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Nielsen, Sanne Skov; Kjeldsen, Peter; Jakobsen, Rasmus

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1 **Full scale amendment of a contaminated wood impregnation site with iron water treatment residues**

2
3 Sanne Skov Nielsen^{a)}, Peter Kjeldsen(✉), Rasmus Jakobsen^{b)}

4 Department of Environmental Engineering, Technical University of Denmark, Miljovej 113, DK-2800 Kgs.

5 Lyngby, Denmark

6 e-mail: pekj@env.dtu.dk

7
8 (✉) **Corresponding author:**

9 Peter Kjeldsen

10 Tel. +45 45251561

11 Fax. +45 45932850

12 e-mail: pekj@env.dtu.dk

13
14 a) Present address: Orbicon, Ringstedvej 20, DK-4000 Roskilde, Denmark (e-mail: sann@orbicon.dk)

15 b) Present address: Geological Survey of Denmark and Greenland, Geological Survey of Denmark and
16 Greenland, Øster Voldgade 10, DK-1350 Copenhagen K, Denmark (e-mail: raj@geus.dk)

17
18 **Abstract**

19 Iron water treatment residues (Fe-WTR) are a free by-product of the treatment of drinking water with high
20 concentration of iron oxides and potential for arsenic sorption. This paper aims at applying Fe-WTR to a
21 contaminated site, measuring the reduction in contaminant leaching, and discussing the design of delivery
22 and mixing strategy for soil stabilization at field scale and present a cost-effective method of soil mixing by
23 common contractor machinery. Soil contaminated by As, Cr, and Cu at an abandoned wood impregnation
24 site was amended with 0.22% (dw) Fe-WTR. To evaluate the full scale amendment a 100 m² test site and a
25 control site (without amendment) were monitored for 14 months. Also soil analysis of Fe to evaluate the
26 degree of soil and Fe-WTR mixing was done. Stabilization with Fe-WTR had a significant effect on
27 leachable contaminants, reducing pore water As by 93%, Cu by 91% and Cr by 95% in the upper samplers.
28 Dosage and mixing of Fe-WTR in the soil proved to be difficult in the deeper part of the field, and pore
29 water concentrations of arsenic was generally higher. Despite water logged conditions no increase in
30 dissolved iron or arsenic was observed in the amended soil. Our field scale amendment of contaminated
31 soil was overall successful in decreasing leaching of As, Cr and Cu. With minor improvements in the
32 mixing and delivery strategy, this stabilization method is suggested for use in cases, where leaching of Cu,
33 Cr and As constitutes a risk for groundwater and freshwater.

34 **Keywords** Field experiment, Iron oxide, Metal, Stabilization, Wood preservation sites

35 Running title: **Amendment of a wood impregnation site with iron water treatment residues**

36

37 1 Introduction

38 Throughout Europe brownfields are present as remnants of industrial production. As early industrial sites
39 from a time with no environmental protection laws, the sites may be heavily contaminated, and often the
40 contamination consists of heavy metals, that are, by nature, not degradable in the environment. The sheer
41 volume of soil is frequently too large for excavation and when the sites are situated in isolated locations,
42 development is not economically feasible. These sites may pose a threat to aquifers and surface waters by
43 leaching of contaminants. Cleaning and reutilization technologies of metal(loid) polluted soils including
44 soil washing [1, electrochemical remediation [2], phytoremediation [3] and combinations thereof are only
45 scarcely used [4].

46 Stabilizing or amending metal(loid) contaminated soil involves adding an amendment to the
47 contaminated soil layers that reduces leaching of contaminants from the soil by sorption or precipitation,
48 and is useful for brownfields and cases where there are no special requirements for the land use. In cases
49 where such circumstances can be fulfilled, the method is considered a cost effective way to minimize the
50 impact of mobile element contamination on the recipients [5]. Bioavailability of contaminants at the site
51 may also be limited [5,6] which prevents spreading of contaminants in the food chain.

52 At former wood impregnation sites especially arsenic (As) is often very mobile in soil and
53 groundwater systems [7,8]. Iron oxides have a strong affinity for arsenic and other trace elements [9,10]
54 and several iron oxides has been evaluated as soil amendment for reducing arsenic and heavy metal
55 leachability: Ochre from mining activities [11], goethite [12], and water treatment residues [13,14]. In cases
56 of multi element contamination a mix of amendments may prove the best option and can be assessed in a
57 strategic selection framework [15]. However, the long-term ability of the amendment to reduce leachability
58 should also be considered since slow transformation of the reactive minerals to less reactive minerals may
59 occur over longer time [16,17].

60 Iron water treatment residues (Fe-WTR) are a common waste product in Denmark, where the
61 water supply is based entirely on groundwater. With the main constituent (60-70%) being ferrihydrite, an
62 iron hydroxide, it is proposed here as a cheap and efficient soil amendment. No pH buffers are required as
63 for iron(II)sulphate, and the cost is limited to a control element analysis and transport to the site. Numerous
64 laboratory studies with soil amendments using iron oxides have been carried out, but few have tested the
65 methods at field scale [14,18] and applicability has not been discussed and evaluated. Laboratory
66 experiments are often carried out under optimal conditions, and their results may not directly be transferred
67 to full-scale scenarios in the field. Also impacts on the soil amendment such as geochemical processes in
68 the soil influenced by soil moisture and biota are lacking in laboratory experiments. For iron oxide
69 amendments prone to microbial iron reduction it is necessary to test their persistency under natural
70 conditions.

71 For full scale amendments large areas need to be treated so choosing a cost-effective and simple
72 way to mix the treated soil and the amendment is crucial. In considering the options for soil mixing, the
73 depth of the contaminated soil layers to be treated is an important factor. Soil mixing by augers is routinely

74 used in the delivery of zero valent iron (ZVI)-clay mixtures for degradation of chlorinated solvents [19] at
75 depths down to 8 m below ground. However, the equipment is highly specialized and therefore expensive
76 to rent. Trench ploughing, with a common use in forestry and a working depth of about 0.9 m, is an option,
77 but the trench plough has a considerable turning radius and will only reach the maximum working depth
78 after 50 m of ploughing. Another option is to use a screening bucket, a tool used in waste management and
79 soil treatment at construction sites. A screening bucket consists of a screen, capable to hold about 0.5 m³ of
80 soil that is passed through the screen by rotating it. Soil fractions >50 mm (usually stones, but for fill also
81 bricks and concrete pieces) is then retained inside the screen and can be discarded. Adding Fe-WTR as
82 slurry, soil and slurry mixture would pass faster through the screening bucket.

83 This study evaluates the full scale amendment with Fe-WTR at a brownfield contaminated with
84 high levels of As, chromium (Cr) and copper (Cu). To our knowledge this is a novel technology, not tested
85 at full scale before. In designing the full scale approach, emphasis was put on making a low cost method
86 easily applicable to a brownfield, thereby maximizing the options for wide-spread professional use. For
87 evaluation of the retention capacity of the amendment, soil pore water samplers were installed at the site
88 and trace element composition monitored for 12 months.

89

90 **2 Materials and methods**

91 **2.1 Field site**

92 The Collstrop wood impregnation site close to Hillerød, Denmark, has previously been used for soil
93 stabilization with WTR at a small scale [14]. Wood impregnation using As, Cr, and Cu was initiated in
94 1955. Heavily contaminated with As, Cr, and Cu, the site is left as a brownfield in the forest. A sketch of
95 the site with vegetation cover is presented in Fig 1. A profound correlation between vegetation cover and
96 contaminant concentration was found in an earlier study [20] with only very limited vegetation growing at
97 contamination hotspots. For this experiment a bare dripping pad in the eastern part of the site was chosen as
98 test site. At dripping pads the treated wood items were placed for drying. Fig. 1 shows the configuration of
99 the test site and location of the 10 pore water samplers, more than 40 soil samples and 4 shallow wells.

100

101 **2.2 Amendment**

102 Fe-WTRs were collected at Sjælsø Waterworks in Northern Zealand, Denmark, which supplies water to
103 large parts of the greater Copenhagen area. Groundwater is extracted from wells 50 to 120 m below surface
104 in a limestone aquifer, and the water is then aerated and passed through a sand filter for separating iron and
105 manganese oxides from the drinking water. Freshly precipitated Fe-WTR slurry with a natural water
106 content (91.2%, n=5) was used as amendment.

107

108 Chemical analysis and BET (Brunauer–Emmett–Teller) surface area of the solids can be found in Table 1.
109 For further information on the Fe-WTR composition, we refer to the earlier publication [14].

110

111 **2.3 Soil mixing procedure at field scale**

112 Before considering the options for soil mixing, an estimate was made of the volume of soil that needed to
113 be treated at the site. The contaminants originate from dripping of impregnation liquids and as most of the
114 contaminant masses are present in the upper 1 m of the soil profile [14], an estimated 80% of the
115 contaminant mass would be captured by treating the upper 1 m of the soil. Additionally, previous studies at
116 the field site had revealed a hanging water table 1-1.5 m below ground [14]. Adding Fe-WTR below the
117 water table will have little effect, as the highly reactive ferrihydrite is expected to be easily dissolved by
118 reductive dissolution and presumably destroy the effect of the amendment, as the iron oxides are dissolved,
119 releasing all captured contaminants. Thus a treatment depth of 1 meter was chosen. A rotary screening
120 bucket mounted on an excavator was used to mix soil and Fe-WTR slurry. A test field of 10 by 10 m with
121 amendment of Fe-WTR was established. Adjacent to that a 10 by 10 m test site without amendment was
122 established, to act as a control plot for the evaluation of the Fe-WTR amendment efficiency. Pore water
123 was also sampled from an undisturbed soil profile within a few meters from the test fields. For
124 configuration of the test fields see Fig. 1. Fig. 2 shows the rotary screening bucket in action.

125 A slurry-trailer carrying a 4.5 m³ basin, installed with mixers, kept the WTR slurry in suspension
126 to make sure the solids were applied evenly at a rate of 0.12 m³·min⁻¹. Soil and Fe-WTR was mixed in 2
127 steps; excavating to 0.5 m and mixing with half the Fe-WTR slurry, then backfilling and mixing again
128 down to 1 meter depth and adding the other half of the Fe-WTR slurry. A total of 4 m³ was added to the
129 amended field, which was the maximum amount possible to not increase the volume of the stabilized soil
130 significantly. The average added dry Fe-WTR percentage to the dry matter of soil in the 10 m by 10 m by 1
131 m is estimated to 0.22 %(dw). The control field was also mixed in 2 steps, but with no Fe-WTR addition
132 and therefore more difficult to mix because the slurry made it easier for the soil to pass through the
133 screening bucket.

134 During mixing greenish colored concrete pieces were separated from the soil, which are likely
135 remains of the impregnation basins and their greenish color presumably copper-arsenate precipitates. For
136 brownfield management, removing waste fractions like this will improve the esthetic value of the site.

137

138 **2.4 Sampling and monitoring**

139 After soil mixing in late April 2011, the site was left to settle. Soil samples were taken at random spots in
140 the amended and the control plots in May 2011. In total nine composite samples representing the depth 0-
141 0.5 meters depth and 0.5-1 meter depth were sampled for both plots (in total 36 samples). The average
142 composition of the soil in the mixed plot and in the control plot was compared using t-test (P=0.05, n=18).
143 Groundwater wells and soil pore water samplers were installed in early May 2011. As according to the
144 manufacturer of samplers the first 2 L of samples has to be discarded; only samples after June 2011 were
145 analyzed. The experiment was concluded in July 2012 after collecting and analyzing more than 200 water
146 samples.

147 To monitor the composition of soil pore water, 10 PrenArt® pore water samplers were installed at
148 an angle of 45° (to limit rapid flow along the tubing) at depth 0.5 and 1 m below surface. Each sampler was
149 connected to a 1 L Bluecap bottle with 1 kPa vacuum. The bottle was changed every 21-31 d, when the
150 collected amount was sufficient for analysis. Total sample volume and pH were measured and 20 mL
151 samples were filtered through a 0.45 µm hydrophilic PTFE filter and stored at 5°C until analysis. The soil
152 pore water concentrations in the amended and the unamended field plot and in an undisturbed reference site
153 a few meters away were sampled over a 14 month period to monitor potential temporal changes. Both test
154 fields were divided in a 3x3 sampling grid (Fig. 1). Soil samples were collected using a hand auger. A 100
155 g composite sample was taken from each of the 0.5 m homogenized cores at depths 0-0.5 m and 0.5-1.0 m.
156 The samples were dried at 105°C for 24 h and homogenized in an agate mortar. From the homogenized
157 sample 2 g was taken for acid digestion in 7 N HNO₃.

158 A hanging secondary water table was present at the site due to clay layers in the glaciofluvial
159 formation [14]. At the time of soil mixing in late spring it was observed about 1 meter below the soil
160 surface. To measure the water table 2 shallow wells (PE tubing Ø2.2 cm) were installed by hand augering
161 at 1 m depth with 20 cm screen. Water table measurements were done with the same frequency as water
162 sampling.

163

164 **2.5 Element analysis of soil and water**

165 Element content in soil and water samples was determined using a Varian 5000 ICP-OES. A standard
166 reference soil was included for every 30 samples and all measurements of those found to be within 10%.
167 Detection limits for water samples were 0.7 µg·L⁻¹ and for soil samples 35 mg·kg⁻¹ at wavelengths 259.940
168 (Fe) 293.931 (Mn) 327.395 (Cu) 205.560 (Cr) and 188.980 (As) nm.

169 For the last 3 rounds of pore water sampling the speciation of Cr(VI)/Cr(III) and As(V)/As(III)
170 was measured. Visual light spectrophotometric screening for Cr(VI) was done using s-diphenylcarbazide as
171 an indicator (EN 196-10:2006, 2006) with a detection limit of 10 µg·L⁻¹. As(V)/As(III) speciation was
172 done by filtering through an aluminosilicate-containing cartridge, retaining As(V) [21]. The As(V)
173 concentration was then calculated as the difference between As(III) and the total As content.

174

175 **2.6 Physical properties of soil and WTR**

176 BET surface area was measured by the N₂ adsorption method [22]. For soil and WTR properties such as
177 geological characterization, grain size and distribution see [14].

178

179 **3 Results and discussion**

180 **3.1 Distribution of the amendment**

181 The analysis of the homogenized core samples showed only a slight difference in iron content with an
182 average of 4815 mgFe·kg⁻¹ (range 1193-6124 mgFe·kg⁻¹) in the control field and 5360 mgFe·kg⁻¹ (range
183 3805-13304 mgFe·kg⁻¹) in the amended (Table 1). A difference of 0.13 wt % Fe was found in the upper 0.5

184 m of soil between the treated and the untreated field and there was no significant (*t*-test, $P=0.05$, $n=18$)
185 difference between iron concentrations in the lower parts of the two fields. The iron amendment was not
186 sufficiently distributed, as the upper 0.5 m in the treated field has a mean value of $6140 \text{ mgFe}\cdot\text{kg}^{-1}$ and the
187 lower only slightly more than the natural background value of $4815 \text{ mgFe}\cdot\text{kg}^{-1}$. Iron distribution in soil
188 layers is shown in Fig. 3, which also reveals a high variability in the background level of iron content with
189 high iron content at the bottom of the control field, may be a soil horizon formed by the natural
190 pseudogleyic conditions in the soil.

191

192 **3.2 Leaching of contaminants in the amended soil**

193 Soil pore water concentrations are a tool to evaluate the most mobile fraction of trace elements in soils [23].
194 Pore water concentrations of As (Fig. 4b+c), Cr (Fig. 5a+b) and Cu (Fig. 5c+d) are decreased as the
195 addition of Fe-WTR significantly reduces the mobile fraction of contaminants in the soil. Comparing all
196 data points for the full year of sampling, the soil amendment reduces pore water concentrations in the
197 mixed fields with 93% for As, 91% for Cu and 95% for Cr in the shallow (50 cm below ground) samplers
198 and 75% for As, 89% for Cu and 97% for Cr in the deeper samplers when comparing with the control site.
199 This difference shows that the upper soil has obtained a larger retention for As and that the lower part of
200 the treated field did not receive a sufficient amount of the Fe-WTR. In terms of the Danish groundwater
201 quality criteria, the dose of Fe-WTR was not sufficient. The average As concentration for amended soil
202 (upper samplers) is $328 \mu\text{g}\cdot\text{L}^{-1}$ and does not comply with the groundwater criteria of $8 \mu\text{g}\cdot\text{L}^{-1}$ [24], but the
203 leaching of contaminants has been significantly reduced. Studies using iron oxide amendment for
204 stabilization has typically used a higher percentage of iron oxides added to the soil to obtain better
205 contaminant retention: 5-15 wt% [25] or 1-8% [18] oxygen scarfing granulate (69% magnetite) or 2.5-5.0
206 wt% ochre (likely ferrihydrite, calcite and aragonite) [11]. Average Fe-WTR addition obtained in this full
207 scale study was about 0.22 wt % of the amended soil. The amendment is to be increased to a range of 1-2
208 wt% in future full scale projects.

209

210 **3.3 Speciation of As and Cr**

211 As toxicity and mobility in soil and groundwater is hugely dependent on speciation, a chemical speciation
212 As and Cr was done in the last 3 rounds of pore water sampling as mentioned in the material and methods
213 section. As no Cr(VI) was found in the pore water, all chromium at the site is assumed to be Cr(III) which
214 is consistent with the low solubility of chromium hydroxides in soil [26] and the observed low pore water
215 concentrations. Only two samples contained more than 5% As(III), which means that the overall speciation
216 of arsenic at the site is consistent with aerobic conditions. These two samples with 8.5% and 20% As(III)
217 were from the deep sampler in the untreated field. This correlates well with the fact that the deep samplers
218 at 90 cm below ground are likely to be below the water table and that this field had the high iron
219 concentrations in the pore water, suggesting somewhat reducing conditions.

220

221 3.4 Effect of water logged conditions

222 Reductive dissolution of iron oxides can happen as the soil gets saturated with water and release of sorbed
223 arsenic takes place accordingly [27-29]. The rate of reductive dissolution of iron (hydr-)oxides depends on
224 mineral type, crystallinity and aggregate size [30,31]. For Fe-WTR amendment the reaction rate is expected
225 to be very high as the main constituent is ferrihydrite, the most reactive iron hydroxide for the above
226 mentioned reasons.

227 Water table measurements are shown in the top right corner of Fig. 4a, which also shows the total
228 iron concentration of the sampled pore water in Fig 3 d+e. Only for the unamended field did iron
229 concentrations in the pore water increase (up to around $400 \mu\text{g}\cdot\text{L}^{-1}$) in the period from late August to
230 December. Small amounts of iron (up to $100 \mu\text{g}\cdot\text{L}^{-1}$) were found after December, despite the water table
231 only slowly decreased during the months of January to March. Temperature dependence of iron reduction
232 rates in soil with the release of Fe and As have been reported to strongly slow down when the temperature
233 decreases from 23°C and 14°C to 5°C [29]. If this is part of the explanation it implies that a coincidence of
234 the cold season with the infiltration season, as seen here, is beneficial where waterlogging may occur.

235 As no increase in dissolved iron is seen in the iron amended soil, not even during water logging, it
236 suggests that the iron amendment is resistant to iron reducing conditions. Microbial activity in the soil may
237 be low due to the high contents of contaminants [32]. Especially copper has been shown to have a toxic
238 effect on iron reducing bacteria, thereby halting iron reduction [33]. However as the copper concentration is
239 almost identical in the fields, this cannot be the sole explanation. If the reduction of iron oxide in the soil is
240 not complete due to an excess of iron oxide in the soil (which is likely to be the case for the Fe-WTR
241 amended soil), it is possible that iron and arsenic is retained in the soil. Fe^{2+} competes for arsenate on the
242 ferrihydrite surface [34], so the Fe^{2+} released by iron reduction may not be released to the water phase in
243 the amended soil. Likewise the release of As to the aqueous phase does not happen until the number of
244 surface sites on the ferrihydrite surface is too small to adsorb all arsenic [28].

245 Another approach is to study the manganese concentrations in the soil pore water (Fig. 3f+g). Fe-
246 WTR contains a substantial amount of manganese oxides, precipitated with the iron oxides, and the
247 background concentration of manganese (in average $198 \text{ mg}\cdot\text{kg}^{-1}$) is relatively smaller compared to the
248 amount of WTR added to the soil. Manganese reduction is thermodynamically favored over iron reduction,
249 so a high porewater concentration of manganese indicates WTR dissolution, as can be seen in Fig. 3, where
250 a peak in the Mn concentration is correlated with a high water table (Fig. 4a).

251

252 3.5 Mechanical treatment of soil

253 Based on the As and Fe (Fig. 4bcde) as well as the Cr and Cu (Fig. 5abcd) pore water concentrations, the
254 mechanical treatment of mixing the soil without adding Fe-WTR has a significant effect on the levels of all
255 measured elements in the soil pore water. This indicates that the mixing of contaminated soil increases the
256 leaching of elements, possibly due to release of fine colloids mobilized with the mechanical treatment of
257 the soil. Addition of iron oxides to a soil do change the mechanical properties of soil and ferrihydrite, the

258 main constituent of Fe-WTR, has even been proposed as a clearing agent to reduce turbidity in fresh water
259 [35]. A cementing effect of Fe-WTR may limit the colloidal transport of elements and this effect can
260 account for some of the difference in metal(loid) leaching in the two mechanically treated fields. This
261 observation suggest that the mechanical treatment of soil, for instance in the case of excavation and
262 landfilling, may increase the leaching of contaminants, but this effect can be avoided with the addition of
263 Fe-WTR.

264

265 **4 Conclusions**

266 Stabilization with Fe-WTR in full scale proved to be fairly simple to apply to the contaminated site.
267 Despite insufficient application of amendment, the field experiment provides valuable insight in the
268 practical application of an iron oxide based soil amendment. Leaching of As, Cr, Cu, as measured by pore
269 water concentrations, was significantly reduced in the Fe-WTR amended soil compared to both a
270 mechanically mixed, but not amended, soil and an undisturbed soil. Even with an iron addition of only 0.22
271 wt%, the amendment caused a significant stabilization, but more Fe-WTR than applied in this study is
272 needed to comply with ground water quality standards. Despite water logged conditions in the lower parts
273 of the soil, no clear signs of iron reduction and subsequent contaminant release were observed. Manganese
274 was however released from the treated soil, suggesting that the Fe-WTR is subject to partial reductive
275 dissolution.

276 The distribution of soil amendment achieved with a screening bucket was satisfying for the upper part of
277 the soil, but it proved more difficult, at least in this very first attempt, to amend the soil from 0.5 to 1 m
278 below surface. In any case, mechanical treatment or mixing of metal(loid) contaminated soil should be
279 avoided as it mobilizes dissolved (or colloiddally transported) contaminants into the soil pore water.
280 However Fe-WTR treatment prevents this, possibly because of inter-particulate cementation processes. As
281 the dose of WTR and difficulties with proper mixing are rather easy obstacles to overcome, we propose this
282 method for use *in situ* at other contaminated sites.

283

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289

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291

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377 **Tables**

378

379 **Table 1** Average solid concentrations and BET surface area of soil and Fe-WTR and average speciation of
 380 pore water in the amended field, control field and undisturbed soil. Number of samples, *n*, are given in
 381 parenthesis). For pore water numbers in parenthesis are lowest and highest measured value of As(III) in
 382 $\mu\text{g}\cdot\text{L}^{-1}$. Basic soil properties are given in [Error! Bookmark not defined].

		As	Cr	Cu	Mn	Fe	BET	As(III)/As(V)	Cr(III)/Cr(VI)
		[mg·kg ⁻¹]				[mg·kg ⁻¹]	[m ² ·g ⁻¹]	[-]	
Amended field	0-0.5 m (<i>n</i> =9)	563	205	598	325	6140	1.654	2.3 (0.1-3.7) (<i>n</i> =7)	>99.9 (<i>n</i> =7)
	0.5-1 m (<i>n</i> =9)	430	133	423	227	4580	1.632		
Control field	0-0.5 m (<i>n</i> =9)	539	156	378	198	4830	1.859	11.1 (4.2-20) (<i>n</i> =3)	>99.9 (<i>n</i> =3)
	0.5-1 m (<i>n</i> =9)	572	149	386	189	4800	1.911		
Undisturbed field		-	-	-	-	-	-	1.2 (0.4-3.5) (<i>n</i> =4)	>99.9 (<i>n</i> =4)
Fe-WTR	(<i>n</i> =5)	46.1	13.0*	36.6	8489.8	28.6%	160.3	-	-

*below analytical quantification limit - not measured

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Figure captions

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393 **Fig. 1** Sketch of vegetation Collstrop Brownfield, a former wood impregnation plant. Vegetation is drawn
394 based on observations from [Error! Bookmark not defined.], but is generally in agreement with author
395 observation within recent years (left). Configuration of the full scale soil stabilization experiment with
396 location of pore water samplers, shallow wells and soil samples. Two soil samples were taken at each
397 sampling point (top right) .

398

399 **Fig. 2** Pictures from the amendment action showing the used rotary screening bucket.

400

401 **Fig. 3** Total iron concentration in the two test fields after application of water treatment residues (WTR)
402 amendment to the northern field. The size of the bubble denotes the iron concentration

403

404 **Fig. 4** Soil pore water concentrations of redox sensitive elements As(b+c), Fe(c+d) and Mn(e+f) and
405 average water table (a). Left column shows pore water samplers in 50 cm depth and the right 100 cm depth.
406 Data points are average of two samplers for elements and four for the water table. Error bars denotes the
407 high and low value. If no error bars are shown, the data point consists of a single measurement from one
408 sampler

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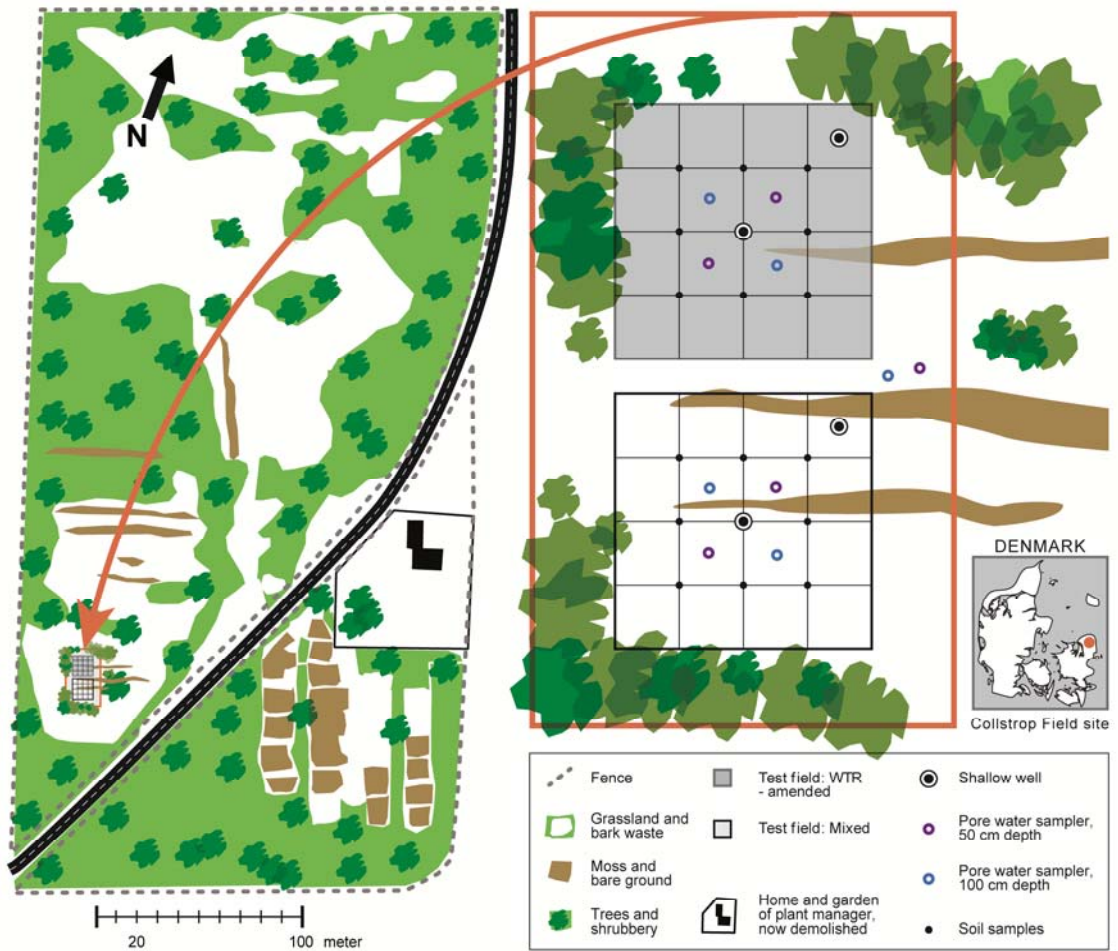
410 **Fig. 5** Soil pore water concentrations of Cr (a+b) and Cu (c+d). Data points are average of two samplers.
411 Error bars denotes the high and low value. If no error bars are shown, the data point consists of a single
412 measurement from one sampler

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Fig.1



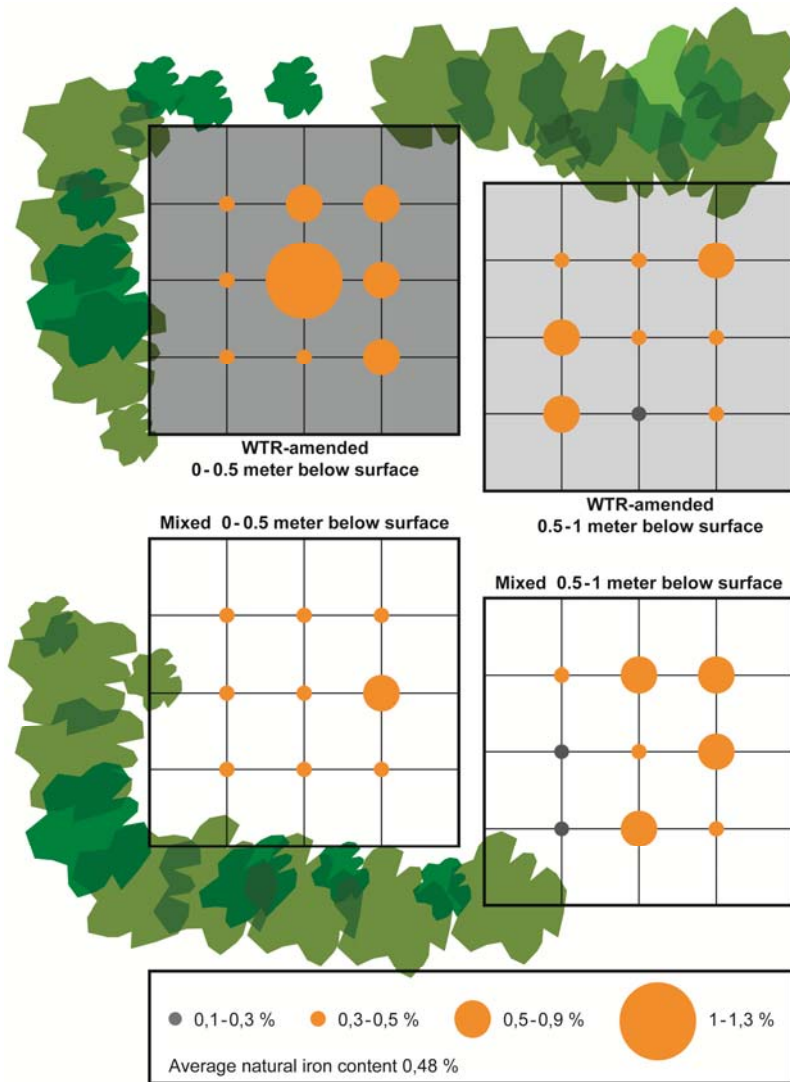
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Fig. 2a



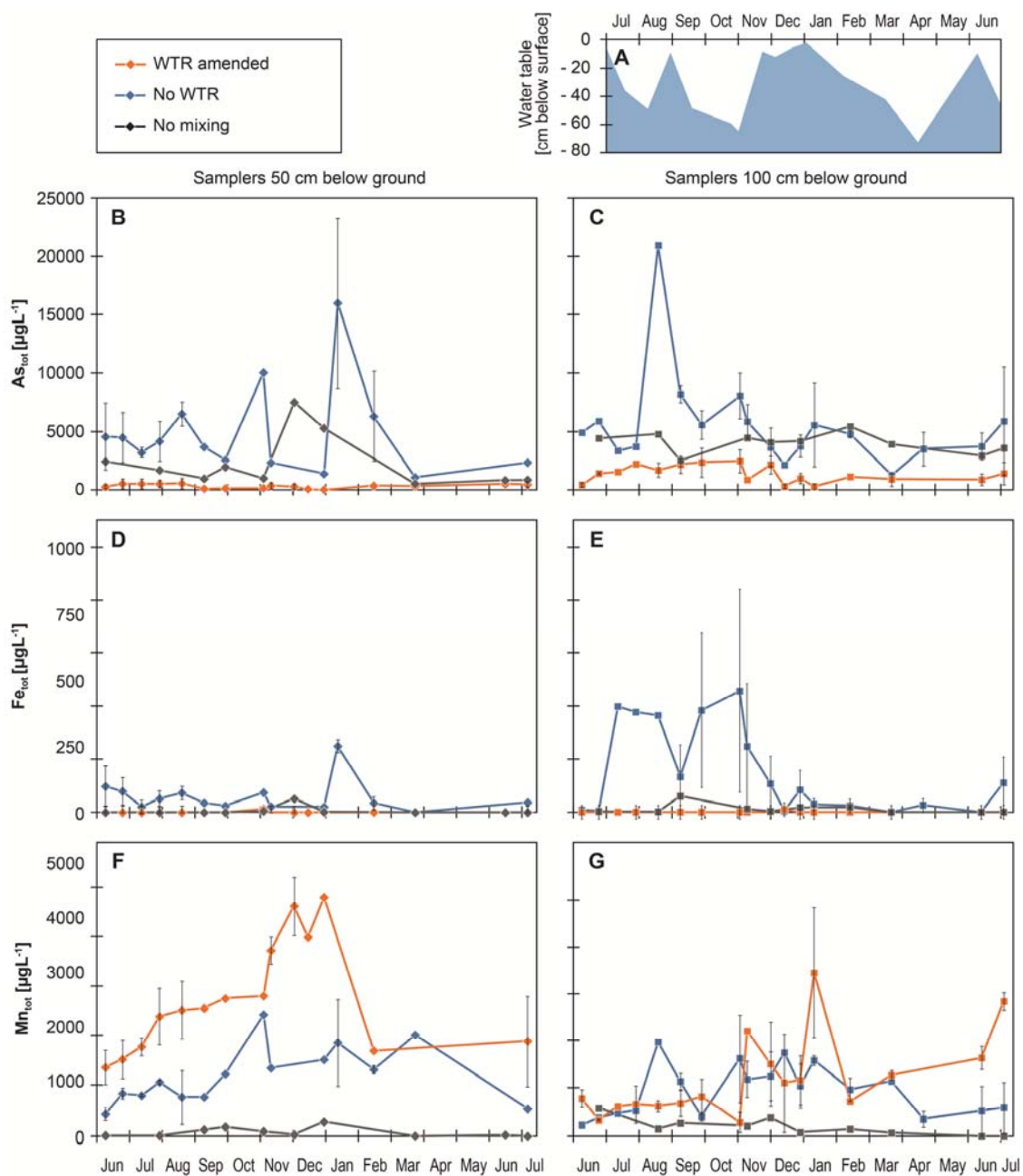
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Fig. 2b



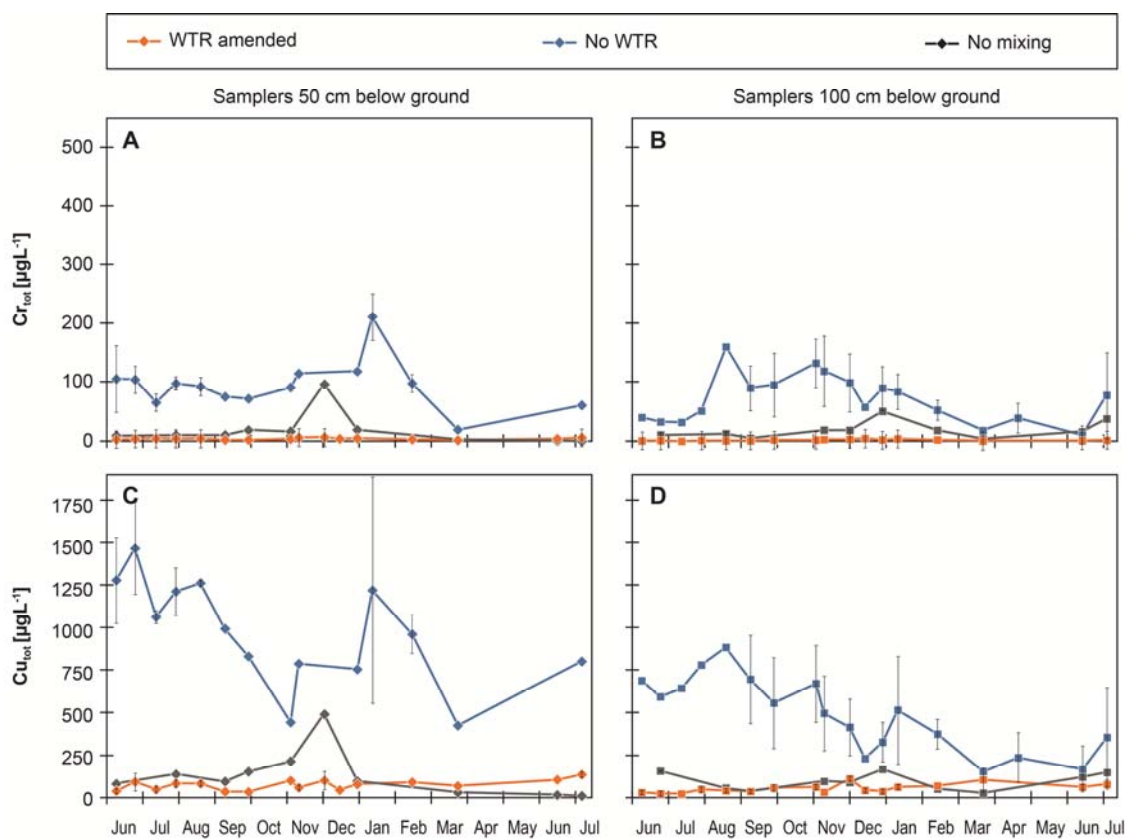
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Fig. 3



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Fig. 4



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Fig. 5