters to collect leachate are highlight in red.

To perform the sequential extraction soils samples were collected in June 2013 from the field. Three composite samples were taken with a spade at different spots of the surface of each area. Leachate samples were collected from lysimeters by pumping out the accumulated water.

For phytotoxicity test, soil pore water analysis and the bioaccessibility test, the soils collected directly after mixing the materials in field and stored in laboratory were used.

3.2 Soil basic characterization

Soil pH and electrical conductivity (EC) of the samples from the field were measured in suspensions of fresh soil and distilled water in the ratio 1:2. For the other tests, the samples were air dried and homogenized.

Total solids (TS) were assessed after drying at 105°C for 24 h, according to Swedish Standard SS 02 81 13. Volatile solids (VS) were measured after ignition at 550°C for 2 h. All the measurements were made in triplicates.

Water holding capacity (WHC) is the amount of water that the studied material can keep against gravity. To determine WHC, a filter paper was place on the permeable bottom of cylindrical beakers and then weighted. The three types of soils (one untreated and two treated soils) were place into the bakers and left in a vessel filled with water for 1 h, in this way the samples were water-saturated from the bottom. The saturated samples were placed into a vessel with wet sand for 3 h to let the excess water to drain. The weight of all samples was registered and then they were placed in the oven at 105°C for 20 h. The procedure was performed in triplicates. An empty beaker was used to adjust the calculation of the saturated

samples, taking into account the water held by the filter paper and the beaker bottom itself. The dry weight was recorded and WHC was measured as the ratio between the water content in saturated sample and the weight of dry soil, all multiply by one hundred.

Soil density was measured by weighting a known volume, filled with loose air dried soil. The measurements were done in triplicates.

3.3 Evaluation methods

3.3.1 Sequential extraction

Distribution of As between soil fractions and sorption to Fe compounds largely affect the accomplishment of the stabilization. Knowing the total concentration is not sufficient to assess the environmental impact of contaminated soil. Through sequential extraction it is possible to examine the association between Fe and As.

The basic idea of sequential extraction procedure is to use different chemical reagents to obtain the release of different metal(loid) fractions from soil by destroying the bond between metal(loid) and soil solids. The strength of the chemicals is increased with each consecutive step to counteract the increasing binding strength of an element in different soil fractions. The analysis of the extracted supernatant gives an estimation of the potential element mobility under different environmental conditions (Balasoiu et al., 2001).

The sequential extraction procedure was performed on three soils: untreated As contaminated soil, soil amended with Fe⁰ and soil amended with Fe⁰ and peat.

A six-step sequential extraction was performed, following the procedure given by Kumpiene et al. (2012). The method given by Dold (2003) was modified with an additional step to assess the fraction bound to Fe - Mn oxides (Tessier et al., 1979), since not all iron oxides were dissolved during the crystalline Fe (III) (oxyhydr)oxides dissolution step (Kumpiene et al., 2012).

The extraction was carried out on homogenized and sieved to <2 mm size soil. 1 g of air dried soil was placed in a 50 ml Teflon centrifuge tube. The method was applied in triplicates and is summarized in Table 1. Separation of the liquid from the solid phase after each extraction step was performed by centrifugation at 10 000 rpm for 15 min. An exception was made in step (IV) that was centrifuged at 10 000 rpm for 30 min, as described by Tessier et al. (1979). The solid residue after the washing phase was used in the next step. The sample from the last step (VI) was not centrifuged but was filtered through paper filter and then diluted to total volume of 100 mL using deionized water.

All the extracts were filtered through 0.45 µm cellulose acetate syringe filters and stored at 4°C prior to analyses by inductively coupled plasma optical emission spectroscopy (ICP-OES).

In some fractions the element concentrations were below instrument detection limits. In these cases, the detection limit value was taken to calculate means and standard deviations.

Table 1. Sequential extraction steps

	Dissolved Fraction	Chemical reagent	L/S	Extraction procedure	Washing step
I	Exchangeable	1 M NH ₄ acetate, pH=4.5	25	shaking for 2 h at room temperature	10 mL of deionized water
II	Poorly crystalline Fe(III)-oxyhydroxide	0.2 M NH ₄ -oxalate, pH=3	25	shaking for 2 h at room temperature in darkness	12.5 mL of 0.2 M NH ₄ -oxalate, pH=3
III	Crystalline Fe(III) (oxyhydr)oxide	0.2 M NH ₄ -oxalate, pH=3	25	heated in water bath at 80°C for 6 h	12.5 mL of 0.2 M NH ₄ -oxalate, pH=3
IV	Fe – Mn oxide	0.04 M NH ₂ OH-HCl in 25% HO-acetate pH=2	20	heated in water bath at 96°C for 6 h	10 mL of deionized water
V	Organic matter and secondary sulphide	35% H ₂ O ₂	25	heated in water bath at 85°C for 1 h	10 mL of deionized water
VI	Residual	Aqua Regia (HCl:HNO ₃ , 1:3 v/v)	15	Digestion in microwave at 195°C for 10 min	-

The total As concentration in soil from the field was calculated as a sum of concentrations of all the fractions determined by the sequential extraction. The total As concentration in soil samples used for the phytotoxicity tests was determined by digesting 1 g of soil in 15 ml of aqua regia (HCl-HNO₃, 3:1, v/v) using microwave digester at 195°C for 10 min. The samples were filtered through 0.45 µm filter prior analysis. All the measurements were performed in triplicates.

3.3.2 Phytotoxicity test and soil pore water analysis

Phytotoxicity was assessed using the method described by Vangronsveld and Clijsters (1992). Seeds of dwarf beans (*phaseolus vulgaris*) were left for 1 day in refrigerator, for vernalization, and then they were submerged into distilled water for 4 h, for the imbibition phase. Four pots (Ø=120 mm, volume 0.9 L) were prepared for each type of studied soil and a Rhizon soil moisture sampler (polymer, 10 cm long, Ø 2.5 mm, 0.1 µm pore size, Eijkelpamp, the Netherlands) was placed in each pot. The soils were kept humid for 1 week before sowing to recover the balance of nutrients and microbiological system. Four seeds were sown in each pot. The experiment lasted 14 days, during which the water moisture was kept between 47% and 53% of soil water holding capacity, and 12 h of artificial light were supplied.

After 14 day morphological parameters were measured for each plant: shoot length, fresh shoot weight and primary leaf area.

Plant shoots (the above ground parts) were harvested and the fresh weight was measured. The shoot and root then were washed with distilled water, dried at 50°C for 96 h, and weighted for

the dry weight determination. The primary leaf area was calculated by estimating the leaf shape to an ellipse and measuring the main axis. The element concentrations in the biomass were analyzed by ALS Scandinavia AB.

Soil pore water was collected the third day and the fourteenth day to assess the element availability in soil. The pH and EC were measured immediately after the sampling on a small aliquot of the sample. The remaining volume was stored at 4°C until element concentration analysis using ICP-OES.

3.3.3 Bioaccessibility and bioavailability

The bioaccessibility of As in untreated and treated soils was evaluated using *in vitro* SBRC method. Only the gastric phase was applied, because as showed by Juhasz et al. (2009), Basta et al. (2007), and Rodriguez and Basta (1999), extending the procedure to intestinal-phase does not increase the extraction of bioaccessible As fraction. The chosen method was validated by Juhasz et al. (2009), comparing *in vitro* assay and measured As concentration in swine's blood after oral administration of contaminated soil (Juhasz et al., 2007). Air dried bulk soils were sieved, and only $\phi < 250 \mu\text{m}$ particle size fraction was used for this analysis. It is considered that only particles of this size can adhere to children hands and be ingested through a hands-to-mouth path.

1 g of soil and 100 ml of gastric solution, consisting of 0.4 M of glycine solution at pH 1.5, were put in high density polyethylene bottles. The samples were intermittently shaken for 1 h in a water bath at 37°C. The samples were filtered through 0.45 μm cellulose acetate syringe filters and stored at 4°C before analysis with ICP-OES. The procedure was performed in triplicates. The bioaccessible fraction is calculated as follows:

$$\textit{in vitro bioaccessibility} (\%) = \frac{\textit{in vitro As}}{\textit{total As}} * 100$$

To estimate the bioavailable As fraction, a linear regression function model, proposed by Juhasz et al. (2009) was applied:

$$\textit{in vivo relative As bioavailability} (\%) = 1.656 + 0.992 * \textit{gastric} (\%)$$

3.3.4 Leachate collection in field

The leachate from the lysimeters placed under the soil layer (at 2 m depth) was collected by pumping out the accumulated water on three occasions, the 4th and the 27th of June, and the 21st of August 2013.

4 RESULTS

4.1 Soil characterization

The main soil characteristics of the samples collected in the field experiment are summarized in Table 2.

Table 2. Main characteristics of untreated and treated soil collected from the field experiment (n = 3, ± SD)

Soil Proprieties	Unit	Untreated soil	Soil + Fe	Soil + Fe + peat
pH (1:2 H ₂ O)	-	7.85 ± 0.13	7.89 ± 0.06	7.72 ± 0.15
Electrical conductivity (EC)	μS cm ⁻¹	403.5 ± 10.6	297.3 ± 36.5	272.3 ± 45.5
TS (bulk soil)	wt.%	99.0 ± 0.2	98.2 ± 0.6	97.5 ± 0.8
VS (bulk soil)	% of TS	1.3 ± 0.4	3.7 ± 1.1	7.3 ± 0.5

The soil amended with peat shows a higher presence of volatile solids, due to the addition of organic matter.

The measured pH values for treated soil did not deviate significantly from untreated one. The EC values decreased for treated soils, most likely due to the adsorption of ions to the amendments.

The main properties of soils used to perform the phytotoxicity test are presented in Table 3.

Table 3. Main characteristics of untreated and treated soils collected directly after the mixing with amendments (n = 3, ± SD)

Soil Proprieties	Unit	Untreated soil	Soil + Fe	Soil + Fe + peat
TS (bulk soil)	wt.%	90.8 ± 0.2	89.2 ± 0.2	90.0 ± 0.3
VS (bulk soil)	% of TS	1.2 ± 0.0	1.3 ± 0.0	6.6 ± 0.2
Water holding capacity (WHC)	%	19.7 ± 0.3	22.2 ± 1.4	33.3 ± 1.1
Density	g cm ⁻³ dw	1.35 ± 0.01	1.33 ± 0.01	1.25 ± 0.01
Total concentration of elements				
As	mg kg ⁻¹ dw	136.71 ± 39.84	148.75 ± 4.36	125.07 ± 6.66
Fe	g kg ⁻¹ dw	23.23 ± 3.75	36.92 ± 3.63	38.32 ± 4.82

The soil treatments have significantly improved WHC. The soil stabilization with Fe⁰ increased WHO by 13% with respect to the untreated soil, while Fe⁰-peat treated soil had WHC that was 70% higher than in the untreated soil.

The soil density did not change by the addition of Fe⁰, but significantly decreased by amending soil with a combination of Fe⁰ and peat (Table 3).

4.2 Sequential extraction

The total element concentration, calculated as the sum of each fraction, is shown in Figure 2. The total As concentration was on average higher in the soil stabilized with Fe⁰ and peat ($224.56 \pm 43.97 \text{ mg kg}^{-1} \text{ dw}$) than in the untreated soil ($189.72 \pm 12.06 \text{ mg kg}^{-1} \text{ dw}$) and soil treated only with Fe⁰ ($191.75 \pm 6.29 \text{ mg kg}^{-1} \text{ dw}$). The data variability in soil with Fe⁰ and peat was quite high, which made the differences between all the samples statistically not significant.

As shown in Figure 2, the total Fe concentration in both samples containing Fe⁰-amendment increased by ca 1.6% compared with the untreated soil.

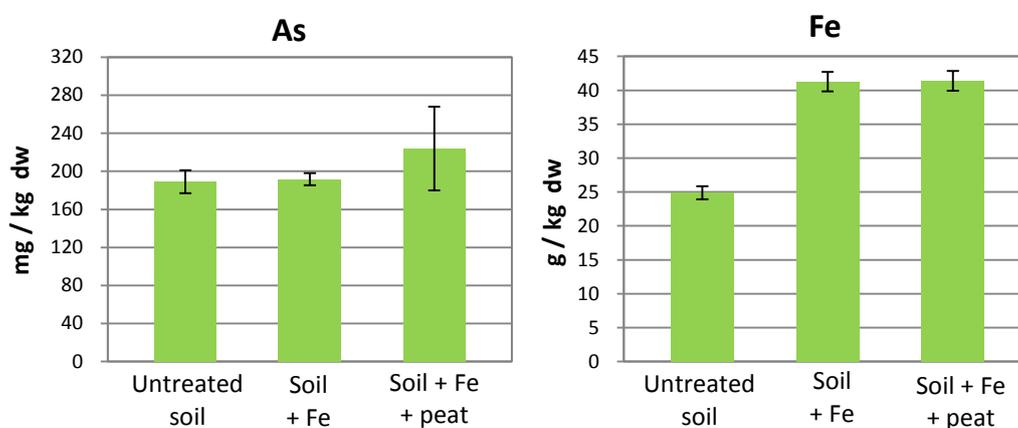


Figure 2. Total arsenic and iron concentration calculated as sum of each fraction measured by the sequential extraction. Error bars represent standard deviations of means, n=3.

Arsenic and iron fractionations are shown in Figures 3 and 4, respectively.

The exchangeable As fraction in both stabilized soils decreased when compared to the untreated soil (Fig. 3). The decrease was larger in Fe⁰-peat containing soil (46% lower concentration than in the untreated soil) than in soil amended only with Fe⁰ (28% lower concentration than in the untreated soil).

No differences between the soil samples regarding the concentrations determined in all the other fractions were found. The Fe⁰-peat amended soil shows on average an increase in the fraction bound to crystalline Fe oxides (Fig. 3). But as mentioned above, Fe⁰-peat containing samples had the highest variability between the replicates, which made this difference insignificant. Arsenic bound to organic matter/secondary sulfide fraction was in most cases undetectable.

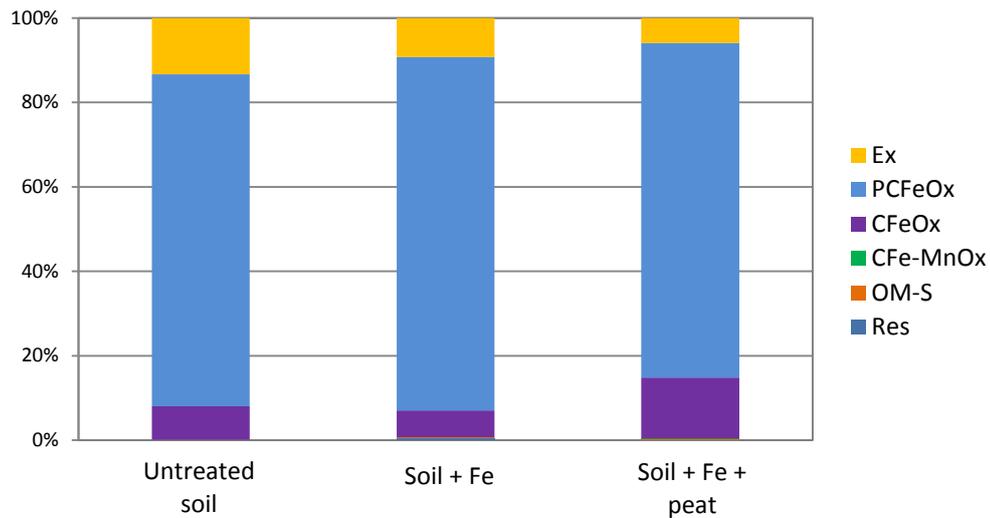


Figure 3. Arsenic speciation in untreated and stabilized soils. (Ex) exchangeable fraction, (PCFeOX) bound to poorly crystalline Fe(III)-oxyhydroxides, (CFeOx) bound to crystalline Fe(III)-(oxyhydr)oxides, (CFe-MnOx) bound to Fe-Mn oxides, (OM-S) bound to organic matter and secondary sulphides, (Res) residual fraction.

The Fe exchangeable fraction increase in both treated soils, from 0.3 ± 0.01 g/kg in the untreated soil to 1.4 ± 0.4 g/kg, and 0.9 ± 0.1 g/kg in Fe⁰ and Fe⁰-peat stabilized soils respectively. The fraction of poorly crystalline Fe(III)-oxyhydroxides shows the greatest difference between treated and untreated soils (concentrations in Fe-amended soils increased 3.5-4 times). All the soils showed the presence of Fe crystalline fraction: untreated soil 7.3 ± 0.2 g/kg, Fe⁰ treated soil 6.5 ± 0.2 g/kg, Fe⁰-peat stabilized soil 7.1 ± 0.7 g/kg. This fraction did not change by the treatments (Fig. 4). No differences between the soil samples regarding the concentrations determined in the Fe-Mn and the residual fraction were observed. The concentration on Fe bound to organic matter increased 6-fold in Fe⁰-peat treated soil and 2-fold in Fe⁰ treated soil. But this fraction is much lower compared to the others and in the Fe⁰-peat treated soil it is only 0.3 ± 0.1 g/kg (Fig. 4).

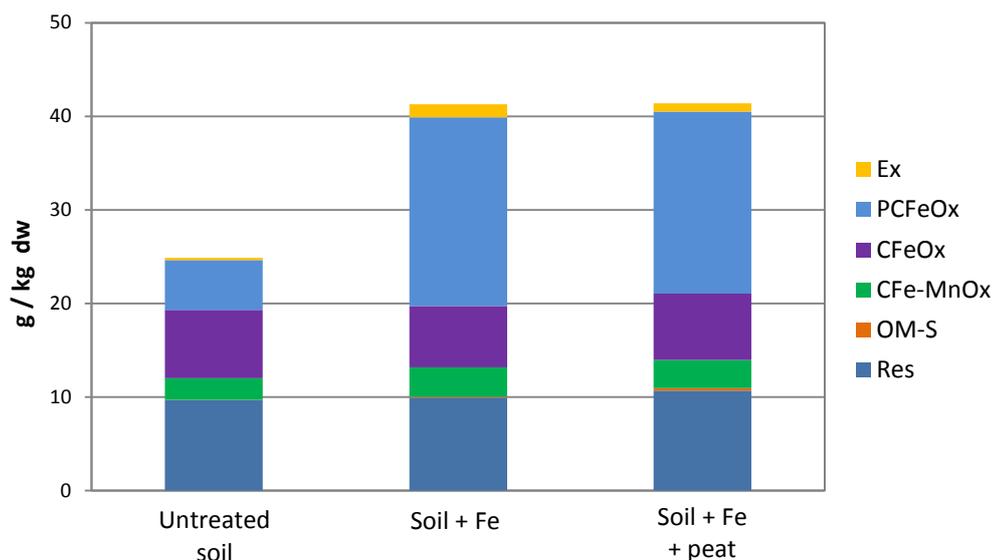


Figure 4. Iron speciation in untreated and stabilized soils. (Ex) exchangeable fraction, (PCFeOx) poorly crystalline Fe(III)-oxyhydroxides, (CFeOx) crystalline Fe(III)-(oxyhydr)oxides, (Cfe-MnOx) Fe-Mn oxides, (OM-S) bound to organic matter and secondary sulphides, (Res) residual fraction.

4.3 Leachate analysis

The pH and EC were measured immediately after the sampling of leachates in field and values are summarized in Table 4. All the pH values measured were around 7-8. Some increase in pH was observed during the second sampling in untreated and Fe⁰ treated soil, followed by a decrease in all samples collected during the third sampling.

The EC increased by nearly one order of magnitude in untreated soil during the second and the third sampling. For Fe⁰ treated soil the mean value did not change, but the standard deviations (SD) were quite high due to variability among replicates. The first leachate sample collected under the Fe⁰-peat treated soil layer showed a high value, but it decreased 13-fold in the second sampling and remained similar during the third sampling (Table 4).

Table 4. pH and EC of leachates collected in field (n=3, ± SD).

		Unit	Untreated soil	Soil + Fe	Soil + Fe + peat
1st sampling	pH	-	7.60 ± 0.21	7.06 ± 0.03	7.15 ± 0.23
	EC	mS cm ⁻¹	0.28 ± 0.249	7.51 ± 2.76	13.05 ± 0.23
2nd sampling	pH	-	7.83 ± 0.18	7.27 ± 0.09	7.03 ± 0.29
	EC	mS cm ⁻¹	2.28 ± 0.69	7.63 ± 3.21	1.47 ± 0.28
3rd sampling	pH	-	7.08 ± 0.14	6.97 ± 0.12	6.97 ± 0.06
	EC	mS cm ⁻¹	1.65 ± 0.13	7.16 ± 2.18	1.82 ± 0.35

The total As and Fe concentrations in the leachates are shown in Figure 5. The As concentration significantly increase in Fe⁰ treated soil (3-fold greater concentration than in the

untreated soil). The concentration from the Fe⁰-peat treated soil did not change compared to the untreated soil, $4.4 \pm 0.9 \mu\text{g/l}$ and $4.4 \pm 1.2 \mu\text{g/l}$ respectively (Fig. 5).

The trend of Fe concentration is similar to that of As. The Fe concentration significantly increased in Fe⁰ treated soil (16-fold greater concentration than in the untreated soil). While the Fe concentration from the Fe⁰-peat treated soil profile did not change compared to the untreated soil $0.2 \pm 0.1 \text{ mg/l}$ and $0.2 \pm 0.1 \text{ mg/l}$ respectively (Fig. 5).

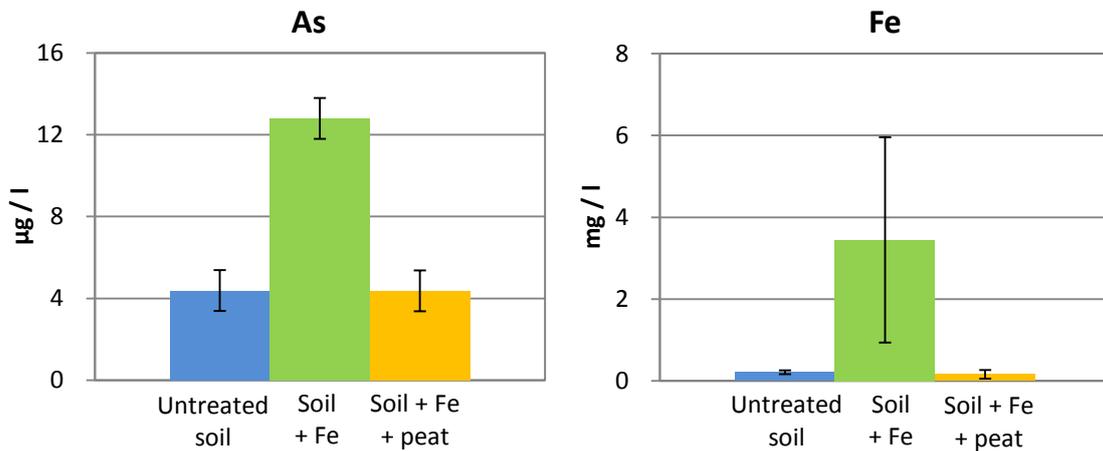


Figure 5. As and Fe concentration in leachates collected during the 1st sampling. Error bars represent standard deviations of means, n=3.

The analysis of the leachate from the second sampling showed one strongly deviating value in the Fe⁰-peat treated soil leachate. This value ($23.3 \mu\text{g/L}$) was substantially higher than in any other analyzed sample (Fig. 6). The reason for this deviation is not clear. If considering this value as an outlier, the As concentration was consistent with the values measured in the first leachate. The average As concentration in the leachate from Fe-peat treated soil did not differ from the untreated soil, while the leachate from Fe⁰ treated soil had on average a substantially higher As concentration than untreated soil. In the leachate from the second sampling the values varied greatly, which made the difference between all samples statistically not significant (Fig. 6).

The Fe concentration decreased significantly and was about 3 orders of magnitude lower than in the leachates from the previous sampling. A standard deviation in the Fe-treated soil indicates the strong variability between the replicates (Fig. 6).

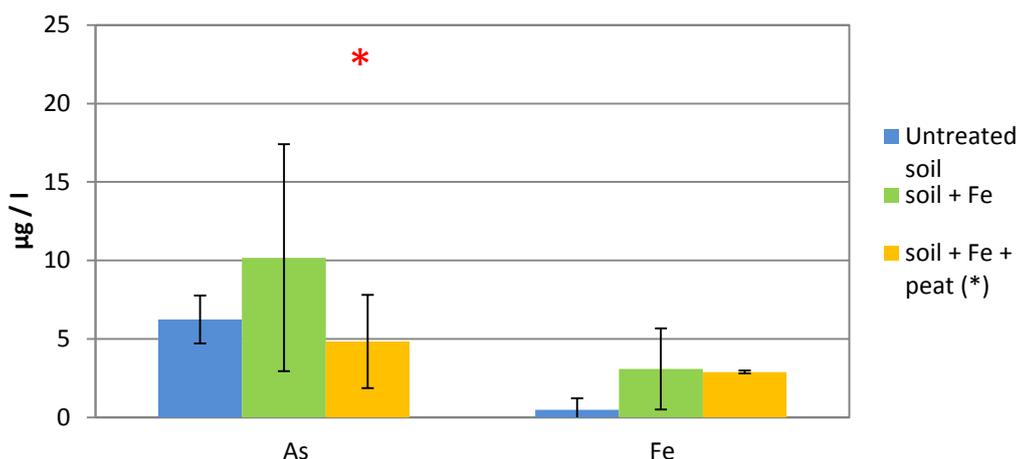


Figure 6. As and Fe concentration in leachates collected during the 2nd sampling. The mean value for Fe-peat treated soil is calculated excluding the deviating value. Error bars represent standard deviations of means, $n = 3$.

The samples collected during the 3rd sampling showed some changes with respect to the previous samplings (Fig. 7). The average As concentration in the leachate percolating through the Fe⁰-amended soil decreased and became equal to the dissolved As in Fe⁰-peat containing soil. Arsenic concentration in both treated soils exceeded that of the untreated soil, but the difference between the leached As in the untreated soil and soil treated with Fe⁰-peat was not significant. No outliers were detected, the sample with the greatest As concentration was 9.9 µg/L. The standard deviation for Fe⁰-peat treated soil was still large, indicating a large variability of As concentration. All the average values were below the As concentration limit for drinking water that is 10 µg/L.

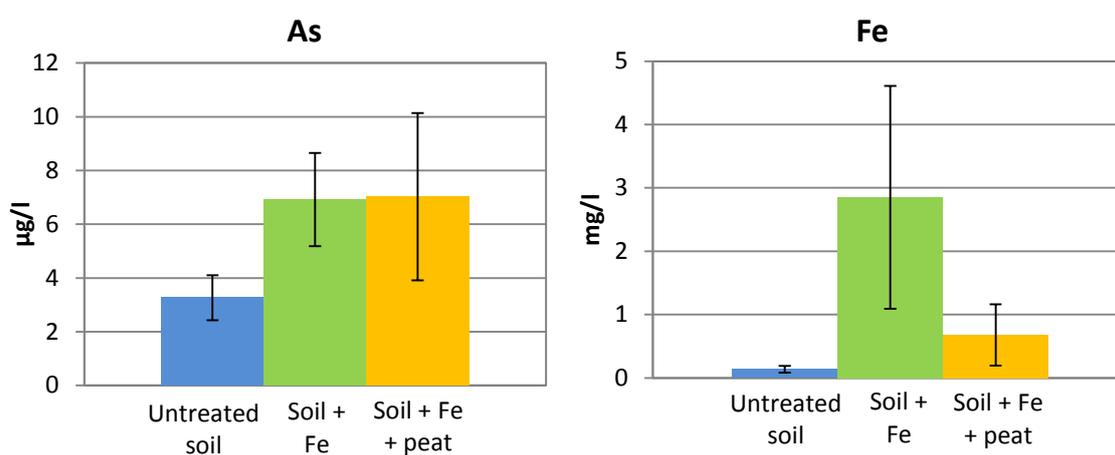


Figure 7. As and Fe concentration in leachates collected during the 3rd sampling. Error bars represent standard deviations of means, $n = 3$.

Considering the three samplings the As concentration in the leachate from Fe⁰ treated soil was the highest, but it showed a gradually decreasing trend. The Fe⁰-peat treated soil had As concentration comparable to the untreated soil. The leachate of the untreated soil showed the

most stable values (the lowest and the highest As concentrations were 3.3 $\mu\text{g/L}$ and 6.2 $\mu\text{g/L}$, respectively).

4.4 Phytotoxicity test

4.4.1 Morphological parameters

Morphological parameters of plants, determined right after harvesting, are shown in Figure 8. The general trend for all the parameters indicates an improvement of plant growth conditions in Fe^0 -peat treated soil, and an impairment of the conditions in Fe^0 treated soil, when compared to the untreated soil. The high variability between the replicates made the differences of shoot length and root dry weight not significant. Primary leaf area, fresh biomass and dry shoot weight showed a similar trend among the different soils. These parameters decreased for plants grown in Fe^0 treated soil by 46%, 40% and 43%, respectively when compared to the plants grown in untreated soil. The plants in the Fe^0 -peat treated soil developed twice as large primary leaf area, fresh biomass and dry shoot weight compared to the untreated soil (Fig. 8).

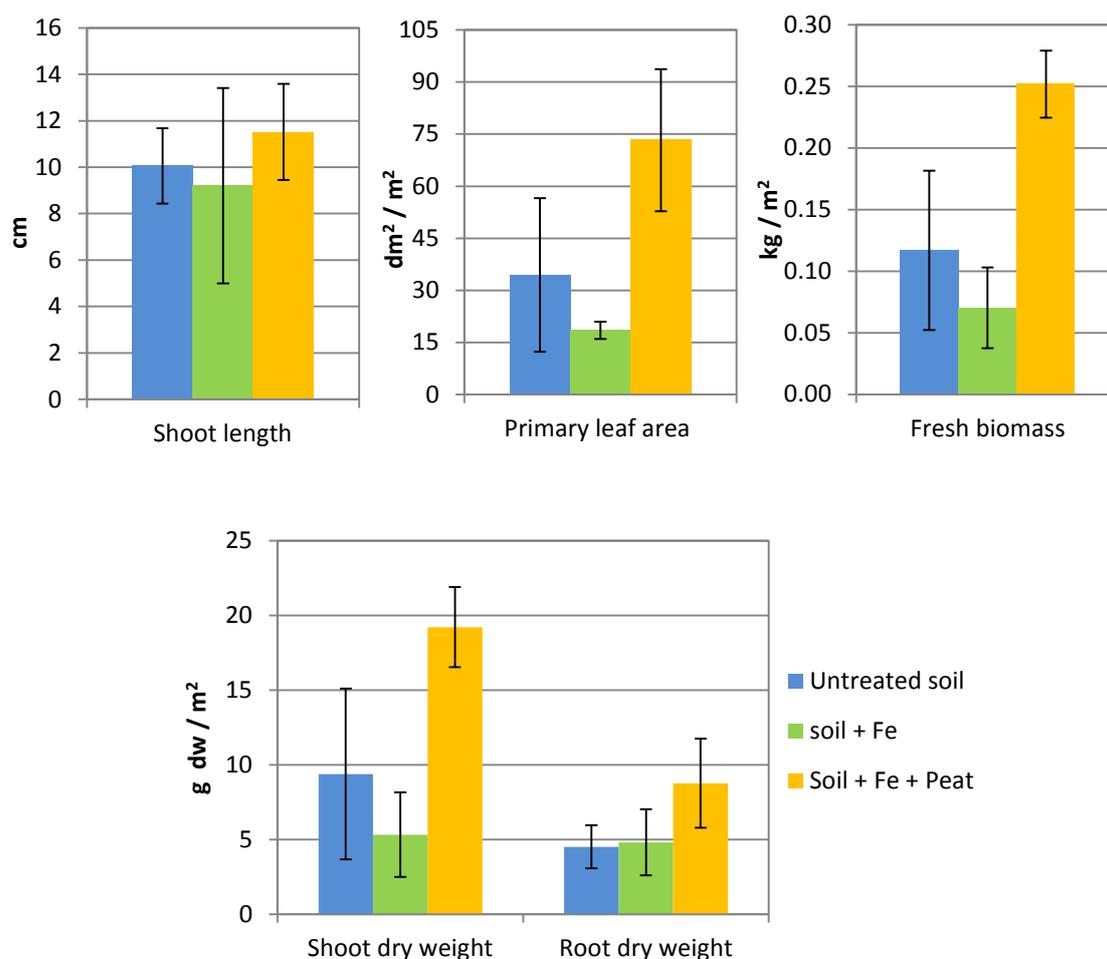


Figure 8. Morphological parameters of dwarf beans developed in untreated soil and soil treated with Fe^0 and Fe^0 -peat: shoot length, primary leaf area, fresh biomass, shoot and root dry weight measured at the end of the phytotoxicity test. Error bars represent standard deviations of means, n = 4.

4.4.2 Element concentration in plants

Element concentrations in the dried shoot and root samples are presented in Figures 9 and 10. The average of As concentrations in plant shoots from the untreated and Fe⁰ treated soil were similar (2.2 mg/kg and 2.1 mg/kg, respectively). The As concentration in the plants from the Fe⁰-peat stabilized soil decreased by 70% when compared to plants from untreated soil. The variability of the data was quite high in Fe⁰-treated soil (Fig. 9).

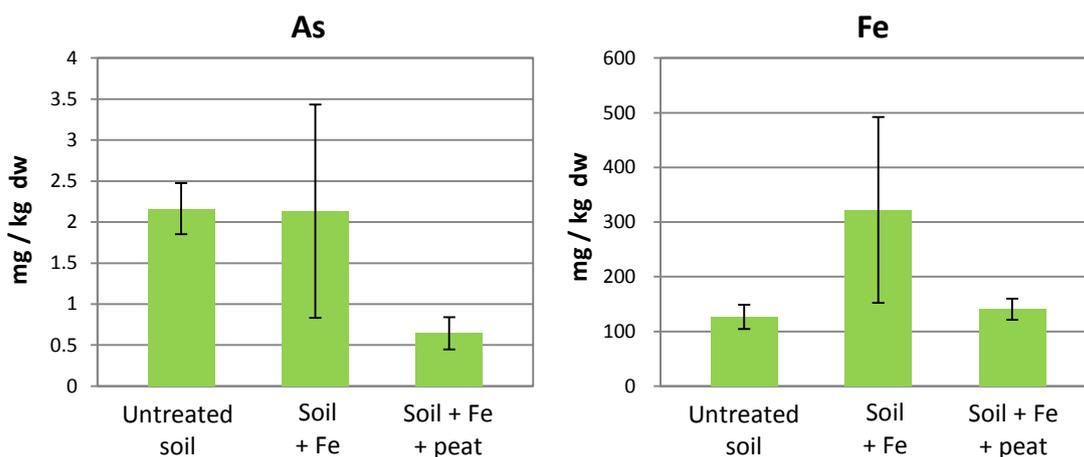


Figure 9. Total arsenic and iron concentration measured in plant shoots. The error bars represent standard deviations of means, n=4.

The As concentration measured in plant roots was by one order of magnitude higher than in the shoots. The data variability was the lowest for the soil stabilized with Fe⁰ and peat. The differences in As concentration between the untreated and the Fe⁰-treated soil was not statistically significant, while As concentration in roots decreased by 55% in plants grown in Fe⁰ and peat stabilized soil (Fig. 10).

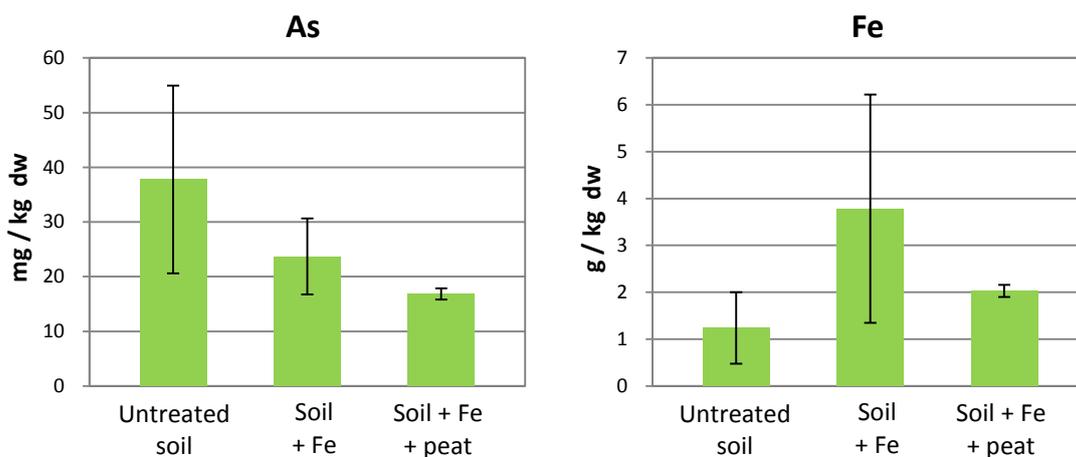


Figure 10. Total arsenic and iron concentration measured in plant roots. The error bars represent standard deviations of means, n=4.

4.4.3 Soil pore water analysis

The electrical conductivity of soil pore water was lower at the end of the phytotoxicity test, while the pH was relatively constant (Table 5).

Table 5. pH and EC of soil pore water collected during the phytotoxicity test (n=4, \pm SD).

		Unit	Untreated soil	Soil + Fe	Soil + Fe + peat
1st sampling	pH	-	6.76 \pm 0.08	7.83 \pm 0.13	7.71 \pm 0.02
	(Day 3)	EC	mS cm ⁻¹	2.24 \pm 0.03	1.27 \pm 0.10
2nd sampling	pH	-	6.83 \pm 0.08	7.91 \pm 0.07	7.59 \pm 0.09
	(Day 14)	EC	mS cm ⁻¹	1.63 \pm 0.19	1.05 \pm 0.09

The concentrations of elements in pore water samples collected in the beginning of the test (day 3) are presented in Figure 11. The As concentration was lower in both Fe⁰ (38.6% lower concentration than in the untreated soil) and Fe⁰-peat treated soils (54% lower concentration than in the untreated soil). The Fe concentration did not show any significant differences among the treatments.

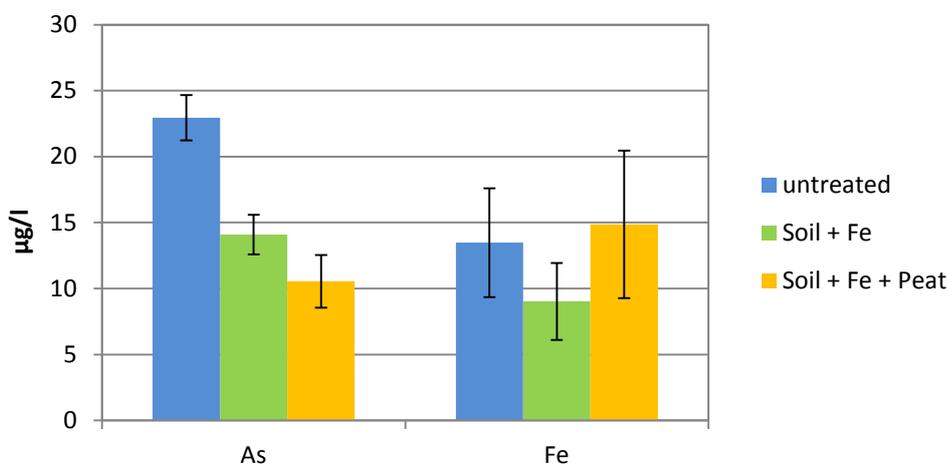


Figure 11. As and Fe concentration in soil pore water samples collected in the beginning of the phytotoxicity test. The error bars represent standard deviations of means, n=3.

The second sampling, at the end of the phytotoxicity test (day 14), showed a similar elements concentration trend than the first samples. The As concentration decreased by 34% in Fe⁰ treated soil, and it was 51% lower in Fe-peat treated soil (Fig. 12).

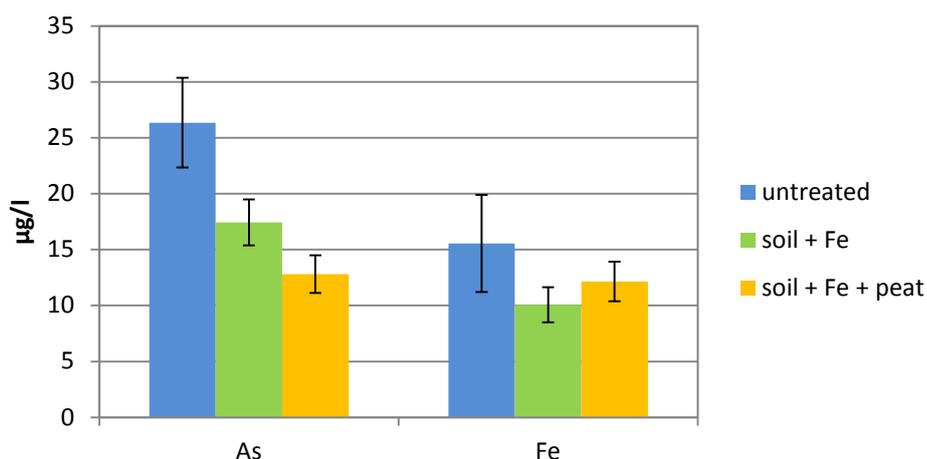


Figure 12. As and Fe concentration in soil pore water samples collected at the end of the phytotoxicity test. The error bars represent standard deviations of means, $n=3$.

4.5 Bioaccessibility

Comparison between the bioaccessible As concentration of untreated and treated soils is presented in Figure 13. The As bioaccessibility decreased in both treated soils, by 3% in the Fe^0 -treated soil and by 23% in the Fe^0 -peat treated soil compared to untreated soil (Fig. 13).

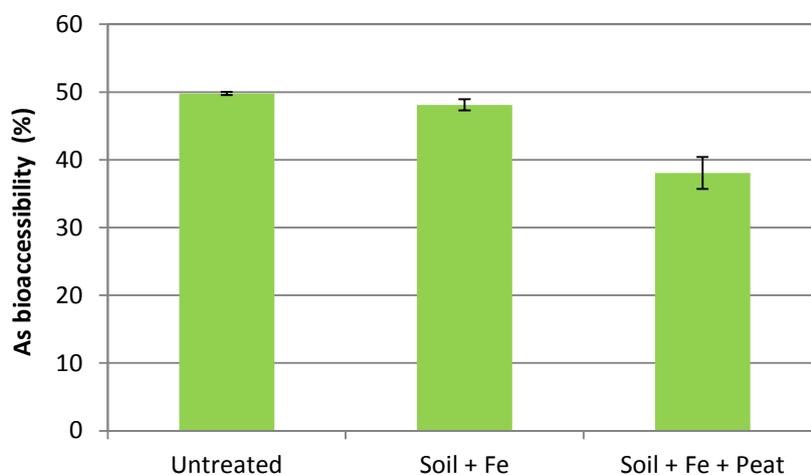


Figure 13. Bioaccessible As fraction measured in untreated and treated soils as percent of the total As concentration. The error bars represent standard deviations of means, $n=3$.

The bioavailability was calculated using the linear regression model. The obtained values are shown in Figure 14. The calculated bioavailable As fraction (%) was by 2.5% - 3.5% larger than the measured bioaccessible fraction.

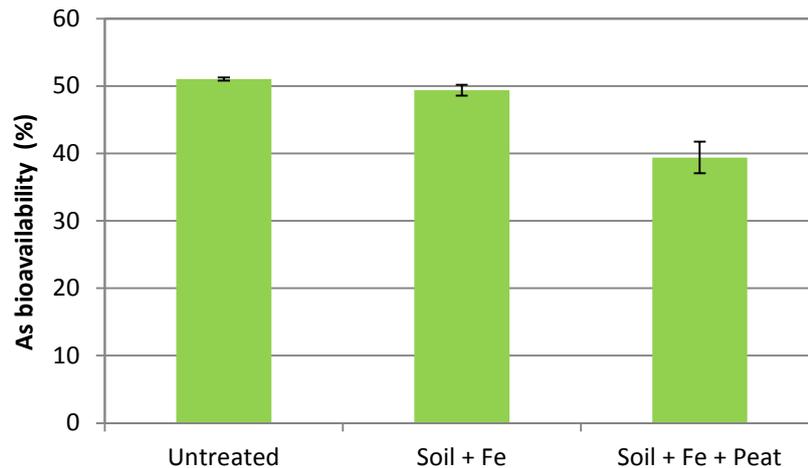


Figure 14. The calculated bioavailable As fraction in untreated and treated soils as percent of the total As concentration. The error bars represent standard deviations of means, $n=3$.

5 DISCUSSION

The aim of the stabilization of contaminated soil is to reduce the contaminant availability to leaching and plant uptake, as well as to decrease the contaminant bioaccessibility to humans. By this, the risk of contaminated soil for the environment and human health can be reduced. Stabilization of contaminated soil should be followed by ecosystem recovery and re-vegetation of the area, aiming to reduce the risk for the soil erosion by wind and surface runoff (Geebelen et al., 2003). The concentration of contaminants in plants is one of the significant exposure pathways for human health. It represents the step through which the contaminants enter into the food chain, but plants themselves can also be considered as a target.

The combination of Fe^0 and peat improved the soil quality by increasing soil water holding capacity, decreasing dissolved As in soil pore water, providing with the best results for all the morphological plant parameters and decreasing As uptake by plant shoots and roots. Lower plant uptake of As is consistent with the decreased concentration of the exchangeable As in the Fe^0 -peat treated soil. Furthermore, a significantly decreased As bioaccessibility and bioavailability in Fe^0 -peat treated soil indicates reduced risks to human health in case of a direct ingestion of soil particles.

The soil treated only with Fe^0 did not show any significant improvement of morphological plant parameters and was less efficient in decreasing As availability and bioaccessibility than Fe^0 combination with peat. Soil amendment with Fe^0 showed even increased As leaching in field. Such behavior was reported earlier (Kumpiene et al., 2013) and the suggested explanation was the higher susceptibility of newly formed Fe oxyhydroxides from oxidation of Fe^0 to dissolution at slightly reduced soil conditions. Arsenic that is bound to colloidal Fe is then leach from the soil along with Fe.

This study shows that soil amended with a combination of Fe^0 and peat can be effective even in a 2 m thick soil layer, but only in a short term. Decreased soil density by the addition of Fe^0 -peat seems to favor air penetration through the soil profile during some time. However, the As concentration in leachate increased over time, most likely due to the gradual establishment of

the reduced conditions in the deeper soil layers. Water saturation of soil and development of low redox has been shown to substantially increase As mobility in Fe-treated soils (Maurice et al., 2007, Kumpiene et al., 2009, 2013). In this study, the leachate was collected below the whole soil layer and the As mobility was affected by the redox conditions occurring along the entire soil profile.

At the end of the first sampling season none of the samples exceeded the As concentration limit for drinking water of 0.01 mg/L (WHO, 2010). The leachate, however, needs to be monitored for a longer time in order to determine whether the As immobilization in soil will be effective during an extended time duration.

6 CONCLUSION

This study demonstrated that the stabilization of As-contaminated soil with Fe⁰ in combination with peat can effectively reduce As phytotoxicity, bioaccessibility and As accumulation in plant shoots and roots. The risks connected to the As spreading to the environment through uptake by plants and through the direct ingestion of contaminated soil have substantially decreased due to this soil treatment. The bioavailable As fraction was only a half of the total As concentration in soil.

Using Fe⁰ amendment alone, the positive impact on the measured indicators was considerably smaller or not significant.

The field study of using the stabilized soil as a landfill top cover shows, however, that this method might be restricted to a thin soil layer. That is, the As immobilization is efficient only in the oxidizing soil environment. Thick soil layers increase the risk for development of low redox conditions in soil profile and consequent mobilization of As. Addition of iron alone in such case can even increase the As mobilization as shown by the field observations.

Applying chemical immobilization of As in soil, the risks to the environment and human health can be substantially reduced, but it is crucial to maintain the soil layer exposed to air in order for the method to maintain providing positive results.

7 OUTLOOK

Further research on long-term and large-scale applicability of stabilization is needed to investigate the occurrence of anaerobic conditions, and the suitability of Fe⁰ combined with others ameliorants for As immobilization. It needs to be assessed at which depth changes in redox condition occur, evaluating the As concentration in pore water sampled at different depths.

8 ABBREVIATIONS

WHO	World health organization
Fe ⁰	Zerovalent Iron
CCA	Chromated copper arsenate (wood impregnation chemical)
BS	Blasting Sand
EC	Electrical conductivity
TS	Total solids
VS	Volatile solids
WHC	Water holding capacity
ICP-OES	Inductively coupled plasma optical emission spectroscopy
SD	Standard deviation

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10 APPENDIX I: LITERATURE REVIEW

10.1 Introduction

The arsenic (As) contamination is a widespread problem and it is a high environmental and toxicological concern. The European Commission classified soil contamination as a priority for further investigation and collection of policy-relevant data at Europe scale. The number of potential contaminated sites in Europe is assessed at 2.5 million, and there are *ca* 342 000 sites in which the contamination has been verified and it is already confirmed that they represent a risk to human, water and ecosystem (Panagos et al., 2013). 35% of the sites are contaminated with heavy metals and metalloids. The management of contaminated sites is estimated to cost around 6 billion Euros per year (Panagos et al., 2013). The EPA has classified As as a Class A human carcinogen. Ingestion of inorganic As can result in both cancer and non-cancer health effects (NRC, 1999). Chronic exposure to low arsenic levels (less than 0.050 mg/L) has been linked to health complications, including cancer of the skin, kidney, lung, and bladder, as well as skin diseases and neurological and cardiovascular system conditions (US EPA, 2000).

The natural content of As in soil is *ca* 5-6 mg kg⁻¹, depending on the type of soil considered (Matera and Le Hecho, 2001; Miretzky and Cirelli, 2010).

The main source of As contamination in soil may be parent rock from the erosion of natural deposit, and anthropogenic activities as mining, smelting of sulfide ores, use of agricultural pesticides, timber and wood preservation and disposal of industrial waste (Miretzky and Cirelli, 2010; Stilwell and Gorny, 1996).

Arsenic is present in several minerals: arsenopyrite (FeAsS) the most abundant, but other sulfide minerals, phosphate minerals and oxide minerals are also common (Garelick et al., 2008).

Chromate copper arsenate (CCA) is a wood preservative that has been used for over 60 years (Nico et al. 2004). Lately the use of CCA is no longer accepted for wood utilized in residential area in USA, Canada, Europe and Australia. The composition of CCA slightly varies from fresh to aged wood, on the average the compound concentrations are; 47.4% CrO₃, 18.5% CuO and 34% As₂O₅ (Nico et al., 2004; Dobran and Zagury, 2006).

10.2 Arsenic chemistry

10.2.1 General information

Arsenic has the outer electron configuration of s^2p^3 and belongs to the subgroup V of the periodic table. Arsenic occurs in environmental system at oxidation state (III) and (V) as arsenite and arsenate. Since the mobility, solubility, bioavailability and toxicity of As is strongly influenced by its oxidation state, it is fundamental to study the speciation of arsenic to better understand the behavior of As in soil (Masscheleyn et al., 1991). In general As is more mobile under alkaline and more saline conditions (Matera and Le Hecho, 2001).

Arsenic occurs naturally in the environment deriving from weathering of soil parent materials, as arsenopyrite (*FeAsS*), orpiment (*As₂S₃*), realgar (*AsS*) and also As metal. Variation in

background concentration is function of the presence of parent material and the mineralization (Wilson et al., 2010).

Soil is a complex system, the main factors influencing As chemistry in soils are soil solution chemistry, solid phase formation, adsorption and desorption, effect of redox conditions, biological transformation, volatilization and cycling of As in soil (Sadiq, 1997). Arsenic becomes a health issue when is in aqueous phase rather than solid phase. The processes involve in this transition are mainly adsorption/desorption, precipitation/co-precipitation and changing from aerobic to anaerobic condition (Fendorf et al., 2010). As can be strongly retained in soil, and the extent of retention influence its bioavailability and mobility. Understanding the geochemical As cycling leads to a better assessment the risks associated to different targets (Wilson et al., 2010).

The World Health Organisation has set the Acceptable Daily Intake(ADI) for As at $2.1 \mu\text{g kg}^{-1}\text{day}^{-1}$ per kg of body weight (WHO, 2011), while the limit of As concentration in drinking water is 0.01 mg L^{-1} .

10.2.2 Conditions affecting arsenic valence and speciation

Arsenic can be found in organic and inorganic forms. As oxidation state is largely influence by pH, redox potential and environment reactions in soil system controlled, among others, by the presence of iron, sulfur and calcium ions, and microbial activity (Sadiq, 1997; U.S. EPA, 2002).

The speciation of As in soil is essential to understand the behavior of arsenic compounds. In general As(V) dominate in oxidizing conditions, while As(III) prevail in reducing environment and are the main forms of inorganic As. In soil they coexist due to the variation of environmental condition and due to the slow transition rate from one species to the other. In general As(V) is less biologically toxic (Mok and Wai, 1990), less soluble and mobile than As(III). Moreover, As(V) sorbs more strongly than As(III).

Within an environmental acceptable pH range as $2 < \text{pH} < 9$, the predominant arsenic species are: H_3AsO_4 for As(III), H_2AsO_4^- and HAsO_4^{2-} for As(V). That means arsenic compound can be neutral or negatively charged based on the As oxidation state (Matera and Le Hecho, 2001).

The most widespread species of organic forms are methylated ones, though organoarsenical complexes are a minor fraction of total dissolve As in soil solution (Sadiq, 1997). The order of toxicity is given as: organoarsenicals(methylated species) < arsenates (As(V)) < arsenites (As(III)) (Wilson et al., 2010).

The combined values of pH and redox potential affect the As forms found in soil. As shown in fig. 1, under oxidizing condition the predominant species is As(V) with a charge that depend on pH value, but mainly negatively charged at common environmental conditions. While under moderately reducing conditions, As(III) is the predominant species, and it is present as uncharged form (Sadiq, 1997). In the graph the redox couple $\text{Fe}(\text{OH})_3/\text{Fe}(\text{II})$ and $\text{MnOOH}/\text{Mn}(\text{II})$ are marked, as both are important in regulating As mobility. Since both iron and manganese oxides and hydroxides exist in several degrees of crystallinity, those boundaries may vary among different soils (Masscheleyn et al., 1991).

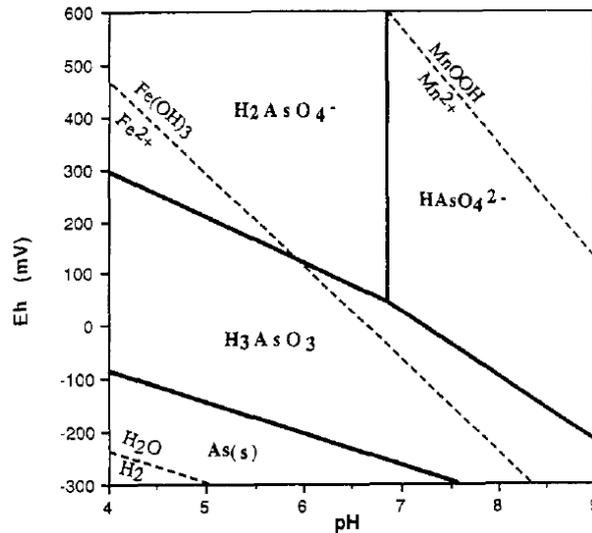


Figure 1: Eh – pH diagram for As - H_2O system (Masscheleyn et al., 1991)

In environmental biogeochemical system the speciation is not at equilibrium, then the analysis of pH and Eh influence is not as sharp as shown in this type of diagram (Mok and Wai, 1990). In this context the total As concentration is not a good indicator of mobility and toxicity of the contamination. Sequential chemical soil extractions can be used as a tool to assess different As forms present in soil (Ascar et al. 2008).

10.2.3 Processes affecting As mobility

10.2.3.1 Adsorption/desorption

These processes affect the As solubility and thus As mobility in the environment. The main compounds involved in the As adsorption are clay, carbonaceous materials, oxides of aluminum, iron and manganese (Sadiq, 1997; U.S. EPA, 2002). The main factors affecting the adsorption are affinity of As for the adsorbent, temperature at which the process occurs and presence of competitive compounds for the available sites (Carabante et al., 2009). Furthermore the partitioning of As onto soil solids depend on its oxidation state: As(V) can strongly bind to mineral and sediment in soil, while As(III) retention is related to specific soil condition (Fendorf et al., 2010).

10.2.3.2 Precipitation/co-precipitation

Direct precipitation of As solid phase can occur in contaminated soil, but more common is the precipitation of soil colloids after As adsorption (Sadiq, 1997). Adsorption and precipitation of As with Ca phases in neutral to alkaline calcareous soils possible As retention mechanism (Matera and Le Hecho, 2001). Both As(V) and As(III) may precipitate in soil, but the constituents inducing precipitation change. As(V), similar to phosphate, tends to precipitate with hard, multivalent cations such as aluminum and ferric-iron under acidic conditions and calcium and magnesium under alkaline conditions; arsenate may also replace SO_4^{2-} or, in

particular, PO_4^{2-} in minerals due to similar size and charge characteristics (Smedley and Kinniburgh, 2002).

10.2.3.3 Aerobic/anaerobic condition

The greatest probability of As release in soil is when the transition from aerobic to anaerobic conditions occur. Under aerobic conditions (100-200 mV), the prevalent species is arsenate, but in saturated soil, e.g. due to extended flooding periods, it may reach reducing condition ($E_h < 100$ mV), and the predominant species is arsenite (Ascar et al. 2008). Under saturated conditions, the consumption of O_2 by aerobic microbes combined with the decrease of available O_2 , induce anaerobic bacteria to utilize alternative electron acceptors. In this state As may be transformed from arsenate to arsenite through reduction or through mineralogical transformation of the soil matrix, such as reductive dissolution of ferric oxides and hydroxides (U.S. EPA, 2002).

10.3 Remediation techniques for arsenic contaminated soil

10.3.1 Commonly applied remediation methods

Remediation techniques used to treat contaminated soil can be classified in three main categories: soil treatment *in situ*, soil treatment *ex situ* and containment through landfilling. In the last years, the main focus was laid on how to enhance the first two options, try to reduce the landfilling due to economic and environmental reasons. The main ways to treat soil, both *in situ* and *ex situ*, are by physical-chemical or thermal treatments processes. Biological treatment of soil contaminated with trace elements is very limited due to the indestructible nature of the elements. The biological treatment is restricted to biologically induced changes in element speciation.

The advantage of *in situ* treatment with respect to the *ex situ* one is to avoid the excavation and transport of the material, and so the costs connected with these operations. For *in situ* applications, it is important to control the by-products of the applied process. The elements may be mobilized downward, or become more soluble and toxic. *In situ* methods generally require longer time periods and the uniformity of the treatment is uncertain due to the heterogeneity of the soil and thus the effectiveness of the process is more difficult to monitor (FRTR, 2002).

The most commonly used treatment technologies for As contaminated soil include stabilization (through solidification and stabilization (S/S), or chemical immobilization), acid extraction, excavation and off-site disposal. Excavation and landfilling might become very costly in cases where large areas of moderately contaminated soil need to be treated (Yukselen and Alpaslan, 2001). But even if contaminated soil ends up in a landfill, some pretreatments could be required in order to meet land disposal requirements (FRTR, 2002).

Soil washing is an *ex situ* technology, but it can also be used on site after soil excavation, that exploit the behavior of some contaminants to preferentially adsorb onto the fines fraction of soil. The pollutants tend to bind to clay and silt particles rather than sand and gravel. Physical methods are applied to separate fine particles from the larger ones, because they are mainly

attached through physical bonds. The separation of larger from finer particles leads to reduced volume of soil, but with higher contaminant concentration, that will need further treatment. After the first screening, the soil is washed in a solution of water with or without chemicals. The solution used to wash the soil will need further treatment, but can be reused several times. This process does not destroy the contaminant, so the overall amount of pollutant will be concentrate in the fine particles and in the washing solution, while the contaminant concentration in the remaining soil is reduced. In such case, stabilization would be the most suitable method to reduce As mobility and consequent environmental risks. The method is gaining more attention and is described in more detail in the following chapters.

Besides the above mentioned methods there are other techniques that have been studied, and that could be applied in certain cases. Those techniques include soil flushing, electrokinetics and phytoremediation.

Soil flushing - This technique is an *in situ* treatment where an extractant solution is injected in the soil. The solution percolates through the contaminated area and carries the pollutant up to the well where the fluid is pumped up and collected. The contaminant-bearing fluid can be water with or without further additives. This technique is applicable to soils with relatively high hydraulic conductivity (U.S. EPA, 2002).

Electrokinetics - This treatment exploit the ability of charged species to migrate due to a low-density current between two electrodes that is applied to the contaminated area. The electrical field between the electrodes mobilizes the charged particles, but also induces a water flow from the anode to the cathode that can carry on non-charged compound. This phenomenon is called electroosmosis. The contaminant is collected at the electrodes, and then it can be remove by using electroplanting or electroposition, precipitation or co-precipitation, adsorption, complexing with ion exchange resins or by pumping the fluid surrounding the electrode (Virkutyte et al., 2002).

The main mechanism of As extraction by electrokinetics is desorption of As species that were attached to the surface soil. The efficiency of the treatment depends on several factors, such as soil pH, As speciation and soil permeability. Contrary soil flushing, efficiency of electrokinetics is higher in soil with low permeability (Kim et al, 2005).

Phytoremediation - This is an *in situ* remediation method exploiting the capability of some species of plants to uptake, concentrate and to detoxify pollutants. The sequestration is done by the plant itself (Peng et al., 2009). The applicability of the method is limited to soil with shallow contamination within the depth reachable by plant roots. The main advantages of this technique are the low capital and operation costs, and it needs only standard agricultural equipment. Moreover, it is a less destructive treatment that protects the soil from erosion and dusting (Mench et al., 2005). The main disadvantages are the long treatment time required and the higher availability of the pollutant to animals due to the translocation to the above ground plant parts (U.S. EPA, 2002).

10.3.2 Stabilization

Stabilization techniques aim to rendering the metal(loid) fractions less available and thus decreasing the risks associated with their leaching, ecotoxicity, plant uptake and human exposure. The contaminant concentration will be the same after the remediation, but it is in less toxic and more inert forms. For this reason, further studies are required about the long term stability of the immobilized compound (Komarek et al., 2013). This is related to the stability of new As compounds formed over time, which in turn depends on many factors, such as site characteristics, particle crystallinity, grain size distribution and presence of other compounds (Miretzky and Cirelli, 2010), as well as the soil saturation degree (Kumpiene et al., 2009).

The contaminant fractionation, or distribution between various soil fractions, becomes one of key factors in As mobility. The target soil fractions include the mobile, soluble, bioavailable for biota or bioaccessible for humans (Kumpiene et al., 2008).

The reduction of the leachability can be achieved through physical and chemical processes. The stabilization/solidification process refers mainly to physical binding of the contaminant in the soil matrix. The chemical stabilization is related to a chemical reactions that aim to decrease the mobility of As and transform it to less toxic forms by adding and mixing different amendments to the contaminated soil. This technique can be applied *in situ* or *ex situ* (Mulligan et al., 2001; Yukselen and Alpaslan, 2001). It can be chosen as final or interim treatment, combined with other techniques or used on its own. It can be applied to several target contaminants, but mainly inorganic ones (FRTR, 2002).

The stabilization can involve several processes as adsorption onto mineral surface, formation of stable complexes with organic ligands, ion exchange, precipitation as salt and co-precipitation with metal oxides (Kumpiene et al, 2008).

The main advantage of this remediation method is that it is a cost-effective treatment and it is considered as non-disruptive to natural pedagogical and hydrological conditions (Peng et al., 2009).

Several amendments have been studied to reduce As contamination in soils, such as Al and Mn oxides, clays and organic matter, but the most extensively examined are oxides of Fe or combinations with them.

10.3.2.1 Aluminum oxides

The information about application of Al compound as amendment for As remediation is scarce, in spite of it showed significant adsorption capability. The maximum adsorption of As(V) on amorphous and crystalline Al oxides occurs within a pH range from 3 to 4, and it decreases with increasing pH (Moore et al., 2000). Although synthetic amorphous Al oxide have a larger specific surface area than some Fe oxides, they show a similar immobilization potential to Fe oxides when applied as amendment to a contaminated soil (Komarek et al.,2013).

10.3.2.2 Manganese oxides

Although Mn oxides have shown to be important trace element scavengers, they are not so many studies available in literature on their utilization as amendment for contaminated soil

(Komárek et al, 2013). Applicability of Mn oxides as ameliorant is limited by the fact that they strongly affect the speciation of redox-sensitive contaminants by increasing the mobility and toxicity of certain elements, e.g. chromium. So its applicability is strongly related to the pollutants present in soil (Manning et al., 2002). Considering soil contaminated with only As, the use of Mn oxides can significantly reduce As mobility and toxicity (Kumpiene et al., 2008).

10.3.2.3 Fly ashes

Fly ashes are a pozzolanic material generated as residual product of combustion. Depending upon the source and composition of the coal being burned, the components of fly ash vary considerably, but all fly ash includes substantial amounts of silicon dioxide SiO_2 (both amorphous and crystalline) and calcium oxide CaO. Ashes have been studied as potential amendment for As contaminated soil. Since the final results are strongly dependent on both the nature of the fly ash and the type of soil, the conclusions cannot be generalized. A detailed study required to provide a better evaluation of the treatment effectiveness. The application of fly ashes can lead to a significant increase in soil pH, which can have varying effect on As. Moon and Dermatas (2007) have studied fly ashes produced by coal burning at electric utility facilities. The experiment have shown a significant immobilization of As, that was supposed to be related to the alkalinity of fly ash leading to the formation of insoluble Ca-As precipitates.

10.3.2.4 Cement and Lime

Cement and lime have been studied as amendments due to their high sorption capacity and potential to form pozzolanic reaction products (Dermatas et al., 2004). Dutrè et al. (1998) have treated As contaminated soil with cement, lime and a combination of them. The solidification/stabilization treatments have shown a decrease in the As leaching, but it was also demonstrated to strong increase of pH and Ca concentration in the leachate. This experiment demonstrated that cement was a more effective amendment than lime. Dutrè and Vandecasteele (1996) have also shown that cement and lime used as ameliorants decreased the As leaching, but in this case lime was more effective than cement. The main mechanism was reported to be the formation of slightly soluble compound $CaHAsO_3$.

10.3.2.5 Iron amendments

Although several amendments have been studied to remediate As contaminated soils to reduce As mobility and toxicity, iron minerals and iron industrial by-products show great potential for *in situ* soil remediation (Miretzky and Cirelli, 2010).

Due to their important sorption properties, Fe oxides have been extensively studied as potential stabilization amendments in soils contaminated with metals and As. Their application, either directly or indirectly through the application of their precursors (e.g., iron grit or Fe sulfates) is supposed to decrease mobile, bioavailable and bioaccessible fractions of As (Komárek, 2013).

The mechanism involved in the adsorption of As species into iron oxides, is the replacement of OH_2 and OH^- for the anionic As species in the coordinate spheres of surface structural Fe

atoms. The adsorption of As(V) and As(III) anions (AsO_3^{-4} and AsO_3^{-3}) on iron hydroxides depends also on pH: the oxides are positively charged for pH lower than 6, while above pH 8 the iron oxide surface is negatively charged. This mechanism and how it affects the As adsorption, can be easily represent as follow:

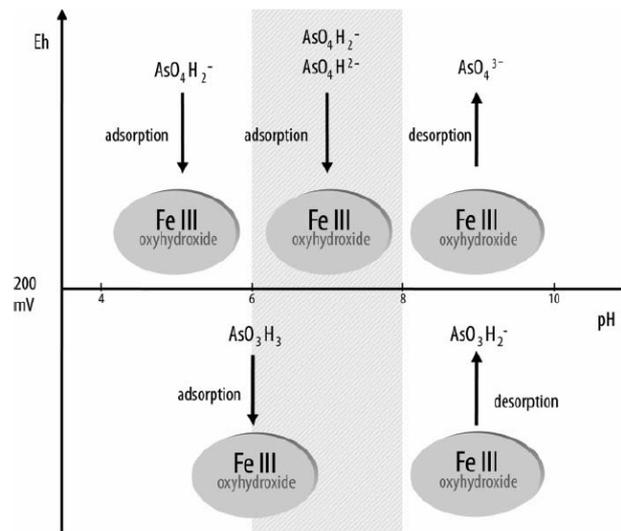


Figure 2: Effect of pH and Eh on arsenate and arsenite adsorption onto Fe oxides (Miretzky and Cirelli, 2010)

Arsenic can also co-precipitate with Fe(III) ions forming amorphous iron arsenates and insoluble secondary oxidation minerals (Fendorf et al., 2010).

The Fe amendment can be applied as Fe oxide, Fe sulfates or Fe^0 . Generally the efficiency of As retention increases with greater amount of Fe oxides. On the other hand Mench (2000) showed that applying a rate greater than 1% could negatively affect vegetation growth.

Fe sulfates have been studied as feasible amendment because it is a commercially available product. It undergoes processes that lead to the formation of Fe oxides as follow:



Using this amendment, however, leads to the acidification of the soil, which negatively affect the mobility other metal contaminants (e.g. Cu, Cr). For this reason, the application of Fe sulphates was studied in combination with lime that neutralizes the soil pH (Moore, 2000; Warren, 2003).

Fe^0 is a largely available material that contains several times more Fe per unit weight than the most common Fe salts. Moreover its oxidation does not lead to strong fluctuation of pH in soil (Miretzky and Cirelli, 2010). This amendment showed good result in immobilizing As in soil when oxidizing condition occurs. Different by-product from steel industry were studied as steel abrasive, oxygen scarfing granulate, blasting sand, and Fe grit. In these studies showed the

capability of these amendments to lower the As concentration in pore water (Mench et al., 2006; Maurice et al., 2007; Lidelöw et al., 2007; Kumpiene et al., 2009). In reducing conditions, an adverse effect on As mobility occurs (Kumpiene et al., 2009, Kumpiene et al., 2013). The principal concern is that changing redox condition can significantly change the solubility of arsenic (Miretzky and Cirelli, 2010). Also, changes from poorly crystalline Fe forms to more crystalline Fe oxides can occur over time, which influences the availability of adsorption sites: the higher the Fe crystallization degree, the lower the density of adsorption sites (Miretzky and Cirelli, 2010). Aging of Fe oxides might increase the risk of As release. Further studies, however, are needed to substantiate this hypothesis.

10.4 Bioaccessibility

The aim of the stabilization technique is to lower the risk related to a contaminated site, and the target of major concern is the human being. There are several exposure pathways for human: ingestion, dermal contact, inhalation or dietary consumption, just to mention some of them. The oral intake is one of the most important, due to the exposure of children to incidental ingestion of small soil particles. In particular, particles with $\varnothing < 250 \mu\text{m}$ are evaluated in all the procedures proposed. Two fundamental definitions need to be pointed out:

- *bioaccessible fraction* is the contaminant amount available for absorption by the internal human body system, so the compounds soluble in gastric or gastrointestinal solution.
- *bioavailable fraction* is the amount of contaminant that is actually absorbed by humans or animals. In *in vivo* test are applied to measure the As concentration in blood plasma and urine, or accumulation in organs, such as kidney, liver and bones.

10.4.1 Regulations

So far the established regulations to consider the bioavailable amount equal to the total As concentration. Generally, the bioavailable quantity differs from the total concentration, because the availability of a contaminant for the uptake by human body is related to the free element activity rather than the overall content, and only the bioavailable fraction is potentially toxic to human.

Considering the total concentration to be bioavailable, the risk might be overestimated. The only adjustment accepted by the regulation is through *in vivo* bioassessability tests. In particular, juvenile swine have been suggested because of its digestive mechanism close to that of humans.

In vivo assay is a long and expensive assessment, and animals are used by definition. A cost and time effective alternative is *in vitro* assay, and lately several tests have been proposed. Since they should substitute the *in vivo* ones, those tests have to be validated, showing a good predictive ability of animal As bioavailability.

In vitro test has already been established for bioaccessibility of lead in risk assessment of contaminated soil (US EPA method 9200), while for As methods are still being validated.

10.4.2 Methods

Several methods have been proposed to estimate As bioaccessibility to humans, but it is possible to subdivide them in two main groups: physiologically based test and glycine-buffered method (Musier et al., 2010).

The first method proposed was PBET, physically based extraction test (Ruby, 1996). This method simulates the gastric or gastrointestinal conditions of human digestion system to assess the bioaccessibility of As. Several factors are monitored, solution composition, pH, anaerobic condition, mixing mechanism, transition time, temperature. The digestive system is so complicated that actually is not possible to recreate the same environment. The studies show a strong results dependency on stomach pH, but also on L/S ratio applied, in particular for glycine-buffer tests.

The digestion method has been simplified. One of the most commonly applied methods was proposed by Basta et al. (2007), so called IVG-OSU, in vitro gastrointestinal Ohio State University. Juhasz et al. (2009), evaluated the performance of four different assays. Those methods were validated, comparing the in vitro and in vivo results, and linear regression models were proposed for each test. This study shows the higher effectiveness of SBRC and IVG method over PBET.

So far all the studies present procedures for both gastric and gastrointestinal tract, but it is demonstrated that the gastric phase is the worst case scenario for As bioaccessibility (Basta et al., 2007; Juhasz et al., 2009; Rodriguez and Basta, 1999). In particular in presence of iron, the extension to gastrointestinal method shows a decrease of As bioaccessibility due to precipitation of amorphous Fe, dissolved at acid pH during the gastric phase. Consequent availability of adsorption sites occurs following the same mechanism as during the remediation process (Juhasz et al., 2009).

The factors of the main bioaccessibility methods are summarized in Table 6.

Table 6: Main factors of in vitro bioaccessibility methods (Juhasz et al., 2009)

Method/phase	Composition (g L^{-1})	pH	L/S ratio	Extraction time (h)
SBRC				
gastric	30.03 of glycine	1.5	100	1
intestinal	1.75 g of bile, 0.5 g of pancreatin	7.0	100	4
IVG				
gastric	10 g of pepsin, 8.77 g of NaCl	1.8	150	1
intestinal	3.5 g of bile, 0.35 g of pancreatin	5.5	150	1
PBET				
gastric	1.25 g of pepsin, 0.5 g of sodium citrate, 420 μL of lactic acid, 500 μL of acetic acid	2.5	100	1
intestinal	1.75 g of bile, 0.5 g of pancreatin	7.0	100	4

SBRC = Solubility Bioaccessibility Research Consortium (Kelley et al., 2002); IVG = In Vitro Gastrointestinal, Ohio State University (Rodriguez and Basta, 1999; Basta et al., 2007); PBET = Physiologically Based Extraction Test (Ruby et al., 1996)

10.5 References

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