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LONG-TERM stability of arsenic in iron amended contaminated soil[☆]

Jurate Kumpiene^{a,*}, Ivan Carabante^a, Alfreda Kasiuliene^a, Annabelle Austruy^{b,d}, Michel Mench^c

^a Waste Science and Technology, Luleå University of Technology, 97817, Luleå, Sweden

^b PIAF - Laboratoire de Physique et Physiologie Intégratives de l'Arbre Fruitier et Forestier, INRAE, Université Clermont-Auvergne - Clermont-Ferrand, France

^c Univ. Bordeaux, INRAE, BIOGECO, Bât. B2, allée Geoffroy St-Hilaire, CS50023, F-33615, Pessac cedex, France

^d Institut Ecocitoyen pour la Connaissance des Pollutions - Centre de Vie La Fossette, RD 268, 13270, Fos-sur-Mer, France



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ABSTRACT

This study aimed at elucidating the long-term efficiency of soil remediation where chemical stabilization of arsenic (As) contaminated soil using zerovalent iron (Fe) amendments was applied. A combination of chemical extraction and extended X-Ray absorption fine structure (EXAFS) spectroscopy technique was applied on soils collected from five laboratory and field experiments in Sweden and France. All soils were treated with 1 wt% of zerovalent Fe grit 2–15 years prior to the sampling. The results indicate that all studied soils, despite the elapsed time since their amendment with Fe grit, had substantial amounts of ferrihydrite and/or lepidocrocite. These metastable and the most reactive Fe (oxyhydr)oxides (mainly ferrihydrite) were still present in substantial amounts even in the soil that was treated 15 years prior to the sampling and contributed most to the As immobilisation in the amended soils. This increases confidence in the long-term efficiency of As immobilisation using zerovalent Fe amendments. Both applied methods, sequential extraction and EXAFS, were in line for most of the samples in terms of their ability to highlight As immobilisation by poorly crystalline Fe phases.

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Soil amendment with zerovalent iron was still effective for arsenic immobilisation 15 years after the soil treatment.

1. Introduction

Nowadays the established concept that bioavailability of contaminants, and not their total soil concentrations, is one of the main environmental risk-defining factors has led to a broader application of in situ stabilization technique for remediating metal(loid)-contaminated soils. Stabilization of metal(loid)s (also so called trace elements, TE) and hence reduction of their mobility and bioavailability, can be achieved by changing TE chemical state using soil amendments that can promote TE precipitation, sorption, and complexation as well as the build-up of new minerals (Mench et al., 2006; Kumpiene et al., 2019). The formation of insoluble phases leads to a reduction of metal(loid) mobility, bioavailability, and thus pollutant linkages in line with risks to the environment and to

human health.

There are numerous successful studies published on TE immobilisation performed in laboratory and full scale (e.g. reviews by Vangronsveld et al., 2009; Mench et al., 2010; Austruy, 2012; Kumpiene et al., 2019). Iron (Fe) is often considered as a suitable soil amendment. The importance of Fe oxides for TE geochemistry is widely acknowledged and is a potential cornerstone for mitigating environmental and health risks caused by metal(loid)-contaminated soils and groundwater (e.g. Schwertmann and Cornell, 2000). Numerous studies (e.g. Kumpiene et al., 2006, 2009; Komárek et al., 2013) show that leaching of TE, especially of As, in Fe amended soil can be reduced by as much as 99%. Nevertheless, there is still some contention against the widespread acceptance of TE immobilisation as a soil remediation method, which lies on uncertainties on the long-term stability of the immobilized contaminants. One key question to address is therefore whether in situ TE stabilization is effective on a long-term or not. Two scenarios can be expected when using zerovalent (metallic) Fe for TE immobilisation: (1) corrosion of metallic Fe added to soils produces Fe oxyhydroxides, which react with dissolved TE (e.g. As, Cu, Zn) and reduce their mobility (e.g. Tiberg et al., 2016). Usually the main corrosion product is ferrihydrite, a

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* Corresponding author.

E-mail address: jurate.kumpiene@ltu.se (J. Kumpiene).

metastable oxyhydroxides, which will slowly transform into more crystalline Fe oxides (e.g. goethite, hematite) that have lower specific surface area. This might cause a release of sorbed TE and increase their leaching over time; or (2) various sorbates (e.g. silicates, phosphates, and organic compounds) can influence Fe crystallization by passivating Fe oxide surfaces (Schwertmann and Cornell, 2000). This might retard or even block ferrihydrite transformation in soils by out-competing sorption reactions involving TE. Sorbed TE themselves can also inhibit further crystallization and dissolution of Fe-(hydr)oxide minerals (Paige et al., 1997; Melitas et al., 2002), by this maintaining TE immobilisation efficiency over prolonged time periods.

Hence, to assess potential TE release and leaching in Fe-stabilized soils, an accurate description of newly formed mineral phases as well as their changes over time is needed. Commonly used methods to quantify the relative abundance of Fe oxides in soils according to their crystallinity are selective dissolutions and extractions (Dold, 2003). As with all chemical extraction methods, TE fractions are operationally defined. This means that TE fractions are bulked together depending on their solubility in the selected chemicals and different Fe oxides are assigned to the same fraction. For example, crystalline Fe oxide fraction can contain goethite, hematite and magnetite, which have significantly different sorptive properties. For more accurately determining solid phase fractionation and contaminant binding mechanisms, sample analysis using molecular-level analytical methods is needed (Walker et al., 2009). Synchrotron based X-ray absorption spectroscopy (XAS) is gaining popularity in environmental studies and offers a possibility for analyzing the relative abundance of Fe phases in bulk soil (Arçon et al., 2005; Fan et al., 2014). Other than qualitative information on the presence of Fe oxides, a quantification of their abundance is possible, making this approach an ideal complement to chemical extractions or other soil analysis methods.

This study aimed at elucidating the long-term efficiency of soil remediation where chemical stabilization of As contaminated soil using Fe amendments was applied. To reach this aim, a combination of chemical extractions and extended X-Ray absorption fine structure (EXAFS) spectroscopy technique was applied on soils collected from laboratory and field experiments in Sweden and France.

2. Materials and methods

2.1. Materials

Soil samples were collected from soil stabilization experiments implemented at laboratory, semi-field (outdoor lysimeters) and field sites in Sweden and France. Brief descriptions of each site and references to the more detailed descriptions of the experimental conditions are given in Table 1. All sites were treated with 1 wt% of zerovalent iron grit (composed of ca 97% of Fe⁰ and some impurities) 2–15 years prior to the sampling.

Three soils (Auzon, Robertsfors and Forsmo) had pH below neutral (pH 5.5–6.0) and two soils (La Combe du Saut and Reppel) were slightly alkaline (pH 7.7–8.2) (Table 1). Auzon soil had the highest amount of organic matter (11–14%), followed by La Combe du Saut (4.4–4.9%), while the remaining three soils had relatively low amount of organic matter (1.2–2.6%).

All soils were highly contaminated with As (310–8360 mg/kg), but the sources of contamination differed. La Combe du Saut is a former site of mining and processing of arsenopyrite, Reppel site is affected by secondary smelting of As, Auzon site was used for manufacturing and storage of pesticides, and both sites in Sweden (Robertsfors and Forsmo) were affected by wood impregnation chemicals (Table 1).

2.2. Methods

2.2.1. Sequential extraction

The detailed procedure of sequential extraction is described in Kumpiene et al. (2012). Briefly, six fractions were extracted as follows: (1) Exchangeable fraction: extracted with 1 M NH₄-acetate at pH 4.5, (2) Poorly crystalline Fe(III)-(oxyhydr)oxide fraction: extracted with 0.2 M NH₄-oxalate at pH 3.0, (3) Crystalline Fe(III) (oxyhydr)oxide fraction: extracted with 0.2 M NH₄-oxalate pH 3.0 at 80 °C, (4) Fe/Mn oxide fraction: extracted with 0.04 M NH₂OH–HCl in 25% (v/v) HO-acetate pH 2 at 96 °C, (5) Organic matter and secondary sulfide fraction: extracted with 35% H₂O₂ at 85 °C, and (6) Residual fraction: extracted with aqua regia (HNO₃:HCl, 1:3 v/v) at 195 °C in a microwave digester (CEM Microwave Sample Preparation System, Model MARS 5). All extracts were filtered through 0.45 mm cellulose acetate syringe filters and stored at 4 °C prior to analyses with ICP-OES (Perkin–Elmer Optima 2000 DV).

2.2.2. EXAFS

Data collection. Extended X-ray absorption fine structure spectroscopy (EXAFS) measurements of Fe were implemented at the wiggler beamline I811 at MAX-lab, Lund University, Sweden. The beamline was equipped with a Si[111] double crystal monochromator, and operated at 1.5 GeV (MAX-II ring) and a maximum current of 250 mA. Iron K-edge EXAFS spectra were collected in fluorescence mode using a Lytle detector. Iron metal foil was used as an energy calibration reference and was run simultaneously with the samples in absorption mode. Higher-order harmonics were reduced by detuning the maximum intensity of the second monochromator crystal by 50%. A Mn filter was used to reduce Fe fluorescence and scattering contributions. Spectra for standard oxides were collected separately at the same beamline. The air-dried samples were mounted on aluminium frame holders using kapton tape and fixed at ca 48° angle to avoid XRD peaks in the scans. All measurements were carried out at ambient-room temperature. Five to ten scans were collected per sample.

Data analysis. The collected XANES data were processed using Athena software (Ravel, 2008) including data normalization based on the Cromer-Lieberman calculations, background removal using the AUTOBK algorithm, alignment and merge of scans. Linear combination fitting (LCF) in k-space between 3 and 12 Å was performed using the same software, showing R factors below 0.01 for all fittings. The following minerals were used for LCF in all spectra analysis (chemical formulas are provided in Table S1): metallic Fe, goethite, hematite, clinocllore, augite, vermiculite, hornblende, biotite, phlogopite, iron(II) sulphide, pyrite, iron oxalate, nontronite (ferrosmeectite), siderite, magnetite and vivianite.

3. Results and discussion

3.1. Distribution of iron in soils

A generic trend occurred in all soil samples: Fe-amended soils had significantly higher concentration of Fe and larger fraction of poorly crystalline Fe oxides (by 6–36%) than the unamended ones (Fig. 1). The fraction of crystalline Fe oxides remained in general unchanged and only in some samples was slightly smaller than in the untreated samples (e.g. for Reppel). These results suggest that zerovalent Fe added to the soils increased the fraction of poorly crystalline Fe oxides, which are the most reactive towards sorption of many trace elements. Although this fraction is considered as metastable and transformation to more crystalline phases is expected over time, it was substantial even in the oldest samples from Reppel treated 15 years before the sampling. It is likely that other

Table 1
Main properties of the studied untreated soils from laboratory and pilot scale field experiments.

	La Combe du Saut (France)		Auzon (France)		Reppel (Belgium/France) ^a	Robertsfors (Sweden)	Forsmo (Sweden)
Source of contamination	Mining and processing of arsenopyrite		Manufacturing and storage of pesticides		As(III)-secondary smelter	Wood impregnation with CCA ^b	Wood impregnation with CCA ^b
Experiment duration, years	8		2		15	8	2
Sub-plots	Zone 1	Zone 2	Plot 1	Plot 2			
Scale of experiment	Field plot, 100 m ²	Field plot, 100 m ²	Field plot, 10 m ²	Field plot, 10 m ²	Outdoor lysimeter, located in Villenave d'Ornon, France 312 kg, 1 m ²	Outdoor lysimeter, located in Luleå, Sweden 100 kg	Laboratory columns, 13 kg
pH (1:2 H ₂ O)	7.7 ± 0.3	8.2 ± 0.0	5.5 ± 0.0	5.9 ± 0.0	7.9 ± 0.1	5.6 ± 0.0	6.0 ± 0.0
EC, µS/cm	110 ± 15	97 ± 5	314 ± 7	212 ± 6	291 ± 4	7.0 ± 1.1	439 ± 26
Redox, mV	198 ± 9	192 ± 8	264 ± 3	248 ± 17	213 ± 15	469 ± 4	278 ± 20
Loss on ignition, %	4.9 ± 0.1	4.4 ± 0.1	11.0 ± 0.2	13.8 ± 0.2	2.6 ± 0.0	1.9 ± 0.0	1.2 ± 0.0
Total organic carbon (TOC), %					7.05	0.15	0.95 ± 0.18
Elements, mg/kg dw ^c							
As	1962	5066	3200	1045	324	8360	310
Fe, %	5.0	6.4	3.4	2.9	0.9	1.8	1.9
References to the experiment descriptions	DIFPOLMINE programme (2006)		Austruy (2012)		Ascher et al. (2009)	Kumpiene (2006)	Kumpiene et al. (2009)

^a Original site is in Belgium, but the soil was transported to France where the experiments were performed.

^b CCA-chromium copper arsenic.

^c Calculated from sequential extraction results as a sum of all fractions.

soil properties, such as high soil pH (i.e. presence of carbonates) and organic matter contributed to the slower crystallization of Fe oxyhydroxides. Nevertheless, this contribution was not obvious as the studied soils had a relatively broad variation of soil properties (Table 1). It is therefore reasonable to assume that metastable Fe species were stabilized mainly by the sorbed trace elements as suggested by e.g. Paige et al. (1997) and Melitas et al. (2002). This means that immobilized As might remain in soil as bound to poorly crystalline Fe oxides over extended periods of time if stable redox conditions prevail.

Fractions of exchangeable Fe and Fe associated with organic matter (OM) were negligible in all samples (Table S2). These fractions were 1% or less of the total soil Fe and only in the Auzon samples the fraction of OM-bound Fe was between 0.5 and 2.8%. The fraction of residual Fe varied in various samples: either increased, decreased or remained unchanged due to soil treatment (Fig. 1).

3.2. Arsenic fractionation in soils

In several cases, amended soil contained higher total soil As, e.g. Robertsfors, Forsmo, and Auzon, compared to unamended soils (Fig. 2). Although it could be argued that soil heterogeneity is the reason for these differences, the more plausible reason is that the soil treatment by immobilisation is fulfilling its function. That is, in the untreated soil the leaching of As is still continuing over the years, while amended Fe is keeping contaminants bound in soil.

Soil amendment with Fe grit has changed the As distribution in the majority of soil samples by slightly decreasing the most soluble fraction (I) by 3–9%, while somewhat increasing the fraction bound to poorly crystalline Fe (oxyhydr)oxides (II) by 1–11% (Fig. 2). This indicates that As (most likely arsenate) immobilisation in soils has occurred mainly due to its sorption to the most reactive Fe (oxyhydr)oxide fraction (II). In general, the largest As fraction in all soils was that bound to poorly crystalline Fe oxides (II) (39–82% of total soil As). The changes in As fraction bound to crystalline Fe oxides varied across the soil samples and no generic trend could be observed. Arsenic in residual fraction was found only in the samples from La Combe du Saut and in one Auzon sample (Auzon + Fe 3, Fig. 2).

3.3. EXAFS analyses

3.3.1. La Combe du Saut

In general, all spectra of samples from La Combe du Saut site were very similar suggesting similarities in the composition of the Fe compounds. There were however slight differences in amplitude and frequencies in the Fe-EXAFS oscillations in *k* range between 7 and 9 Å⁻¹ (Fig. 3a). These differences were also observed in the Fourier Transform (FT) spectra for distances larger than 3 Å (Fig. S1). This means that some differences in the amount of Fe compounds existed between the samples. This is confirmed by the Fe phase partitioning results obtained by the linear combination fitting (LCF) analysis (Table 2). Although all minerals and compounds were considered during the analysis (Table S1), only those that were needed to obtain the best fit are presented in tables.

Iron in the soils from La Combe du Saut was present mainly as (alumino)silicates and oxides: vermiculite, nontronite and goethite (Table 2). Hematite and lepidocrocite were also detected, but in much lower amounts. Despite that, the differences in the abundance in these Fe oxides were important in explaining the differences in spectral features between the samples. Samples from amended plots showed 3.2–6.8% of lepidocrocite, while abundance of this mineral was less significant in soil from untreated plots (0.5%). Although the variability in the Fe partitioning between hematite and lepidocrocite was small, the addition of lepidocrocite to the linear combination fitting was crucial to obtain good fits for all spectra. Fig. 3a shows the Fe-EXAFS of all soil samples with their corresponding LCF showing a good agreement between the calculated combinations and the measured spectra. Ferrihydrite was not found in any of these samples. However the fraction of lepidocrocite was in a very good agreement with that obtained by the sequential extraction regarding the abundance of poorly crystalline Fe phases. Extraction results showed the presence of 2–3.4% of poorly crystalline Fe phases in amended samples and 0.6–0.7% in the untreated ones (Table S2) vs 3.2–6.8% and 0.5%, respectively, of lepidocrocite. Besides ferrihydrite, formation of lepidocrocite upon oxidation of metallic Fe may also be expected in soils in the presence of oxic water (Liu et al., 2014).

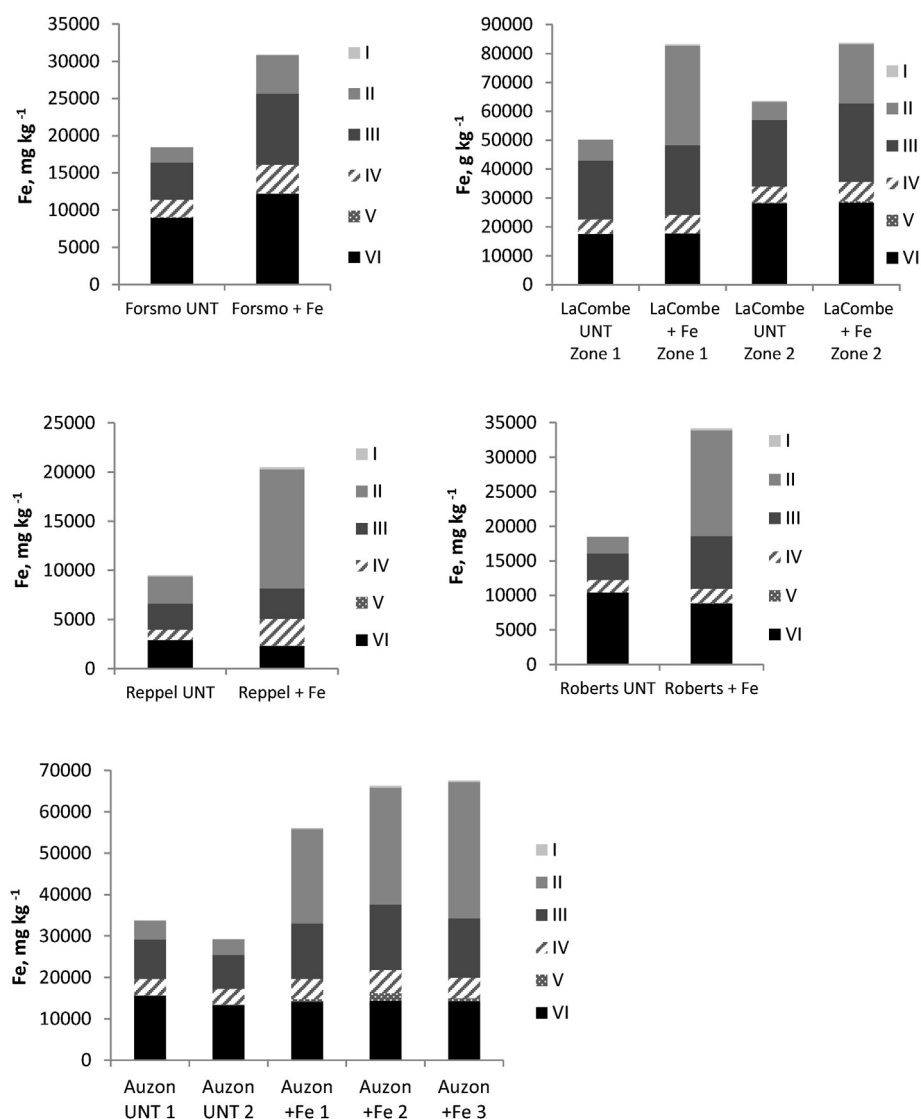


Fig. 1. Distribution of iron in operationally defined soil fractions from the studied sites. (I) Exchangeable fraction, (II) Poorly crystalline Fe(III)-(oxyhydr)oxide fraction, (III) Crystalline Fe(III) (oxyhydr)oxide fraction, (IV) Fe–Mn oxide fraction, (V) Organic matter and secondary sulphide fraction, (VI) Residual fraction.

3.3.2. Auzon

The spectra recorded for the Auzon soil samples were almost identical suggesting very similar Fe mineralogy in all these ones (Fig. 3b). The samples were composed of a relatively broad mixture of Fe compounds (Table 2). Similarly to what was observed in La Combe du Saut, Fe in the Auzon soil was present mainly as aluminosilicates and oxides. Fig. 3b shows a very high similarity between the sample spectra and their respective fit.

A relatively small difference in the abundance of poorly crystalline Fe phases was determined by EXAFS (max 7% increase in amended soil), compared with a much higher amount of poorly crystalline Fe phases determined in Fe-amended samples by the sequential extraction (Fig. 1). According to the extraction results, the fraction of poorly crystalline Fe oxides increased by 28–36% in the amended samples.

3.3.3. Forsmo

The spectra of the Forsmo soil samples were very similar suggesting similarities in the Fe solid speciation (Fig. 3c). There were however slight differences in amplitude and frequencies in the Fe-

EXAFS oscillations for k ranges between 7 and 11 \AA^{-1} , as well as slight changes in shoulders at k 3 and 5.5 \AA^{-1} (Fig. 3c). LCF of the Forsmo soil samples shows that Fe in this soil was mainly in aluminosilicates, silicates and oxides (Table 2).

The increase in ferrihydrite and lepidocrocite in the amended sample indicated that these Fe (oxyhydr)oxides, most likely formed from oxidation of the added Fe grit, were still present two years after Fe amendment. This is in line with the sequential extraction results (Fig. 1), although the latter showed smaller fraction of poorly crystalline Fe oxides in the amended sample (17% of total Fe) than that calculated amount of ferrihydrite from EXAFS data (30.5%).

3.3.4. Robertsfors

Fig. 3d shows the clear differences in the Fe-EXAFS spectra measured in the Robertsfors samples and their corresponding LCF spectra. The spectral differences could be explained by the increased fractions of ferrihydrite, lepidocrocite and ferrosmeectite (nontronite) in the amended soil (Table 2). The oxidation state of Fe in both samples also differed. According to the EXAFS data, the

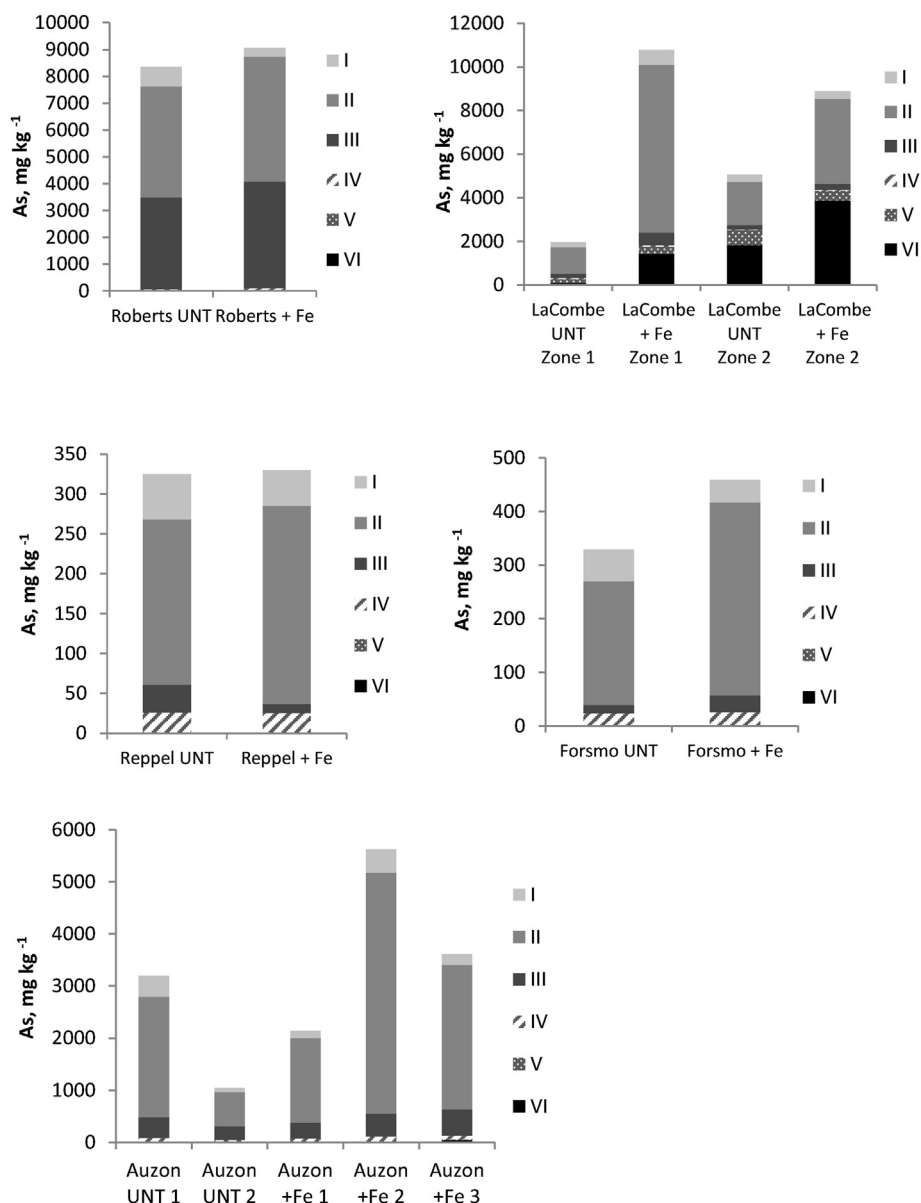


Fig. 2. Distribution of arsenic in operationally defined soil fractions of soils from the studied sites. (I) Exchangeable fraction, (II) Poorly crystalline Fe(III)-(oxyhydr)oxide fraction, (III) Crystalline Fe(III) (oxyhydr)oxide fraction, (IV) Fe–Mn oxide fraction, (V) Organic matter and secondary sulphide fraction, (VI) Residual fraction.

untreated soil was a mixture of Fe(II) minerals, FeS, and Fe(III) minerals, whereas the amended soil was basically composed of Fe(III) minerals (Table 2). Oxidation of Fe(II) to Fe(III) could have occurred upon soil aeration during addition of amendments. An increased formation of goethite, lepidocrocite and ferrihydrite could come thus from the added Fe grit, but also from the oxidation of Fe(II) sulfide. The sequential extraction also showed a higher amount of Fe in residual fraction of the untreated sample (Fig. 1), which could have contained primary Fe(II)sulfides that did not dissolve in the previous steps. Substantially larger fractions of poorly crystalline and crystalline Fe (oxyhydr)oxides were determined in the amended soil through extraction as well. Thus for the Robertsfors soil, EXAFS results were in line with those of the sequential extraction.

3.3.5. Reppel

The linear combination fitting shows that both untreated and amended soils were basically composed of the same components: goethite, ferrihydrite, ferrosmeectite and hornblende, but in different amounts (Table 2). The small spectral variations, seen in Fe-EXAFS spectra in *k*-space (Fig. 3e) and FT (Fig. S5), demonstrated the differences in the abundance of the Fe components. The largest difference between the soil samples was observed for ferrihydrite, its fraction increasing after soil amendment from 19% to 43% of identified Fe compounds. EXAFS results agreed with those of the sequential extraction, which showed a significant increased fraction of poorly crystalline Fe (oxyhydr)oxides in the amended soil (from 29% to 59% of the total soil Fe) (Fig. 1).

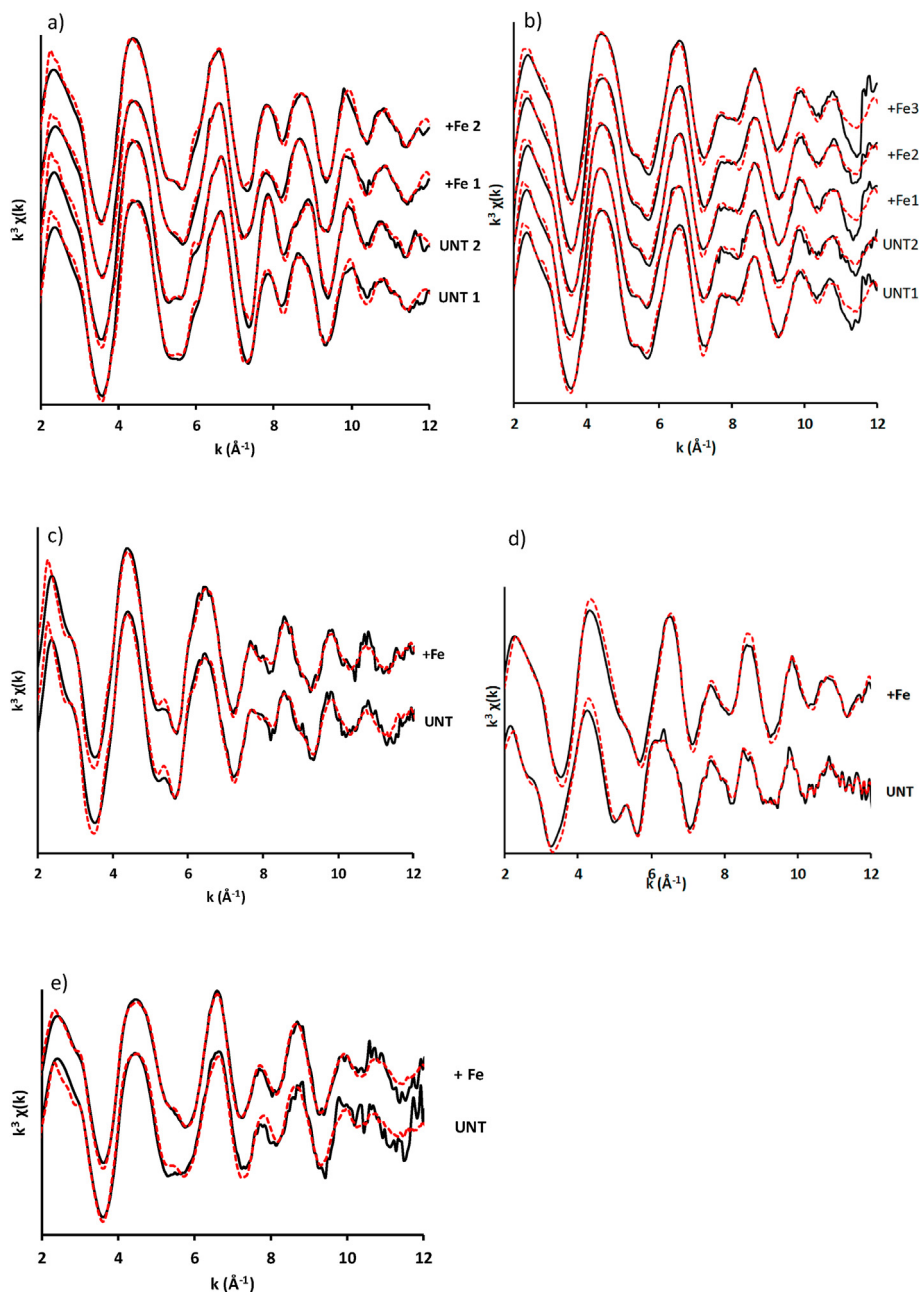


Fig. 3. Fe-EXAFS spectra in k -space (black solid line) together with LCF spectra (red discontinuous line) of soil samples from a) La Combe du Saut, b) Auzon, c) Forsmo, d) Robertsfors and e) Reppel. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.4. Long-term stability of poorly crystalline Fe compounds

The results of the absolute abundance of Fe phases determined by the sequential extraction and EXAFS were not identical. This was expected knowing that both tests are done on a very small amount of soil subsamples, thus differences comprise both natural variation and analytical errors. In addition, the sequential extraction is done by dissolving Fe oxides that are operationally grouped into different fractions. In previous studies, not all fractions that should be dissolved by performing specific steps of the extraction were actually dissolved (Kumpiene et al., 2012). Nevertheless, the more important information is the relative change in the reactive Fe fractions due to soil treatment. That is, whether the difference in poorly crystalline Fe (oxyhydr)oxides between untreated and treated

samples can be detected with any of the used techniques.

All treated soils had higher concentrations of poorly crystalline Fe (oxyhydr)oxides as determined by the sequential extraction and more ferrihydrite as calculated from EXAFS results, than untreated ones. The only exception was samples from La Comb du Saut, which had no ferrihydrite detected by EXAFS either in untreated or treated samples. However, an increase of lepidocrocite was observed after treatment of the soil at La Comb du Saut, which is an iron oxyhydroxite showing great adsorption reactivity towards As (Wang and Giammar, 2015). Thus, identification of poorly crystalline Fe (oxyhydr)oxides obtained by both sequential extraction and EXAFS spectroscopy showed a relatively good agreement, meaning that in all studied sites, except La Comb du Saut, an increase in poorly crystalline Fe (oxyhydr)oxides were observed by both

Table 2
Results of the linear combination fitting for Fe spectra measured in the studied soil samples (as fractions of Fe oxides).

Sample	Goethite	Hematite	Vermiculite	Nontronite	Lepidocrocite	Ferrihydrite	Augite	Clinocllore	Biotite	FeS	Ferrosmeectite	Hornblende
LaComb UNT Zone 1	0.255	0.064	0.431	0.246	0.005							
LaComb + Fe Zone 1	0.198	0.050	0.440	0.279	0.032							
UNT Zone 2	0.237	0.155	0.422	0.167	0.020							
LaComb + Fe Zone 2	0.199	0.089	0.462	0.181	0.068							
Auzon UNT 1	0.066	0.041	0.473	0.239	0.054	0.220						
Auzon UNT 2	0.080	0.053	0.439	0.135	0.093	0.212						
Auzon + Fe 1	0.031	0.043	0.360	0.193	0.092	0.278						
Auzon + Fe 2	0.058	0.048	0.392	0.171	0.093	0.280						
Auzon + Fe 3	0.037	0.024	0.363	0.185	0.090	0.293						
Forsmo UNT	0.039	0.080			0.053	0.265	0.126	0.167	0.174			
Forsmo + Fe	0.030	0.050			0.065	0.305	0.127	0.134	0.170			
Robertsfors UNT	0.103			–	0.099	–			0.387	0.157		
Robertsfors + Fe	0.106			0.017	0.145	0.285			0.240	–		
Reppel UNT	0.243					0.194					0.104	0.455
Reppel + Fe	0.171					0.434					0.243	0.114

techniques. The relative increase in poorly crystalline Fe phases (extraction) and in ferrihydrite fraction (EXAFS) is collectively presented for all samples in Fig. 4. It is suggested that the difference between the results of both techniques becomes smaller the longer time has passed since the soil amendment.

It is unclear though in which step of the sequential extraction dissolves lepidocrocite. When the fraction of this mineral defined by EXAFS was added to the ferrihydrite, the final result of the relative increase became nearly identical to that of the extracted fraction of poorly crystalline Fe (oxyhydr)oxides for the treated Forsmo, Robertsfors and La Combe Du Saut zone 1 samples: 5.6% extracted vs 5.2% defined by EXAFS for the Forsmo sample; 32% extracted vs 33% defined by EXAFS for Robertsfors samples and 27% by both methods in La Combe Du Saut sample. For the remaining samples the results became closer, but not as similar as for the above ones. It is therefore possible that lepidocrocite, which has small size crystals and is very reactive, got dissolved in the second step of the sequential extraction and was assigned to the poorly crystalline Fe (oxyhydr)oxides. The formation of even smaller than usual size lepidocrocite is very likely if precipitation of this Fe oxyhydroxide as a secondary mineral is a result of the oxidation of soil amendment. Since no ferrihydrite was identified in the La Combe du Saut soils, the As immobilisation most likely occurred due to the increased fraction of lepidocrocite (Table 2), which may be as important for As immobilisation as ferrihydrite. Lepidocrocite was identified in all soils, and more in the treated ones, except for the Reppel soil where this mineral was not detected.

A multivariate data analysis was run to identify any correlation between the soil properties (pH, EC, LOI) and the abundance of the identified Fe oxides. No clear patterns were, however, observed which would give any conclusive information about the correlation between these factors and responses.

4. Conclusions

All studied soils, despite the elapsed time since their amendment with Fe grit, had substantial amounts of ferrihydrite and/or lepidocrocite. These are the most reactive Fe (oxyhydr)oxides most likely formed due to the corrosion of the added zerovalent Fe grit particles and responsible for the As immobilisation in the amended soils. This means that metastable Fe oxides (mainly ferrihydrite) were still present even in the Reppel soil that was treated 15 years prior to the sampling. This increases confidence in the long-term efficiency of As immobilisation using zerovalent Fe amendments.

Both applied methods, sequential extraction and EXAFS, were in line for most of the samples in terms of their ability to highlight As immobilisation by poorly crystalline Fe phases. Although the absolute amounts of Fe compounds differed, changes in the fractional distribution of the reactive Fe oxides due to the soil treatment identified by both techniques were similar. Nevertheless, summing up fractions of ferrihydrite and lepidocrocite measured with EXAFS gave even a better similarity than just counting ferrihydrite to the results measured as poorly crystalline Fe phases by the sequential extraction for most of the samples. Thus, lepidocrocite was most likely assigned to poorly crystalline Fe (oxyhydr)oxides by the sequential extraction procedure.

CRediT author statement

Jurate Kumpiene: Conceptualization, Methodology, Data curation, Visualisation, Writing- Original draft preparation, Supervision. **Ivan Carabante:** Investigation, Formal analysis, Data curation, Visualisation, Writing- Reviewing and Editing. **Alfreda Kasiuliene:** Investigation. **Annabelle Austruy:** Investigation, Resources. **Michel Mench:** Investigation, Resources, Writing- Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

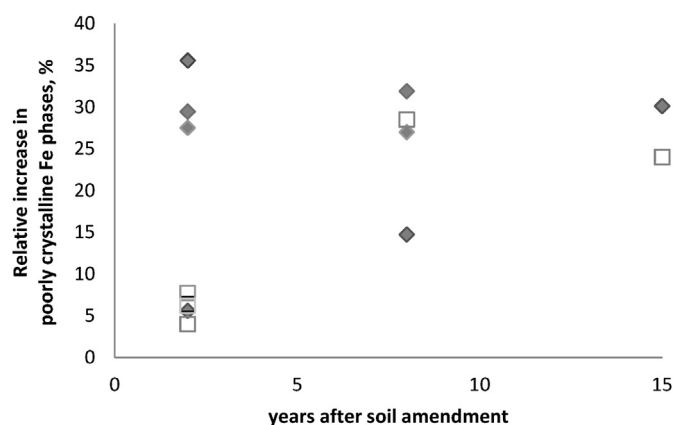


Fig. 4. Relative increase in poorly crystalline Fe (oxyhydr)oxides as determined by sequential extraction (solid diamond) and ferrihydrite defined by EXAFS (hollow squares) calculated as a difference between unamended and amended soils.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2020.116017>.

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