



Degradable organic acids for extraction of As, Cr and Cu from contaminated soils



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Preface

Gentle low cost remediation technologies for simultaneous heavy metal and metalloid removal from soils are lacking and the intention of this project was to investigate the potential and optimal condition for an oxalate based extraction technique for remediation. The oxalate extraction technique was tested on the fine fraction of a soil sample collected from the Collstrop site near Hillerød, to investigate the potential for remediation of the site and the general potential of the method.

The experimental work, data processing and writing of this report were carried out at the University of Copenhagen. The Capital Region of Denmark funded the project, provided access to the Collstrop site and contributed with input to the report. The consultant company Orbicon supplied information about the Collstrop site and assisted in selection of a sampling point at the site.

Table of contents

Summary.....	1
1 Introduction.....	2
1.1 Aim.....	3
2 Experimental.....	4
2.1 Site description, sample collection and pretreatment.....	4
2.2 Extraction experiments	6
2.2.1 Extraction as a function of pH	6
2.2.2 Extraction as a function of oxalate concentration	6
2.2.3 Extraction as a function of L:S ratio and numbers of repeated extractions.....	7
2.3 Analysis and data treatment	7
3 Results and discussion.....	8
3.1 As, Cr and Cu in the fine fraction.....	8
3.2 Extraction with citrate and oxalate as a function of pH	8
3.3 Extraction as a function of oxalate concentration	12
3.4 Extraction as a function of L:S ratio and repeated extractions	13
4 Conclusions.....	16
5 Perspectives.....	17
References:.....	19

Summary

Vast areas of soil contaminated with multiple elements are found around the world due to activities such as mining, industrial processes (e.g. wood impregnation and metallurgy) and diffuse contamination of urban soils. Most research within remediation of toxic elements has focused on heavy metals, the methods show only little or varying effectivity for other elements such as arsenic and are still at laboratory or test stage. There is a strong need to develop a gentle remediation technique which is relatively low cost, can remediate for contamination with mixed elements, is a long term solution and do not add further contamination to the environment or the soil.

The potential for simultaneous extraction of metalloids and heavy metals from contaminated soil by the degradable agents oxalate and citrate was investigated by batch experiments over 24 hours. The investigated soil was the fine fraction ($< 62 \mu\text{m}$) from a Danish CCA contaminated soil collected at the Collstrop site near Hillerød. The fine fraction contained total As, Cr and Cu concentration of 1155, 309 and 750 mg/kg.

Oxalate shows a high potential for simultaneous extraction of As, Cr and Cu from the fine fraction. The maximum extraction efficiency was 75, 28 and 85% of the total soil concentration for As, Cr and Cu, respectively. Citrate shows equally good results for Cr and Cu with removal efficiencies of 25 and 82%, respectively. However, citrate was much less effective for removal of As and only showed an extraction efficiency of 41%.

The extraction efficiency of oxalate was negatively influenced by an increase in pH especially for As. A pH of 5.5 and an oxalate concentration of 0.25 M or higher is recommended for simultaneous remediation of As, Cr and Cu. The liquid:solid ratio should be 10 and two repeated extractions have to be carried out to obtain the optimal extraction.

These results showed that oxalate is a very potent extraction agent for simultaneous remediation of metalloids and heavy metals from contaminated soils. Since oxalate is easily degradable its use should not pose any threat to the environment.

1 Introduction

Vast areas of soil contaminated with multiple elements are found around the world due to activities such as mining, industrial processes (e.g. wood impregnation and metallurgy) and diffuse contamination of urban soils (Gonzalez-Corrochano et al., 2014; Rotting et al., 2014; Li et al., 2013). According to the European Environment Information and Observation Network for soil (EIONET-SOIL) there are about 342,000 contaminated sites and 2,553,000 potentially contaminated sites in Europe and 35% of the contamination is assumed to be due to toxic elements (Panagos et al., 2013).

Still few sites have been remediated and the European annual budget for management of contaminated soils is estimated to be around 6.5 thousand million euros (Panagos et al., 2013). Soils contaminated with toxic elements have many different adverse effects on surrounding environments and humans (Fent, 2004; Cedergreen et al., 2013; Rajaganapathy et al., 2011). Remediation of toxic element contaminated soils have had a strong focus since the 1980ies but the state of the art soil remediation still suffers from many limitations including low effectivity, high costs, adding new contamination to the environment, leading to deteriorated soil quality and not being able to remediate for elements which exhibit different geochemistry (Koptisik, 2014; Yao et al., 2012).

Most research within remediation of toxic elements has focused on heavy metals, the methods show only little or varying effectivity for other metals or metalloids such as arsenic and are still at laboratory or test stage. The method most applied for arsenic remediation has been stabilization with iron oxides, zero valent iron or different minerals; good results have been obtained on short term basis for some soils whereas for others stabilization is not effective, especially changing chemical and physical conditions for these soils can lead to leaching from stabilized soils (Tsang et al., 2014; Garau et al., 2014). There is a strong need to develop a remediation technique which is relatively low cost, can remediate for contamination with mixed elements, is a long term solution and does not add further contamination to the environment.

Chemical soil wash, where the soil is washed with an aqueous solution containing chemical reagents which can extract the contaminants, is a promising remediation technology for toxic elements (Dermont et al., 2008; Qui et al., 2010). Most research within chemical extraction has focused on extractants which are themselves persistent contaminates or which may lead to decreased soil quality e.g. ethylenediaminetetraacetic acid (EDTA), strong acids or base (Dermont et al. 2008; Yang et al., 2009). In the later years the focus has shifted towards soil wash with natural organic matter and biodegradable organic agents which has shown potential for selected elements in some soils and has less negative effects on the soil and environment (Tsang et al., 2013; Wang and Mulligan, 2013; Nair et al., 2007; Qui et al., 2010).

So far little knowledge of how effective degradable low molecular acids are in simultaneous remediation of mixed contaminations of the metalloid arsenic and heavy metals. Formation of complexes between the extracting agent and heavy metals absorbed on the soil surface is believed to be an important release mechanism (Qui et al., 2010). Arsenic does not form strong complexes with extracting agents and other mechanisms such as surface dissolution of iron oxide minerals to which the arsenic is absorbed may become important (Qui et al., 2010).

Agents such as EDTA and strong acids which are very effective in remediation of heavy metals have little effectivity for arsenic (Tsang et al. 2013; Moutsatsou et al., 2006). Oxalic and citric acids are among the most promising extracting agents for arsenic. For oxalic acid extraction efficiencies from 50 to 100% have been seen in different studies (Bhattacharya et al., 2002; Kim and Kim, 2011; Elgh-Dalgren et al., 2009) whereas only a few studies find efficiencies below 20% (Amofah et al., 2010). Citric acid also shows potential for As removal, however, the results are much less consistent with most extraction efficiencies being below 50% and ranging from 6 to 100% (Alam and Tokunaga, 2006; Amofah et al., 2010; Kim and Kim, 2011; Oh et al., 2011).

There is a need to investigate the potential of anions of degradable low molecular weight acids as oxalate and citrate for simultaneous extraction of heavy metals and arsenic from contaminated soils. Further, there is a need to identify the optimal chemical and physical conditions for the extraction.

1.1 Aim

The aim of the study was to test if the two degradable low molecular weight organic acids anions oxalate and citrate can be used for simultaneous remediation of As, Cr and Cu from the fine fraction of a Danish contaminated soil. This included identifying the optimal chemical and physical conditions for the extraction with regards to the pH, concentration of extractant, liquid:solid ratio (L:S ratio) and number of extractions carried out.

2 Experimental

2.1 Site description, sample collection and pretreatment

The soil was collected from the Collstrop site at Stenholtsvang 5 km northeast of Hillerød, Denmark. The site had been used for wood preservation for about 40 years from 1936 to 1976. The first 19 years it was operated according to the Boucherie process applying sodium fluoride, arsenic(III)oxide and dinitrophenol as preservation agents. In 1955 the operation was changed to the Dr. Gewelkes process applying arsenic (As), copper (Cu) and chromium (Cr) as preservation agents and this process was continued until the closure in 1976. The site is contaminated with As, Cr and Cu and concentrations of up to 2000, 200 and 400 mg kg⁻¹, respectively, are not uncommon (Nielsen et al., 2010). Figure 1 shows a photo of the contaminated site with indication of the major contaminated areas and the location of the sampling site.

About 10 L soil was collected with a shovel. The grass and moss cover was removed and soil was dug up to a depth of about 25 cm. The soil was dried at room temperature until no further weight loss was observed. After drying, the soil was separated into different particle size fractions by a sieving shaker using the following cut offs 4000, 2000, 500, 249, 149 and 62 µm. After the first separation the fractions between 62-2000 µm was bulked and washed in deionized water, dried and separated again. This resulted in 12.3 and 4.7% of the soil mass in the <62 µm size fraction for the first and second separation, respectively. The resulting 700 g <62 µm fraction was bulked in a 1 L polypropylene container and was carefully mixed by a spoon and stored for use in extraction experiments.

The element concentration and homogeneity of the <62 µm soil fraction was tested by acid digestion and analysis of the As, Cr and Cu pseudo total soil concentrations. Seven grab samples of approximately 3 g soil were collected by a spoon from the <62 µm fraction and each subsample was pulverized in an agate ball mill. Approximately 0.2 g of each subsample was accurately weighted into a Teflon digestion vessel, 5 ml 70% HNO₃ (J.T. Baker, Instra-Analyzed) and 1 ml 15% H₂O₂ (J. T. Baker, Analyzed) were added. The soil was digested in a microwave assisted system with a reaction chamber pressurized to 40 bar for 10 min at 240 °C (Milestone, UltraWAVE). For quality assurance two reference soil materials (Montana soil, NIST 2711a, National Institute of Standards and Technology; Till-3, Canadian Certified Reference Materials Project (CCRMP)) and one blank were included in the digestion. The samples were made up to 50 ml and were then diluted to different degrees depending on the element to be determined.

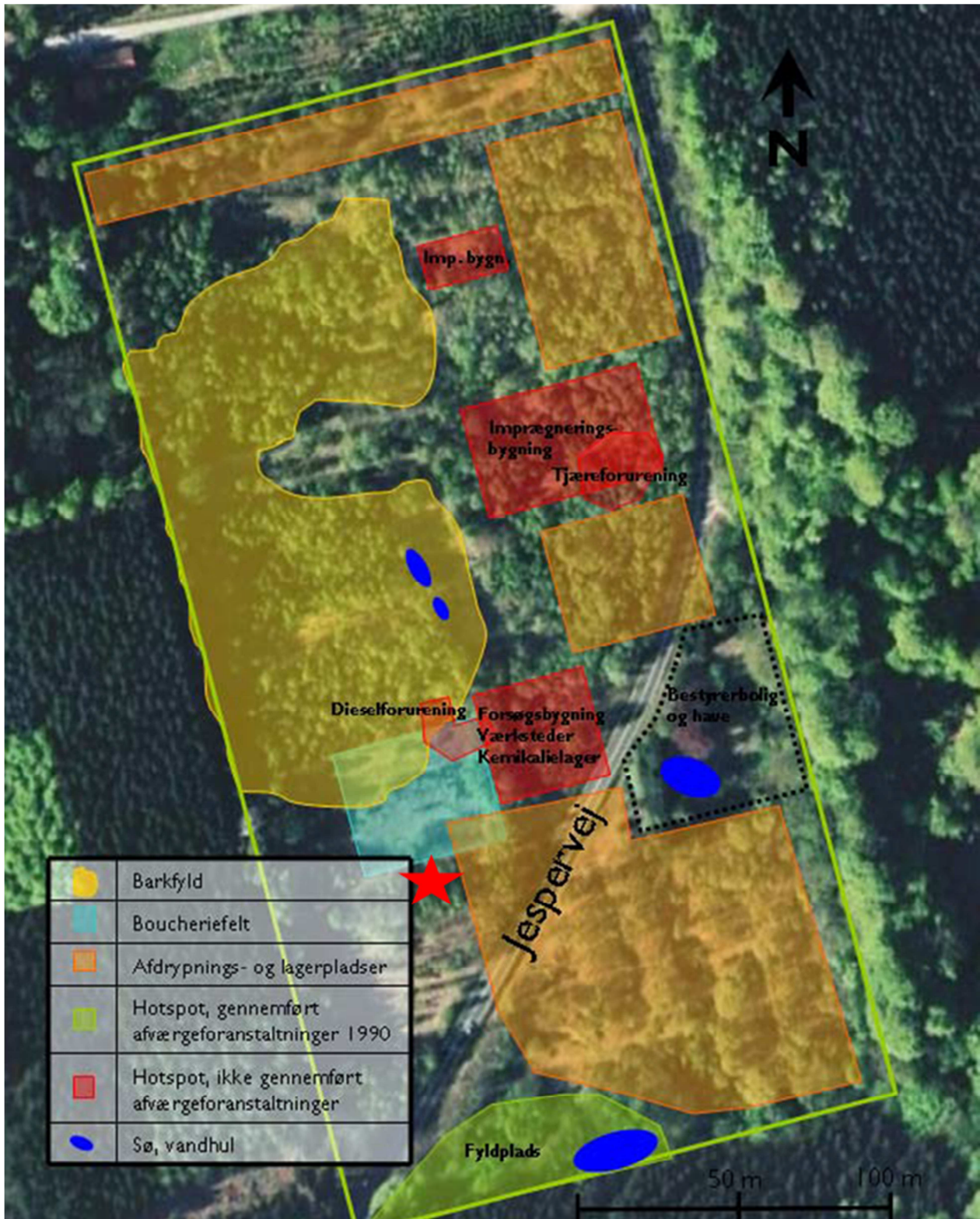


Figure 1. Photograph of the Stenholtsvang site with indication of the sites which have previously been identified as contaminated with different pollutants. The sampling point is indicated with a red star.

2.2 Extraction experiments

2.2.1 Extraction as a function of pH

Extraction as a function of pH was carried out with a liquid to solid ratio (L:S ratio) of 10 using 3 g soil in a 50 ml disposable polypropylene centrifuge tube (Almeco, Sigma-Aldrich). The oxalate and citrate concentration were made up to 0.5 M (Potassium oxalate monohydrate 99%, sodium citrate dehydrate >99%, Sigma-Aldrich, Denmark) and different volumes of 0.1 M HNO₃ or 0.01 M NaOH were added to adjust the pH. The volume was made up to 30 ml with Milli-Q water (Millipore, element) and the suspension was shaken “head over end” for 24 hours at 15 rpm (Heidolph REAX 20, Struers, Denmark) (Figure 2). The samples were centrifuged at 10,720 g for 20 min and the supernatant filtrated through a 0.45 µm nylon syringe filter (Mikrolab Århus A/S). 15 ml of the filtrated supernatant was acidified to 0.2% HNO₃ and used for later As, Cr and Cu determination by GFAAS and the final extraction pH was determined for the left over supernatant (913 pH Meter, combined glass electrode, 6.0262.100, Metrohm). The extraction of As, Cr and Cu in percentage was calculated as the mass of the element in the extraction solution divided by the mass of the element in the soil before the extraction times 100%.



Figure 2. The photograph shows the extraction carried out in 50 ml polypropylene tubes in a “head over end” rotary shaker for 24 hours.

2.2.2 Extraction as a function of oxalate concentration

The extraction as a function of pH with citrate as the extracting agent showed little efficiency for As compared to oxalate why the further experiments only were carried out with oxalate as the extracting agent. The extraction as a function of the oxalate concentration was carried out with the same experimental conditions as described above for the pH experiments except that the pH was kept stable around 5.5 and the oxalate concentrate addition was varied. Different volumes of 1 M oxalate were added to obtain oxalate concentrations of 0, 0.01, 0.05, 0.10, 0.25, 0.50 and 0.75 M. Two replicate extractions were carried out for each oxalate concentration. The extractions without addition of oxalate were both performed with Milli-Q water and in 0.5 M KNO₃ to investigate the possible effect of the ionic strength in the experiments with high concentrations of oxalate. A pre-experiment was performed to determine approximate volumes of 0.01 M NaOH or 1 M HNO₃ needed to obtain a pH of 5.5 and a concentration of 0.02 M MES-buffer was used (2-(N-morpholino)ethanesulfonic acid (MES) monohydrate, Sigma-Aldrich). Further, the pH was controlled and adjusted with small volumes of HNO₃ or NaOH several times during the experiment.

2.2.3 Extraction as a function of L:S ratio and numbers of repeated extractions

Extraction experiments as a function of L:S ratio and number of extractions were carried out as the extraction experiments described above except that the L:S ratio was varied, each soil sample was extracted three times, pH was 5.5 and the oxalate concentration was kept at 0.5 M. The L:S ratios were 2, 5, 10 and 20 by using 15, 6, 3 and 1.5 g soil per 30 ml extraction solution, respectively. The three repeated extractions were carried out by removing as much as possible of the supernatant after the centrifugation and determining the mass of water left in the tube which is transferred to next extraction step. The accumulated mass of extracted element was calculated according the formula:

$$m_i = \sum_1^3 c_i i \cdot (V_i + V_{rem}) - c_i \cdot V_{rem}$$

where “*i*” is the number of the extraction step, “*m*” is the masse of the extracted element, “*c_i*” is the determined concentration at extraction step “*i*”, “*V_i*” is the added volume at extraction step “*i*” and “*V_{rem}*” is the volume remaining from the previous extraction step.

2.3 Analysis and data treatment

The concentration of As, Cr and Cu were determined by graphite furnace atomic absorption spectroscopy (GFAAS) (Perkin Elmer AAS 5100 equipped with a Zeeman magnet) or flame AAS (Perkin Elmer AAS 3100). External calibration with drift correction by one medium standard for every 10 samples was applied. The method of standard addition was used to test for possible matrix interference for the digested soil and oxalate and citrate extractions. No matrix interferences were found.

To investigate if the extraction efficiency was significantly different between two L:S ratios performed after the same number of extractions and if different numbers of extraction significantly influenced the extraction efficiency at the same L:S ratio pairwise student-t test were carried out in Microsoft Excel 2010.

3 Results and discussion

3.1 As, Cr and Cu in the fine fraction

17% of the soil mass was found in the fine fraction after two repeated sieving (<62 μm). However, after the first sieving and the wash of the soil in Milli-Q water the second sieving still resulted in 5% of the soil ending up in the fine fraction indicating that several repeated sieving and washing steps are needed to fully separate the coarse and fine fraction. Therefore, the coarser fraction (62-2000 μm) was found still to contain considerable As, Cr and Cu contamination after the separation. However, as the scope of this work was to study the potential of small organic acids for simultaneous remediation of As, Cr and Cu from the fine fraction, no further effort was put into separation of the remaining fine fraction in the coarse fraction.

The analysis of the fine fraction showed that it was highly contaminated with As, Cr and Cu and the concentrations were 1155 ± 39 , 309 ± 20 and 750 ± 25 mg/kg, respectively. The recovery of the applied digestion and analysis method were within $\pm 10\%$ of the certified value for the reference materials and the concentrations of digestion blanks were below the detection limit for As, Cr and Cu. Many studies have shown that the element concentration in contaminated soil may vary considerable even if considerable effort has been put into homogenizing the sample. Therefore, it is important to determine the homogeneity of a sample before extraction studies are carried out. If the sample is homogenous with regards to the element concentrations the extraction in percentage of the total element content of the soil can be determined by determining the concentration in the extraction solution only and using previously determined total element concentrations for the soil. However, if the soil is heterogeneous with regards to the element concentrations the element concentrations should be determined in the both the extraction solvent and the extracted soil. The relative standard deviation for the seven determinations of the As, Cr and Cu concentrations were 3.4, 6.5 and 3.3% showing that the soil is sufficiently homogenous to only determine the concentration in the extraction solution.

3.2 Extraction with citrate and oxalate as a function of pH

The extraction with oxalate as a function of pH showed high efficiency with a maximum of 74, 25 and 90% for As, Cr and Cu, respectively (Figure 3). For all three elements the highest efficiency was observed at the lowest applied pH value of about 5.5. Of the three elements As extraction was most affected by an increase in pH and a gradual decrease was observed from about pH 6 to 8.3 which resulted in only 24% being extracted at pH 8.3. A gradual reduction in the extraction efficiency of 12 and 15% with increasing pH were observed for Cr and Cu, respectively.

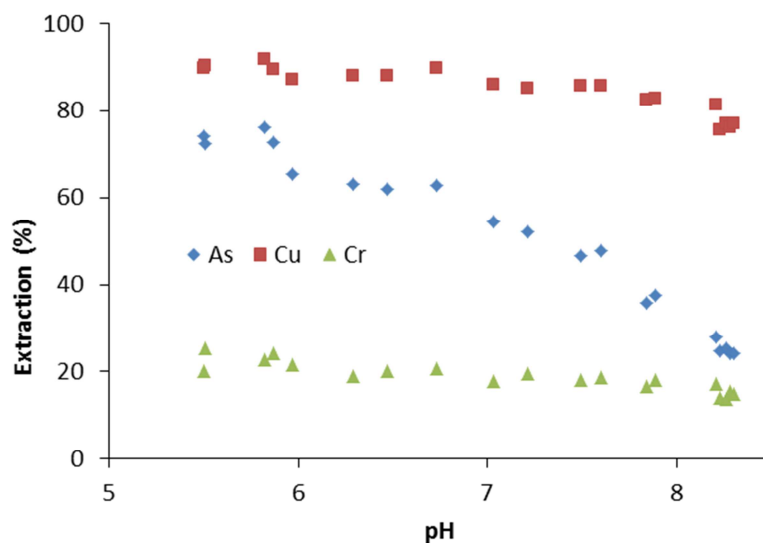


Figure 3. Extraction of As, Cr and Cu as a function of pH at a L:S ratio of 10 and oxalate concentration of 0.5 M oxalate over 24 hours of extraction.

The molecular mechanisms determining the extraction of an element, the efficiency of the extraction and the pH dependency is likely different for the three elements. Copper has a high affinity for surface complexation to soil organic matter by covalent bonding and in Cu contaminated soils the organic fraction is important for the retention of Cu. In surplus of oxalate Cu will form the soluble complex $\text{Cu}(\text{C}_2\text{O}_4)_2^{2-}$ which has a high stability constant of $3.91 \cdot 10^{10} \text{ M}^{-2}$ (at 25° and an ionic strength of 0 M) (McAuley and Nancollas, 1960). Therefore, oxalate acts as a competing complexing agent to the soil organic matter and results in extraction of Cu. Aqueous speciation model calculations shows that the oxalate complexation of Cu increases sharply from pH 4 to the maximum at pH 5 and remains at a stable high level at higher pH values (PHREEQC 3.3.5). As the oxalate-Cu-complexation is more efficient at higher pH values the decreasing extraction efficiency at higher pH values seen in Figure 3 is likely due to the increasing competition from Cu-soil-surface-complexation at higher pH values.

In soils the presence of organic matter in top soils will reduce Cr to the oxidation state 3+ and as seen from Figure 4 Cr(III) will form the none charged complex $\text{Cr}(\text{OH})_3$ at pH values above 5.5 (Rai, Eary and Zachar, 1989). The $\text{Cr}(\text{OH})_3$ complex has a very low solubility and control the concentration of dissolved chromium in soils (Rai, Eary and Zachar, 1989). Therefore, Cr will be found as the $\text{Cr}(\text{OH})_3$ precipitate in top soil and exhibit a very low solubility and mobility. Oxalate forms Cr(III)-oxalato complexes on the surface of Cr(III) hydrous oxides particles which results in a reduced surface redox potential, weakening of surface bound Cr and surface dissolution of the oxide (Rodenas et al., 1997). The observed release of Cr in presence of oxalate is likely due to the surface dissolution of Cr oxides (Figure 3). The oxalate induced dissolution of Cr(III) hydrous oxides have been seen to decrease with increasing pH values (Rodenas et al., 1997). The observed decrease in Cr extraction with increasing pH (Figure 3) can be due to both a decreased formation of surface Cr(III)-oxalato complexes and increasing precipitation of $\text{Cr}(\text{OH})_3$. Therefore, to increase the Cr extraction efficiency significantly above the observed 25% it would be necessary to decrease the pH below the applied 5.5.

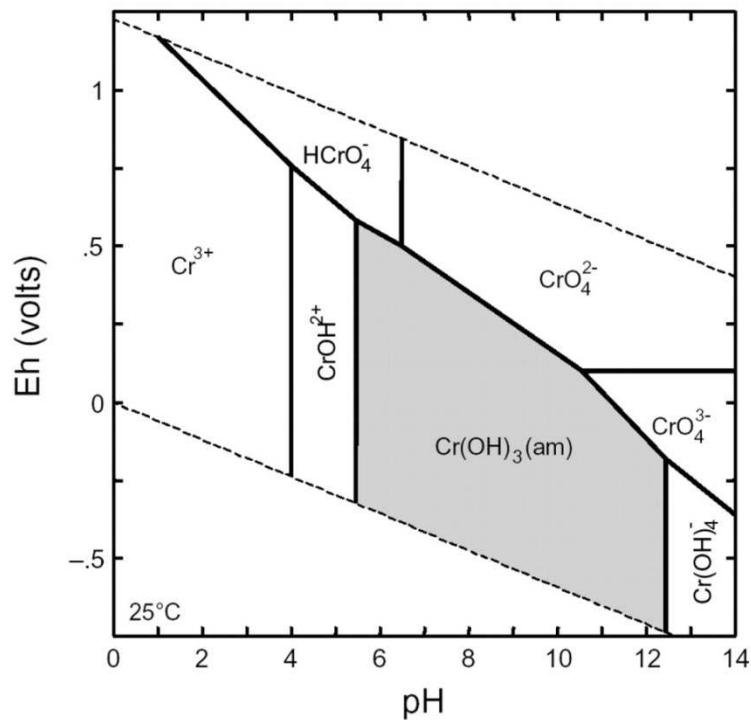


Figure 4. Aqueous speciation of Cr as a function of pH and redox conditions at 1 atm and 25 °C.

The high influence of pH on the As extraction compared to Cr and Cu is due to the difference in As geochemistry. In oxidized soil As is mainly present in the oxidation state 5+, however, since the soil has a high content of organic matter in the form of As contaminated bark filling which may result in reduction of As and the oxidation from As(III) to As(V) has a slow reaction kinetic both reduction states may occur in the soil (Wang and Mulligan, 2006; Smedley and Kinniburgh, 2002). Under the investigated pH conditions As(V) can be present as the oxyanions H_2AsO_4^- and HAsO_4^{2-} and As(III) will be the neutral specie H_3AsO_3 (Figure 5). The mobility of As in soil is mainly controlled by the sorption to metal oxides (Bissen and Frimmel, 2003; Smedley and Kinniburgh, 2002). As(III) has a high affinity for sorption to iron oxides whereas As(V) shows sorption to metal oxides in general and for example has a higher affinity for sorption to aluminum oxides compared to As(III) (Inskeep et al, 2002; Bissen and Frimmel, 2003). The actual binding strength of As for a soil depend on the oxidation state of As, the concentration, type and crystallinity of the oxides and the pH (Dixit and Herring, 2003; Fendorf et al., 1997; Stollenwerk, 2003; Bissen and Frimmel, 2003). Arsenic has been found to form a bidentate-binuclear-complex on the iron oxide surface forming covalent bonds to two surface iron atoms (Jiang et al., 2013). As(III) sorption shows a low degree of pH dependence whereas the sorption of As(V) to iron oxides have been found to have a maximum at about pH 4 (Dixit and Herring, 2003). The observed decreasing extraction at higher pH values is not related to the As binding strength to the soil as this should decrease with increasing pH at least for As(V).

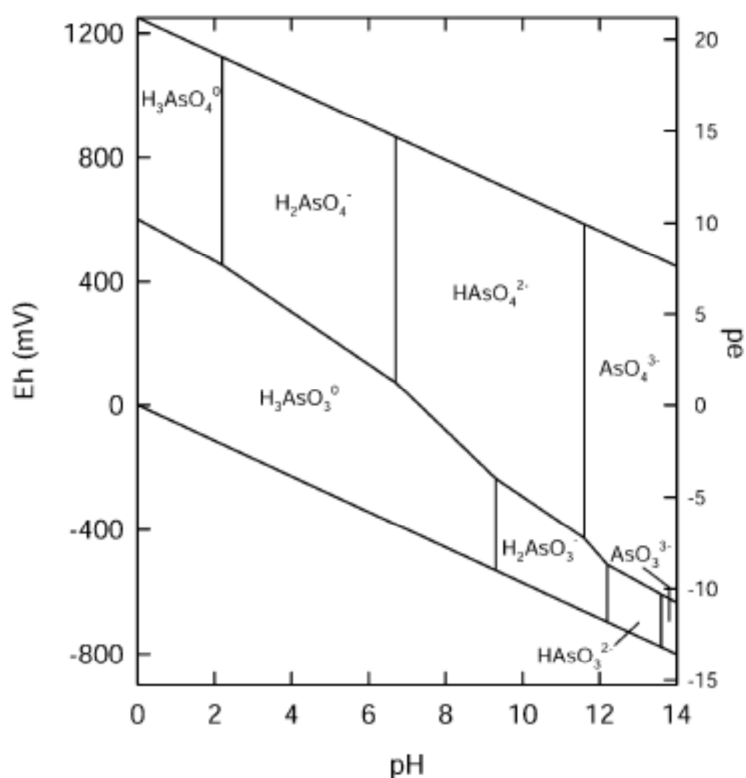


Figure 5. Aqueous speciation of As as a function of pH and redox conditions at 1 atm and 25 °C (Smedley and Kinniburgh, 2002).

Oxalate and arsenic exhibit a similar sorption pattern forming a bidentate-binuclear-complex on the surface of iron oxides and the sorption shows a similar pH dependence which decreases at pH values above 5 for goethite (Mesuere and Fish, 1992; Panias et al., 1996). The sorption of oxalate may further result in non-reductive dissolution of the iron oxide by weakening of Fe-O surface bonds or reductive dissolution of iron oxides by electron transfer from oxalate to the surface-Fe-atom (Panias et al., 1996). The oxalate enhanced dissolution of iron oxides follows a pH trend similar to the sorption of oxalate with decreasing dissolution at higher pH values (Johnson and Loeppert, 2006). The high efficiency of oxalate in As extraction may be due to competition for sorption sites and/or dissolution of reactive surface sites (Figure 3). Oxalate can act as a competing sorbent for the same sorption sites as As and the oxalate adsorption will decrease the zeta potential of the iron oxide and thereby weaken the bonding strength of sorbed As (Panias et al., 1996). Arsenic release may also be a result of dissolution of the iron oxide surface.

Figure 6 shows the extraction efficiency for citrate as a function of pH. The highest extraction efficiency was 41, 25 and 82% for As, Cr and Cu, respectively. Compared to oxalate the extraction efficiency for citrate is similar for Cr, about 10% lower for Cu and 45% lower for As at pH 5.5. The extraction with citrate showed trends similar to the oxalate extraction with a slight drop in efficiency for Cr and Cu with increasing pH whereas the extraction of As with citrate were less influenced by changing pH compared to the oxalate extraction. Citrate sorbes to the iron oxide surface with formation of up to tridentate complexes (Marcussen et al., 2009; Cornell and Schindler, 1980). Citrate exhibits a weaker sorption to iron oxides but the decrease in sorption as a function of pH occurs at higher pH of 6-7 compared to oxalate (Mesuere and Fish, 1992; van Hees et al., 2003; Lackovic et al., 2003). The weaker sorption of citrate can explain why oxalate is a more efficient extraction agent for As compared to citrate; as the competition for surface sites and dissolution of the iron oxide surface will be less for citrate. Since citrate was found to be a much less effective extraction agent for As further extraction experiments were only carried out for oxalate.

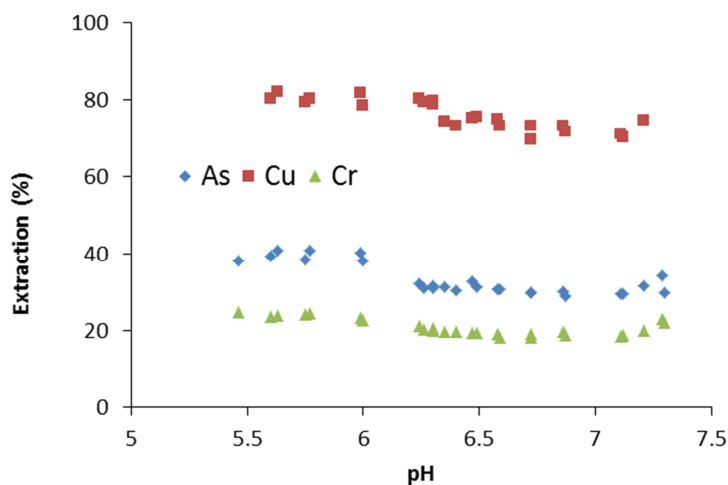


Figure 6. Extraction of As, Cr and Cu as a function of pH at a L:S ratio of 10 and concentration of 0.5 M citrate over 24 hours of extraction.

3.3 Extraction as a function of oxalate concentration

The extraction of As, Cr and Cu as a function of the oxalate concentration at pH 5.5 is shown in Figure 7. Without oxalate in the extraction experiments up to 2% of the total As, Cr and Cu were extracted showing that potent extraction agents are needed to clean the soil. No difference was observed in the extraction with Milli-Q water and 0.5 M KNO_3 showing that the ionic strength has little effect on the extraction. Even though the extraction's efficiency was low without oxalate the washing solutions had concentrations of up to 2.3, 0.6 and 1.5 mg L^{-1} for As, Cr and Cu, respectively. So even though the extraction is not efficient without oxalate very high soil solution concentrations can be expected at the site at a pH of 5.5.

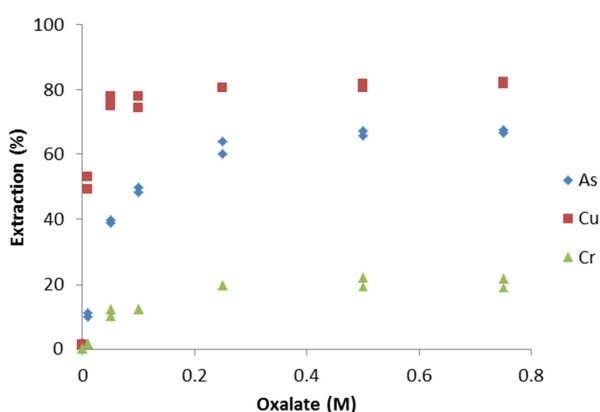


Figure 7. Extraction of As, Cr and Cu as a function of oxalate concentration at pH 5.5 and a L:S ratio of 10 over 24 hours of extraction.

The extraction as a function of the oxalate concentration shows a higher efficiency for Cu compared to As and Cr over the full concentration range (Figure 7). The extraction efficiency for Cu reached 50% at an

oxalate concentration of 0.01 M and it increased to 80% at 0.05 M oxalate; further oxalate addition did not increase the efficiency. If Cu is the only soil contaminant which needs to be remediated this can then be carried out at relatively low oxalate concentrations resulting in more cost effective remediation.

For efficient As extraction higher oxalate concentrations were needed (Figure 7). Arsenic was the element mostly affected by the oxalate concentration and it had a gradual increase in efficiency with increasing oxalate concentration; at 0.01 M oxalate the extraction efficiency was about 10% and this increased to 40% by increasing the oxalate concentration to 0.05 M. The double oxalate concentration of 0.1 M only increased the extraction to 50%, showing that much more is gained in efficiency by an oxalate increase at low oxalate concentrations. The maximum extraction efficiency for As of about 65% was obtained at oxalate concentration of 0.25-0.75 M.

A much lower efficiency was observed for Cr compared to Cu and As; 0.05 M oxalate was needed to increase the Cr extraction significantly above the efficiency of Milli-Q water and 0.5 M KNO_3 (Figure 7). About 12% Cr was extracted at 0.05 M oxalate and the optimum extraction efficiency of 20-22% was obtained at oxalate concentrations of 0.25-0.75 M.

To obtain efficient removal of all three elements an oxalate concentration of 0.25 M was needed whereas higher oxalate concentrations did not improve the extraction efficiency. This shows that at a concentration of 0.25 M the oxalate is in surplus and that the extraction of the three elements is not in competition with each other. This will of course be soil dependent especially the content of iron oxides and organic matter in the soil can influence the oxalate concentrations needed to obtain optimal extraction efficiency. Soils with a high content of iron oxides or organic matter has a high capacity for binding As or Cu, respectively and higher oxalate concentrations may be needed to effectively compete with the binding to the soil. On the other hand less or more oxalate may be needed for soils with low or high concentrations of the investigated contaminants. However, to understand how the soil element, iron oxide and organic matter content influence the oxalate concentration needed for effective extraction of As, Cr and Cu studies of extraction efficiencies for different soils contaminated to different degrees are needed.

3.4 Extraction as a function of L:S ratio and repeated extractions

Figure 8 shows the extraction of As, Cr and Cu as a function of the L:S ratio and three repeated extractions. For all three elements an increase in the extraction efficiency was seen with increasing number of extractions and increasing L:S ratio, however, the effect of increasing the L:S ratio depended on the number of extractions and vice versa.

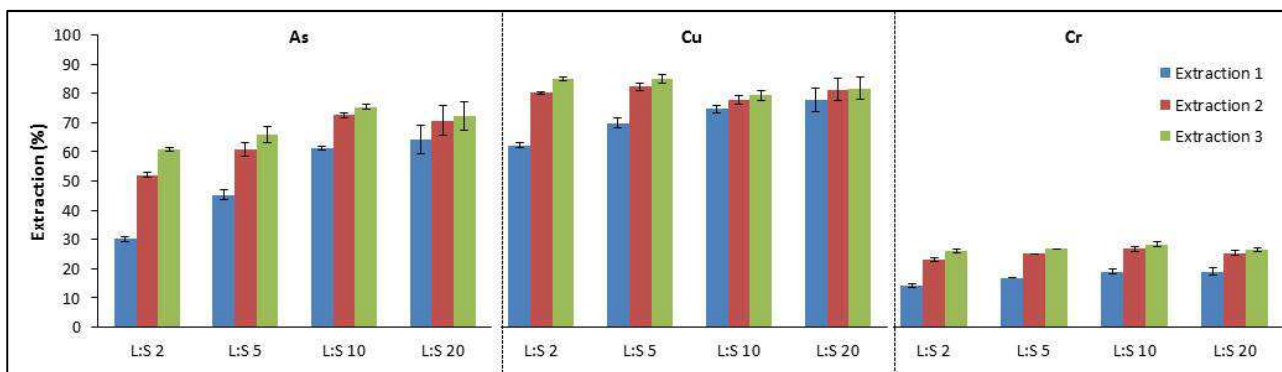


Figure 8. Extraction of As, Cr and Cu as a function of number of extractions and the L:S ratio with 0.5 M oxalate at pH 5.5 over 24 hours.

For As the extraction at a L:S ratio of 2 increased with increasing number of extractions and three or more extractions have to be performed to obtain the maximum extraction efficiency (Figure 8, Table 1). The obtained extraction efficiency at a L:S ratio of 2 and with three repeated extractions was $61 \pm 1\%$ which is significantly below the extraction efficiency at higher L:S ratios for the same number of extractions (Figure 8, Table 2). The extraction efficiency also increased significantly by increasing the L:S ratio from 5 to 10 with efficiencies of 66 ± 3 and 75 ± 1 , respectively for three repeated extractions (Figure 8, Table 2). A further increase in the L:S ratio from 10 to 20 did not result in increased efficiency (Figure 8, Table 2). This shows that the maximum extraction efficiency of about 75% As is obtained at a L:S ratio of 10 with 3 repeated extractions (Figure 8, Table 1). Using three repeated extractions instead of two only added 3% more to the extraction efficiency why it is unlikely that adding further extractions will add significantly to the efficiency. The results indicate that if more extractions are carried out for the lower L:S ratios of 2 and 5 the extractions efficiency may end up having the same efficiency as the L:S ratio of 10. However, to confirm this more extractions have to be carried out for the L:S ratios of 2 and/or 5.

Table 1. Results of student t-tests comparing the extraction efficiency for one, two and three repeated extractions at L:S ratios of 2, 5, 10 and 20. *, **, *** show differences between the extraction efficiencies at the 95, 99 and 99.9% level, respectively, whereas NS shows not significant difference.

		L:S 2		L:S 5		L:S 10		L:S 20	
		Ex. 2	Ex. 3	Ex. 2	Ex. 3	Ex. 2	Ex. 3	Ex. 2	Ex. 3
As	Ex. 1	***	***	***	***	***	***	NS	NS
	Ex. 2	-	***	-	*	-	**	-	NS
Cu	Ex. 1	***	***	***	***	*	**	NS	NS
	Ex. 2	-	***	-	*	-	NS	-	NS
Cr	Ex. 1	***	***	***	***	***	***	***	***
	Ex. 2	-	**	-	***	-	NS	-	NS

Table 2. Results of student t-tests comparing the extraction efficiency for different L:S ratios for 1, 2 and 3 repeated extractions. *, **, *** show differences between the extraction efficiencies at the 95, 99 and 99.9% level, respectively, whereas NS shows not significant difference.

		Extraction 1			Extraction 2			Extraction 3		
		L:S 5	L:S 10	L:S 20	L:S 5	L:S 10	L:S 20	L:S 5	L:S 10	L:S 20
As	L:S 2	***	***	***	**	***	**	*	***	**
	L:S 5	-	***	**	-	***	*	-	**	NS
	L:S 10	-	-	NS	-	-	NS	-	-	NS
Cu	L:S 2	***	***	**	NS	*	NS	NS	**	NS
	L:S 5	-	**	*	-	**	NS	-	**	NS
	L:S 10	-	-	NS	-	-	NS	-	-	NS
Cr	L:S 2	**	***	**	**	**	*	NS	*	NS
	L:S 5	-	**	*	-	**	NS	-	*	NS
	L:S 10	-	-	NS	-	-	*	-	-	*

The extraction efficiency for As at a L:S ratio of 20 did not show a difference between extraction 1, 2 and 3. Part of the reason for this may be that the experiments with a L:S ratio of 20 had higher uncertainties compared to the experiments with lower L:S ratios, as was also seen from the higher standard deviations. Centrifuging and separating the supernatant and soil becomes more effective at lower L:S ratios due to inter-particle-cohesive-forces. Furthermore, a small loss of soil while removing the supernatant will have a higher influence on the extraction efficiency for the next extraction step for a high compared to a low L:S ratio.

The maximum obtained extraction efficiency for Cu was 85% (Figure 8). Using only one extraction the release of Cu increased when the L:S ratio was increased from 2, 5, 10 and 20 to efficiencies of 62, 70, 75 and 78%, respectively, though the increase from L:S 10 to 20 was not statistically significant (Figure 8, Table 1). When the number of repeated extractions were increased to two no statistically significant increase in the extraction efficiency was obtained by increasing the L:S ratio above 2 (Figure 8, Table 2). A small but significant increase in the extraction efficiency of 3% occurred if the number of extractions were increased from 2 to 3 at a L:S ratio of 5 (Table 1).

The maximum extraction efficiency for Cr was about 28% (Figure 8). If L:S ratios of 2 and 5 were applied three repeated extractions or more had to be performed to obtain the maximum extraction of Cr (Figure 8, Table 1). When the L:S ratio was increased to 10 only two replicate extractions were needed and increasing the L:S ratio to 20 did not further increase the extraction efficiency (Figure 8, Table 1).

Two repeated extractions with a L:S ratio of 10 resulted near optimal extraction efficiencies of all three elements which would only be improved by a few percent by including a third extraction step. Further increase of the L:S ratio did not improve the extraction efficiency significantly. If lower L:S ratios must be used due to practical or economic reasons this can be compensated by using a higher number of repeated extractions.

4 Conclusions

The potential for simultaneous remediation of metalloids and heavy metals from contaminated soil by oxalate and citrate was investigated by batch experiments over 24 hours. The investigated soil was the fine fraction (< 62 μm) from a Danish CCA contaminated soil collected at the Collstrop site near Hillerød. The fine fraction contained total As, Cr and Cu concentrations of 1155, 309 and 750 mg/kg, respectively.

Oxalate shows a high potential for simultaneous extraction of As, Cr and Cu from the fine fraction. The maximum extraction efficiency was 75, 28 and 85% of the total soil concentration for As, Cr and Cu, respectively. Citrate shows equally good results for Cr and Cu with removal efficiencies of 25 and 82%, respectively. However, citrate was much less effective for removal of As which only showed an extraction efficiency of 41%.

The extraction efficiency of oxalate was negatively influenced by an increase in pH; especially for As where the efficiency dropped from 74% at pH 5.5 to 24% at pH 8.3. The needed oxalate concentration for optimal extraction conditions depended on the element in question. 0.05 M oxalate was needed to obtain the maximum Cu extraction whereas 0.25 M oxalate was needed for maximum extraction of As and Cr. Therefore, an oxalate concentration of 0.25 M or higher is recommended for simultaneous remediation of As, Cr and Cu.

The influence of the liquid:solid (L:S) ratio and the number of repeated extractions on the same soil sample were investigated under optimal conditions of pH 5.5 and 0.5 M oxalate. Optimal Cu extraction could be obtained at a L:S ratio of 2 when 2 repeated extractions were performed. For As and Cr a L:S ratio of 10 and 2 repeated washings were needed.

These results show that oxalate is a very potent extraction agent for simultaneous remediation of metalloids and heavy metals from contaminated soils. Since oxalate is easily degradable its use should not pose any threat to the environment. The optimized extraction conditions with oxalate resulted in final As, Cr and Cu concentrations of about 290, 220 and 110 mg/kg, respectively in the fine fraction.

5 Perspectives

The Danish EPA have issued two types of soil quality standards, namely the soil quality criteria which set limits to the content of pollutants in soil for the most sensitive land uses such as private gardens and kindergartens and the cut-off criteria which state the pollutant concentration limits above which all contact to the soil must be prevented for sensitive land uses (Miljøstyrelsen, 2014). The soil quality criteria for As, Cr and Cu are 20, 500, and 500 mg/kg and the cut-off criteria are 20, 1000 and 1000 mg/kg, respectively. The study showed that the optimized extraction procedure of two repeated extractions at pH 5.5 with oxalate concentrations of at least 0.25 M and a L:S ratio of 10 resulted in final As, Cr and Cu concentrations of 290, 220 and 110 mg/kg, in the fine soil fraction for the very contaminated soil from the Collstrop site. Remediation of the fine fraction from the Collstrop soil by oxalate extraction would therefore result in Cr and Cu concentration below the Danish soil quality criterion whereas the As concentration would be about a factor 15 above the criterion.

If the fine fraction from the Collstrop site is to be returned to the ground after remediation it must be mixed with a coarser fraction to ensure a texture which will allow for the development of a stable soil structure resistant to soil erosion and which will allow for water transport and offer anchoring support for construction and plant growth. The fine fraction constituted 17% (weight/weight) of the soil collected from the Collstrop site. If a similar texture should be obtained by mixing the fine fraction with a coarser fraction the fine fraction would contribute with about 51, 37 and 19 mg/kg to the final soil concentrations of As, Cr and Cu, respectively. Though the extraction with oxalate shows a high potential for remediation with respect to As and Cu the fine fraction mixed with 83% of a coarse fraction still have concentration above the soil quality criterion for As of 20 mg/kg. To obtain concentrations within the soil quality criterion for As only 6% of the remediated fine fraction can be mixed with 94% coarser fraction.

Even though the oxalate extraction based remediation of As fails to be in compliance with the Danish soil quality criteria the remaining As in the soil may not pose a risk for humans or the environment. The study showed that increasing the number of extractions from two to three had little to no effect on the As release. This indicates that the remaining As after two extraction is strongly bound to the soil material and both the mobility and bioavailability may be low. At low mobility and bioavailability there is little risk of ground water contamination and toxicological effects on soil living organisms. Ingestion of the remediated soil poses an As exposure risk to humans. Soil ingestion may be inadvertent intake e.g. through dust or residual soil on vegetables or children putting dirty hands, soil or gravel into the mouth. The risk of uptake of toxic elements from ingested soil depends on the bioaccessibility which is defined as the quantity which is released in the gastrointestinal tract and becomes available for absorption (Heaney, 2001). Bioaccessibility is usually evaluated by *in vitro* digestion procedures, generally simulating gastric and small intestinal digestion (Courraud et al., [2013](#)).

To understand the environmental risk of As in the Collstrop soil after remediation with oxalate, As-mobility-tests are needed. Mobility test could be performed as batch or column test with extraction agents which differ in their ability to extract As compared to oxalate. Using extraction agents of different strength and chemical behavior could show the risk under different scenarios. Such test should also be performed under anoxic conditions as the release of As may be increased under reduced conditions due to reduction of iron oxides. Bioavailability tests for the remediated soil could also be performed for example with an As

sensitive bacterial biosensor. Bioaccessibility evaluated by *in vitro* digestion tests as described above could be used to evaluate the potential uptake risk from soil ingestion.

This study has only investigated the remediation of As, Cr and Cu from the fine fraction of a highly contaminated soil. The removal efficiencies were moderate for Cr and very high for As and Cu. Even though the Danish soil quality criterion for As was not met the oxalate extraction may have potential to reach this criterion for other soil types or soils with less As contamination. As very few studies with oxalate mediated As extraction have been carried out and these are inconsistent in their methodology it is very difficult to compare their extraction efficiencies and relate these to the soil type and As concentrations. To further develop this technology towards a mature soil remediation technology there is a need to test the extraction efficiency for different soils with different As concentrations.

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