Technical University of Denmark



Test of Tree Core Sampling for Screening of Toxic Elements in Soils from a Norwegian Site

Nielsen, Mette Algreen; Rein, Arno; Legind, Charlotte Nielsen; Amundsen, Carl Einar; Gosewinkel Karlson, Ulrich; Trapp, Stefan

Published in: International Journal of Phytoremediation

Link to article, DOI: 10.1080/15226514.2011.620648

Publication date: 2011

Link back to DTU Orbit

Citation (APA):

Nielsen, M. A., Rein, A., Legind, C. N., Amundsen, C. E., Gosewinkel Karlson, U., & Trapp, S. (2011). Test of Tree Core Sampling for Screening of Toxic Elements in Soils from a Norwegian Site. International Journal of Phytoremediation, 14(4), 305-319. DOI: 10.1080/15226514.2011.620648

DTU Library Technical Information Center of Denmark

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.

- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Test of Tree Core Sampling for Screening of Toxic

2 Elements in Soils from a Norwegian Site

3	
4	Mette Algreen Nielsen ¹ , Arno Rein ¹ , Charlotte N. Legind ¹ , Carl Einar Amundsen ² , Ulrich
5	Gosewinkel Karlson ³ and Stefan Trapp ^{1,*}
6	
7	1 Department of Environmental Engineering, Technical University of Denmark, 2800 Kgs.
8	Lyngby, Denmark
9	
10	2 Bioforsk Soil and Environment Division, Fredrik A Dahlsvei 20, N-1430 Ås, Norway
11	
12	3 National Environmental Research Institute, Aarhus University, Frederiksborgvej 399, 4000
13	Roskilde, Denmark
14	
15	* Corresponding author:
16	Stefan Trapp, Department of Environmental Engineering, Miljøvej building 113, DK-2800
17	Kgs. Lyngby, Denmark, Tel.: +45 4525 1622 Fax: +45 4593 2850 E-mail: sttr@env.dtu.dk
18	

19 Abstract.

20 Tree core samples have been used to delineate organic subsurface plumes. In 2009 and 2010, 21 samples were taken from trees growing on a former dump site in Norway and analyzed for 22 arsenic(As), cadmium(Cd), chromium(Cr), copper(Cu), nickel(Ni) and zinc(Zn). Concentrations in soil were in averages 30 mg/kg dw for Zn, 2 mg/kg dw for Cu, and < 123 24 mg/kg dw for Cd, Cr, As and Ni. The concentrations in wood samples from the polluted test 25 site were compared to those derived from a reference site. For all except one case, mean 26 concentrations from the test site were higher than those from the reference site, but the 27 difference was small and not always significant. Differences between tree species were 28 usually higher than differences between reference and test site. Furthermore, all these 29 elements occur naturally, and Cu, Ni and Zn are essential minerals. Thus, all trees will have a 30 natural background of these elements, and the occurrence alone does not indicate soil 31 pollution. For the interpretation of the results, a comparison to wood samples from an 32 unpolluted reference site with same species and similar soil conditions is required. This 33 makes the tree core screening method less reliable for heavy metals than, e.g., for chlorinated 34 solvents. 35 36 37 38 **Keywords:** Heavy metal; Soil; Wood; Polluted; Plant uptake; Monitoring 39 40

41 **1 Introduction**

42

43 Biomonitoring for heavy metals is an established technique (Markert 1993, Markert et al. 44 1999). Mosses, lichens, but also trees and tree rings have been sampled to determine the 45 concentration level of heavy metals in the environment (Gratani, Crescente, and Varone 46 2008, Markert and Wtorova 1992, Monticelli et al. 2009, Migeon et al. 2009). 47 Phytoscreening is a new term and was given for the use of vegetation samples to screen 48 subsurface pollution (Sorek et al. 2008). The technique to take tree cores to track pollution 49 plumes below surface has been found to be a simple, fast, noninvasive and inexpensive 50 screening method (Vroblesky, Nietch and Morris 1999, Ma and Burken 2002, Schumacher, 51 Struckhoff and Burken 2004, Gopalakrishnan et al. 2007, Trapp et al. 2007, Sorek et al. 52 2008, Larsen et al. 2008). The principle is that roots take up pollutants from soil or shallow 53 groundwater. With the transpiration stream, the contaminants are transported above the 54 surface and into the stem, where they adsorb to the wood and other plant parts. Wood is 55 sampled with a tree corer and analyzed for the pollutants. Elevated concentrations in wood indicate subsurface contamination (Vrobelsky et al. 1999). The method is rapid, simple, 56 cheap, and allows a high sample number in short time without heavy equipment. Tree core 57 58 sampling is thus seen as a reliable and inexpensive alternative method for investigating and 59 monitoring the extent of shallow pollutants (Larsen et al. 2008). Subsequently, tree core 60 sampling was recommended for initial screening of an area (Sorek et al. 2008) and for 61 assessing the presence of pollutants (Larsen et al. 2008), and the method is used frequently in practice now (unpublished engineering work). However, so far all studies have dealt with 62

chlorinated solvents, such as trichloroethylene (trichloroethene, TCE), tetrachloroethene
(PCE) and trichloroethane.

65

66 The purpose of this study was to test the tree core method for toxic elements, such as arsenic 67 and heavy metals. Arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni) and 68 zinc (Zn) are frequent pollutants in soil, mainly from human activities but also from natural 69 sources. At elevated levels, all these are toxic to humans and wildlife, and their occurrence in 70 soil is regulated by legal standards in most countries. Their dissolution in soil solution and 71 the subsequent uptake into vegetation depends on chemical speciation (and thus pH and 72 redox potential), on organic matter, clay content, and on the concentration of other ions 73 (Barber 1995, Hough et al. 2004, US EPA 2005, Swartjes et al. 2007, Legind and Trapp 74 2010). The bioavailable fraction in soils may decrease with time, leading to reduced uptake 75 (Kirkham 2006). Fungi may facilitate transport to roots (Smith et al. 2010).

76

77 The individual elements may - depending on their xylem or phloem transport - move 78 preferably into different plant parts, i.e. roots, stem, leaves and fruits (Thorne, Walke and 79 Maul 2005). Wood was sampled because it is protected from aerial deposition, it is available 80 throughout the whole year (samples were taken in winter) and it does not change much with 81 time (as leaves do). A disadvantage is that little is known about the uptake of toxic elements 82 into wood since most studies focus on edible plant parts such as fruits or leaves. Thus, data about accumulation of toxic elements in wood are needed, also for an assessment of the 83 84 feasibility of phytoextraction.

86	Wood from trees (mainly birch, willow and poplar) growing on a former dump site was
87	sampled and analyzed for As, Cd, Cr, Cu, Ni and Zn. The concentrations were compared to
88	those from trees of the same species growing outside the contaminated area. The objectives
89	of this study were to determine typical concentration levels in wood and to test the tree core
90	sampling method for the screening of subsurface pollution with toxic elements (focus on
91	heavy metals).
92	
93	2 Methods
94	
95	2.1 Test site
96	The Møringa (former) dump site near Horten, Norway, is an artificial half-island at the Oslo
97	fjord created by the dumping of waste. From the 19th century until 1993, it has received
00	waste oil oil distillary waste walding slags blowing sand and building residues, originating

) d waste oil, oil distillery waste, welding slags, blowing sand and building residues, originating 98 99 from ship yards, oil recycling, ship and aircraft maintenance, and lead battery production. 100 Investigations of the site between 1992 and 2005 (Amundsen et al. 2005) revealed that the 101 site is contaminated with large amounts of heavy metals, petroleum products, polycyclic 102 aromatic hydrocarbons and polychlorinated biphenyls. On the site, wild-type pioneer 103 vegetation consisting of grassland and trees (such as willow, poplar, birch and cherry) has 104 developed.

105

106 The depth of the waste deposit is approximately 3 m. The cover at the Møringa waste site

107 consists of 0.2 to 0.5 m clean soil. The concentrations of the elements of interest in this cover

108 are unknown but it can be assumed that they are close to natural soil (background levels).

109 All soil samples from the site are composite samples (30-50 kg), where each was taken from deep (2-4 meters) pits of an area of about 16 m^2 (4 x 4 meter). The main aim of the sampling 110 111 in 2004 (Amundsen et al. 2005) was to investigate the leaching potential of toxic elements in 112 the waste to predict the future influence of the waste site on the local marine environment. 113 Most waste samples were therefore collected from the lower part between groundwater table 114 and 1 m above groundwater table, but some were also taken from the upper part of the 115 deposited waste. Eight risk zones were mapped, each with relatively homogeneous waste filling (Fig. 1). Concentrations of toxic elements in deposited material from the eastern part 116 117 of the landfill (Ø1, Ø2 and Ø3) are significantly higher than in most of the western areas (V4 118 to V8) (Tab. 1), but the concentration level of pollutants seems to be quite uniform with 119 depth.

120

121 <Figure 1>

122 <Table 1>

123

124 2.2 Tree core sampling

Tree core sampling was performed at the Møringa site on the 8th and 9th of July 2009 and on 125 the 30th of March 2010. Trees were sampled in the eastern part of the site which is densely 126 covered by trees. Sampled tree species were predominantly birches (Betula sp.) and willows 127 128 (Salix caprea), but included also cherry (Prunus sp.), aspen (Populus tremula), ash (Fraxinus 129 excelsior) and mountain ash (Sorbus aucuparia) in the first campaign. Only willow (Salix 130 *caprea*) and poplar (*Populus tremula* and other poplar species) were sampled in the second 131 campaign. Reference samples were taken 20 to 50 m outside the area of the dump site, and at 132 a location about 10 km away. All reference samples were closer to urban area (Møringa Submitted to International Journal of Phytoremediation

peninsula is the remotest place in this area), and contamination from other sources thandumped waste can not be excluded.

135

136 All tree cores were taken at a stem height of 1 m using a 6 mm increment borer (Suunto, 137 Finland). Tree cores had a length of 6 cm, where the outer centimeter (containing the bark) 138 was discarded to avoid atmospheric influence. Only in 2009, the next centimeter (cm 1-2 139 towards stem center) was used for mixed samples, and cm 2-6 made up an individual sample. 140 Mixed samples were collected in order to represent subareas, including between 3 and 9 141 individual tree cores. The aim here was to test whether the analysis of one mixed sample (i.e. 142 several trees in the area of interest) instead of many individual samples (one per tree) is an 143 appropriate method for subsurface characterization, as this would save laboratory efforts. 144 During the second campaign, wood from cm 1 to 5 was used as sample, and two replicates 145 from each tree were taken.

146

147 2.3 Extraction and chemical analysis

148

Soil samples were dried at 40 °C to constant weight, extracted with aqua regia (concentrated
hydrochloric acid: concentrated sulfuric acid 3:1) and analyzed using ICP-AES (Amundsen
et al. 2005).

152

Wood samples from the first campaign were extracted using an autoclave. The wood samples were dried at 75-85 °C to constant weight. Between 0.5 and 0.8 g of the dried sample was weighed into 100 ml blue cap bottles, then 10 ml 65% HNO₃ and 10 ml miliQ water were

added. The sample was autoclaved for 30 min at 125 °C and cooled to room temperature afterwards. 5 ml 30 % H_2O_2 were added and the sample was placed on a sand bath for 20 min without cap. The sample was quantitatively transferred to a 50 ml volumetric flask. MiliQ water was added to the total volume of 50 ml. The flasks were shaken for 1 min and the sample was then filtered into a plastic (PE) bottle for storage at room temperature. Before analysis, 7 ml of sample was transferred to a test tube and then analyzed using ICP-OES.

162

Some samples of the first campaign had unusually high concentrations of Cu, Ni and Zn, and we found that the procedure erratically contaminated samples during extraction. Even though these samples could be identified, the results for Ni and Cu from the first campaign were discarded (the results for Zn could be used, though with a high DL, because the concentrations were sufficiently above the laboratory background), and the method was optimized and changed to sand bath extraction for the second campaign.

169

170 For the sand bath method, wood samples were dried as before. Between 0.5 to 0.8 g of the 171 dried sample were weighed into a 50 ml volumetric flask. Then 10 ml 65 % HNO₃ was 172 added, and the flask was placed on a sand bath for 2 hours at 70-80 °C. Samples were then 173 removed and cooled at room temperature for 10 min. Afterwards, 2.5 ml 30 % H₂O₂ were 174 added and the samples were placed back on the sand bath until the gas reaction was completed. The procedure was repeated with additional 2.5 ml 30 % H₂O₂. MiliQ water was 175 176 added to get 50 ml volume. After shaking for 1 min, approximately 5 ml of sample were 177 transferred to a centrifuge glass, shaken and emptied. The rest of the sample was transferred 178 to the same centrifuge glass and centrifuged for 10 min with 2500 rpm. The supernatant was

transferred to plastic (PE) bottles for storage at room temperature. For analyses, 7 ml ofsample were transferred to test tubes and then analyzed at ICP-OES.

181

182 The methods were validated by comparison to the referenced soil standard QC Loam Soil

183 (Sigma Aldrich, DK). All concentrations for soil and wood are given for the dry weight

184 (dw).

185

186 2.4 Statistics

187 The main question of the study was whether the concentration of toxic elements in wood 188 from trees on contaminated sites is elevated, compared to reference sites. This was tested 189 using a one-tailed t-test with an error probability of 0.05 ($\alpha = 5\%$). The distribution of the 190 experimental data was tested using the Kolmogorov-Smirnov (KS) test for continuous 191 distributions, implemented in the software Crystal Ball. Three distributions were tested, 192 namely normal, log-normal and uniform (rectangular) distribution. The assumption of 193 equality of sample distribution and tested distribution was rejected if the distance between 194 both was above a critical distance D_{crit}. These critical distances were taken from Sachs 195 (1991). For calculation of mean, standard deviation, minimum, maximum, F-test and t-test, 196 values below detection limit were replaced by 1/2 detection limit. The data for Ni and Cu 197 from the first campaign were not statistically analyzed, as well as the results for As from the 198 second campaign, which were close or below to detection limit.

199

The statistical difference between the measured concentration in the mixed sample and the concentrations in the corresponding individual samples was tested using the "one-value ttest" (Bahrenberg, Giese and Nipper 1990). The tested t-value is

203

$$204 t_{test} = \frac{\left| x - a \right|}{\frac{s}{\sqrt{n}}}$$

205

206 hereby, x is the mean of the individual samples $(n \ge 3)$ and a is the concentration of the mix

207 sample (n = 1, i.e. the fixed value). The null hypothesis H_0 is rejected if t_{test} is above the t-

208 distributed t_{crit} with degree of freedom (df) = n-1 and α = 5%.

209

211 **3 Results**

212

Table 2 shows the overall characterization of the wood samples from Møringa. Highest 213 concentrations were measured for zinc, followed by copper (2nd campaign only). The other 214 215 elements (As, Cd, Cr, Ni) had similar concentrations, most of them below 1 mg/kg. The 216 concentration results from the first campaign were typically more log-normal than normal 217 distributed, which makes a statistical analysis with parametrical methods critical. For all 218 results from the second campaign, normal distribution could be accepted. The measured 219 concentration level was for all elements quite similar in campaign one and two. Only 220 cadmium showed distinctly higher values in wood from the second campaign. The reason is 221 that exclusively willows and poplars were sampled, and those species showed the highest 222 cadmium uptake of all trees that were sampled at the site.

223

224 Table 3a shows the comparison of results from reference and test site from the first 225 campaign. The mean values of arsenic from reference and test site were significantly 226 different, but it should be noted that all values from the reference site were below DL. The 227 concentrations of cadmium were far higher in willow wood than in birch wood. The 228 difference between reference and test site was significant for both birch and willow. For 229 chromium, concentrations in willow wood were also higher than in birch wood, and elevated 230 at the test site, though not significant. For zinc, a significant difference was found only for 231 willow wood, even though concentrations in birch were higher.

232

From campaign one, it became obvious that willow and poplar trees took up most elements in
higher concentration than birch, cherry and ash. Also, the difference of concentrations in
Submitted to *International Journal of Phytoremediation*

wood from the test site, compared to those from the reference site, was more pronounced. This was the reason to choose willow and poplar, both from the family *Salicaceae*, as preferred species for the second campaign. In the second campaign (Table 3b), Cu was found to be significantly increased in the wood from the test site. The concentration for Cd were elevated in samples from test site for willows and reduced for poplar. Ni and Zn were elevated in samples from the test site, and only significantly for poplar. The mean concentrations of Cr were similar in all samples.

242

The test for differences between mixed samples taken during the first campaign (cm 1-2, first campaign only) and the individual samples, by which the mixed sample was composed, yielded that in about half of the cases there was a significant difference (one-value t-test, $\alpha =$ 5%), and in the others not. Mixed samples can reduce the sample number, but due to the relatively small differences between trees from reference sites and those from the test site, a high sample number is preferable, to get better statistics.

249

250 <Table 2>

- 251 <Table 3 ab>
- 252
- 253

254 4 Discussion

255

4.1 Differences in uptake between test and reference site

257 The main objective of the study was to test the feasibility of phytoscreening for toxic 258 elements. This was done by comparing concentrations of As, Cd, Cr, Cu, Ni and Zn in wood 259 samples from the Møringa dump site (test site) with concentrations in samples from nearby 260 reference sites. The results (Table 3) show that in all except one case (Cd in poplar wood), 261 the average concentrations of the investigated toxic elements were higher in wood from the 262 test site. This is promising. However, the differences were sometimes very small, and 263 individual trees from the reference site may show much higher content than trees from the 264 test site. Figure 2 shows some typical results. Figure 2 a (Cr in willow wood) displays a 265 situation where the mean concentrations in wood from the test site (0.41 mg/kg) is much 266 higher than those in wood from the reference site (0.24 mg/kg). Still, the second highest concentration of all samples was measured in wood from a reference tree, and the difference 267 268 of the means is statistically not significant (Tab. 3a). Contrary, Figure 2 b (Cu in willow) 269 shows an example where this difference is statistically significant. Indeed, the concentration 270 level in wood from the test site is clearly elevated. Nonetheless, individual trees from the 271 reference site may have concentrations above individual trees from the test site. This 272 demonstrates that the method - if applied - requires sampling of a many trees to avoid false 273 conclusions.

274

275 Elevated concentrations of toxic elements in trees from contaminated sites were also reported276 by other authors.

277

278 Arsenic in tree rings was measured and related to pollution by Markovic et al. (2009). The 279 concentration in individual tree rings varied largely over the years. The average concentration 280 of arsenic in poplar wood was 12.9 mg/kg in wood from the less polluted and 20.2 mg/kg in 281 wood from the more polluted site. In a study with birch growing on a chromite processing 282 waste site and willows growing on a sewage disposal site. Cr was poorly taken up into the 283 aerial part of the plant (i.e. all values, including wood, were below DL = 5 mg/kg). Cr was 284 measurable only in the roots. Zinc levels in wood from contaminated sites were above 200 285 mg/kg (Pulford, Watson and McGregor 2001).

286

287 < Figure 2 ab >

288

289 4.2 Differences between tree species

The difference between tree species (birch and willow, willow and poplar) was for two heavy metals (Cd and Cr) larger than the difference between test and reference site. For two heavy metals (Ni and Zn), the variation due to species was approximately as large as the difference between the sites, and only for two elements (As and Cu) the site was mainly determining the concentrations in wood. This means that for a comparison between reference and test site, the same tree species must be chosen. This will not always be possible.

296

Some tree species (e.g., willow) were better suited than others (e.g., birch). In the study of Migeon et al. (2009), who measured the uptake of heavy metals into 25 tree species growing on polluted soils, cadmium was highest in Salicaceae family members, identical to our

300 finding. Under unpolluted conditions, the normal Cd concentration level in plants is 0.1 301 mg/kg and the maximum is 0.2 mg/kg (Kirkham 2006). In our study, concentrations in wood 302 were below this range, except for *Salicaceae* (willow and poplar). Large variations between 303 species were also found at a French site (Migeon et al. 2009) for Cd. Cr and Zn, and less for 304 Cu. Concentrations varied with age of the tree ring (Monticelli at el. 2009), and Hagemever 305 and Schäfer (1995) found a variation of the concentrations of cadmium, lead and zinc with 306 season. Riddell-Black, Pulford and Stewart (1997) found a certain natural variability of the 307 accumulation even within the same species. Arsenic uptake into needle trees was measured 308 by Haug, Reimer and Cullen (2004). Spruce tree samples from an arsenic-rich site had total 309 As concentrations between 0.04 and 0.13 mg/kg, i.e., even below the values obtained here, 310 while concentrations in Douglas pine were much higher, up to 176 mg/kg in stem. The 311 concentration in new-grown stem was higher than in old stem.

312

313 Copper, nickel and zinc are essential micronutrients. According to Marschner (1995), the 314 average concentration of copper in plant shoots that is sufficient for adequate growth is 6 315 mg/kg dw. Concentrations of copper found in wood from Møringa ranged from 0.5 to 5 316 mg/kg. Average concentration of nickel in plant shoots that are sufficient for adequate 317 growth are about 0.1 mg/kg (dw). Nickel concentrations in wood from the Møringa site 318 ranged from 0.12 to 0.75 mg/kg. Zinc concentrations in dry shoot of 20 mg/kg are required 319 for growth (Marschner 1995). Measured concentrations in wood ranged from < 10 to 97 320 mg/kg. Plants can not grow without a certain minimum level of these elements (Marschner 321 1995). The presence of these metals alone can therefore never be a proof for soil or 322 groundwater pollution. Furthermore, it is likely that the uptake of the essential elements is

enzyme-regulated and thus follows Michaelis-Menten kinetics (Barber 1995, Chen et al.
2008, Trapp et al. 2008). This means that the uptake decreases with higher environmental
concentrations (Markert et al. 1999). It also follows that the concentration differences in
wood will be smaller than those in soil, making the detection of subsurface contamination
from differences in wood concentrations more difficult.

328

329 4.3 Limitations

330

331 Concentrations of heavy metals in soil at the Møringa site were determined in a separate 332 study, and only at few sample points. It is therefore not possible to compare concentrations in 333 trees to those in soil, i.e., a correlation of concentrations is not possible. Furthermore, the 334 waste with high pollutant concentrations was covered with a less-polluted layer of soil, which 335 was thick enough so that the trees probably were not in contact with the more toxic 336 underground. Only few soil samples were taken from the cover (Tab. 1).

337

In order to allow a conclusion on the subsurface pollution level from vegetation samples, the 338 339 bioavailability of the toxic elements should not be different. Kirkham (2006) reports that the 340 pH of the soil is usually the most important factor that controls uptake, with low pH favoring 341 Cd accumulation. High phosphate and zinc concentrations decrease Cd uptake. The reference 342 site should thus have very similar conditions to the test site (e.g., soil type, pH, nutrient 343 supply, tree species, weather), except, of course, the concentrations of toxic elements. This 344 turned out to be difficult for the Møringa site. A difference in pH is likely, because the waste 345 at the site was partly mixed with bricks, cement debris etc. which leads to alkaline pH (pH 7

to 9), while normal forest has typically pH 5 to 6. Furthermore, the area along the coast is densely populated, and urban waste (such as defect TVs) was found all around, also on the reference area. A fence was close by (eventually releasing zinc, cadmium, nickel and chromium), and a road. Generally, it will be difficult to find totally unpolluted soils in urban areas, and thus well-suited reference sites. Also, no soil samples were taken and analyzed from the reference site, so neither concentrations nor soil conditions are known.

352

353 Concentrations in wood were generally low, typically factor 100 or more lower than 354 concentrations in soil. At the same time, sample volumes were necessarily small (< 1 g). 355 Subsequently, the measured concentrations for some elements (As, Ni) were often close to or 356 even below the detection limit. The use of another analytical instrument (ICP-MS, AAS with 357 graphite oven) might improve the limit of determination. Also, from this aspect, the 358 measurement of leaves might be superior, because concentrations are generally higher than in 359 wood (Vandecasteele et al. 2008, Harada et al. 2010). On the other hand, atmospheric 360 deposition is often an important source for heavy metals in leaves (Gratani et al. 2008) and 361 could disturb the phytoscreening. Indeed, atmospheric deposition (Gratani et al. 2008, Legind and Trapp 2010) could be one reason for the often small difference of concentrations in 362 363 samples from test- and reference site.

364

Toxic elements are also toxic to trees (Marschner 1995). Perhaps, trees avoid growth in polluted soil and extend their roots preferably into cleaner soil areas. Also, maybe trees cannot grow at all in highly polluted soils, which mean in turn that trees cannot be used as indicator for such high pollution. The method is therefore restricted to a certain concentration

range, limited by detection limit at the lower end and by severe toxic effects at the higherend.

371

Uptake from soil into roots is most likely from the bioavailable pool (McLaughlin 2002). This means, elevated levels in wood do not necessarily indicate elevated total concentrations in soil. This can, of course, also be seen as an advantage of the method, because it directly tracks the fraction of the chemical that is freely available for uptake, toxicity and leaching. Legal standards, however, are typically based on total concentration in soil, e.g., in Denmark (Miljøstyrelsen 2009).

378

Toxic metals reside often in soil layers close to the surface and are therefore available for hand-driven borers. It is probably easier and more certain to determine the heavy metal concentrations of soil samples, instead of using the indirect analysis of wood samples. On the other hand, trees do integrate over a large volume (up to $> 100 \text{ m}^3$ root zone per tree) and smooth out inhomogenities of soil contamination. Also, they yield directly the bioavailable (and thus toxic and mobile) fraction.

385

386 5 Conclusions

387

We tested phytoscreening of toxic elements and heavy metals for an abandoned waste site, by comparing concentrations in wood samples from the test site with concentrations in samples from reference sites. In all except one case, the concentrations of the investigated toxic elements were higher in wood from the test site. However, toxic elements occur in

392 higher or lower amounts in any soil. Subsequently, the elements were also present in 393 reference samples. The uptake underlies natural variations and depends on tree species and 394 soil properties. Consequently, the differences between contaminated test site and (nominally) 395 unpolluted reference site were not always statistically significant.

396

Although it is too early to judge the feasibility of the tree core method for toxic metals, it became already apparent that the method is more difficult to use than for chlorinated solvents, which are purely anthropogenic compounds. In particular, the occurrence of a toxic element in wood alone can not be used as criterion for subsurface pollution, a statistically sound comparison to samples from a well-suited reference site (same tree species, same age, similar soil properties, non-polluted) is necessary. This increases the efforts and the uncertainty of the method.

404

405 Acknowledgements

406 This work was funded by the European Union (European Commission, FP7

407 Contract No. 213161, project ModelPROBE). We thank Sinh Hy Nguyen for assistance with

408 the chemical analysis and Bernd Markert for pre-review.

409

411	References
412	
413	Amundsen, C.E., French, H., Aasen, R., Nordal, O. 2005. Supplementary investigations at
414	Møringa waste site, Horten. Risk assessment and remedial action plans (in Norwegian).
415	Jordforsk-report. 19/05. Bioforsk, 1432 Aas, Norway.
416	
417	Bahrenberg, G., Giese, E., Nipper, J. 1990. Statistische Methoden in der Geographie.
418	Stuttgart, Teubner.
419	
420	Barber, S.A. 1995. Soil nutrient bioavailability. A mechanistic approach. John Wiley & Sons,
421	New York, 2nd ed.
422	
423	Chen, W., Li, L., Chang, A.C., Wu, L., Kwon, SI., Bottoms, R. 2008. Modeling uptake
424	kinetics of cadmium by field-grown lettuce. Environ. Pollut. 152, 147-152.
425	
426	Gopalakrishnan, G., Negri, M.C., Minsker, B.S., Werth, C.J. 2007. Monitoring subsurface
427	contamination using tree branches. Ground Water Monitoring & Remediation 27, 65-74.
428	
429	Gratani, L., Crescente, M.F., Varone, L. 2008. Long-term monitoring of metal pollution by
430	urban trees. Atmospheric Environment 42 (35), 8273-8277.
431	

432	Hagemeyer, J., Schäfer, H. 1995. Seasonal variations in concentrations and radial distribution
433	patterns of Cd, Pb and Zn in stem wood of beech trees (Fagus sylvatica L.). The Science of
434	the Total Environment 166, 77-87.
435	
436	Harada, E., Hokura, A., Takada, S., Baba, K., Terada, Y., Nakai, I., Yazaki, K. 2010.
437	Characterization of cadmium accumulation in willow as a woody metal accumulator using
438	synchrotron radiation-based x-ray microanalyses. Plant Cell Physiol. 51(5), 848-853.
439	
440	Haug, C.M., Reimer, K.J., Cullen, W.R. 2004. Arsenic uptake by the Douglas-fir
441	(Pseudotsuga menziesie). Appl. Organometal. Chem. 18, 626-630.
442	
443	Hough, R.L., Breward, N., Young, S.D., Crout, N.M.J., Tye, A.M., Moir, A.M., Thornton, I.
444	2004. Assessing potential risk of heavy metal exposure from consumption of home-produced
445	vegetables by urban populations. Environ Health Persp 112, 215-221.
446	
447	Kirkham, M.B. 2006. Cadmium in plants on polluted soils: Effects of soil factors,
448	hyperaccumulation, and amendments. Geoderma 137, 19-32.
449	
450	Larsen, M., Burken, J., Machackova, J., Karlson, U.G., Trapp, S. 2008. Using tree core
451	samples to monitor natural attenuation and plume distribution after a PCE spill. Environ. Sci.
452	Technol. 42, 1711–1717.
453	

454 Legind, C.N., Trapp, S. 2010. Comparison of prediction methods for the uptake of As, Cd

455 and Pb in carrot and lettuce. SAR/QSAR Env. Res., in print.

456

457 Ma, X., Burken, J.G. 2002. VOCs fate and partitioning in vegetation: Use of tree cores in 458 groundwater analysis. *Environ. Sci. Technol.* 36, 4663-4668.

459

- 460 Markert, B., Wtorova, W. 1992. Inorganic chemical investigations in the Forest Biosphere
- 461 Reserve near Kalinin, USSR III. Comparison of the multielement budget with a forest
- 462 ecosystem in Germany aspects of rejection, indication and accumulation of chemical
- 463 elements. *Vegetatio* 98, 43-58.

464

465 Markert, B. 1993. Plants as biomonitors: Indicators for heavy metals in the terrestrial
466 environment. VCH Weinheim.

467

- 468 Markert, B., Wappelhorst, O., Weckert, V., Herpin, U., Siewers, U., Friese, K., Breulmann,
- 469 G. 1999. The use of bioindicators for monitoring the heavy-metal status of the environment.
- 470 *J. Radioanalyt. Nuclear Chem.* 240(2), 425-429.

471

- 472 Markovic, D.M., Novovic, I., Vilotic, D., Ignjatovic, L. 2009. Determination of As in tree-
- 473 rings of poplar (Populus alba L.) by U-shaped DC arc. Environ. Monit. Assess. (2009) 151,

474 377–382.

475

476 Marschner, H. 1995. Mineral nutrition of higher plants. Academic Press, London.

477

478

479 metals in terrestrial ecosystems: importance of partitioning for bioavailability to 480 invertebrates, microbes and plants, Chapter 3 (Allen, H.E., ed.). SETAC press, Pensacola, 481 FL. 482 483 Migeon, A., Guinet, F., Chalot, M., Blaudez, D., Richaud, P. 2009. Metal accumulation by woodv species on contaminated sites in the north of France. Water, Air, and Soil Pollution 484 485 204 (1-4), 89-101. 486 487 Miljøstyrelsen. 2009. Liste over jordkvalitetskriterier, afskæringskriterier, 488 grundvandskvalitetskriterier og afdampningskriterier. 489 http://www.mst.dk/Virksomhed og myndighed/Kemikalier/Klassificering+og+risikovurderi 490 ng/Graensevaerdier/02350600.htm 491 492 Monticelli, D., Di Iorio, A., Ciceri, E., Castelletti, A., Dossi, C. 2009. Tree ring 493 microanalysis by LA-ICP-MS for environmental monitoring: validation or refutation? Two 494 case histories. Microchim. Acta 164,139-148.

McLaughlin, M.J. 2002. Bioavailability of metals to terrestrial plants. In: Bioavailability of

495

496 Pulford, I.D., Watson, C., McGregor, S.D. 2001. Uptake of chromium by trees: prospects for

497 phytoremediation. *Environmental Geochemistry and Health* 23, 307–311.

498

- 499 Riddell-Black, D., Pulford, I.D., Stewart, C. 1997. Clonal variation in heavy metal uptake by
- 500 willow. Aspects of Applied Biology 49, 327–334.
- 501
- 502 Sachs, L. 1991. Angewandte Statistik. Berlin, Springer.
- 503
- 504 Schumacher, J.G., Struckhoff, G.C., Burken, J.G. Assessment of subsurface chlorinated
- 505 solvent contamination using tree cores at the Front Street site and a former dry cleaning
- 506 facility at the Riverfront Superfund Site, New Haven, Missouri, 1999–2003. U.S. Geological
- 507 Survey Scientific Investigations Report 2004-5049.
- 508 http://pubs.usgs.gov/sir/2004/5049/pdf/complete.pdf
- 509
- Smith, S.E., Christophersen, H.M., Pope, S., Smith, F.A. 2010. Arsenic uptake and toxicity in
 plants: integrating mycorrhizal influences. *Plant Soil* 327,1-21.
- 512
- 513 Sorek, A., Atzmon, N., Dahan, O., Gerstl, Z., Kushisin, L., Laor, Y., Mingelgrin, U., Nasser,
- A., Ronen, D., Tsechansky, L., Weisbrod, N., Graber, E.R. 2008. Phytoscreening: The use of
- trees for discovering subsurface contamination by VOCs. *Environ. Sci. Technol.* 42(2), 536542.
- 517
- 518 Swartjes, F.A., Dirven-Van Breemen, E.M., Otte, P.F., Van Beelen, P., Rikken, M.G.J.,
- 519 Tuinstra, J., Spijker, J., Lijzen, J.P.A. 2007. Human health risks due to consumption of
- 520 vegetables from contaminated sites. RIVM Report 711701040/2007. Bilthoven, NL, National
- 521 Institute for Public Health and the Environment.

- 522 http://rivm.openrepository.com/rivm/bitstream/10029/16413/1/711701040.pdf
- 523
- 524 Thorne, M., Walke, R., Maul, P. 2005. The PRISM Foodchain Modelling Software:
- 525 Parameter Values for the Soil/Plant Model. QRS-1198A-3. London, UK, Food Standards
- 526 Agency. http://www.foodbase.org.uk//admintools/reportdocuments/266-1-487_QRS-1198A-
- 527 3SPDatav1.1.pdf

528

- 529 Trapp, S., Larsen, M., Legind, C.N., Burken, J., Macháčková, J., Karlson U.G. 2007.
- 530 A guide to vegetation sampling for screening of subsurface pollution. Available at
- 531 http://homepage.env.dtu.dk/stt/GuidetoVegetationSampling.pdf

532

Trapp, S., Feificova, D., Rasmussen, N.F., Bauer-Gottwein, P. 2008. Plant uptake of NaCl in
relation to enzyme kinetics and toxic effects. *Env. Exp. Botany* 64, 1-7.

535

US EPA United States Environmental Protection Agency. 2005. Human Health Risk
Assessment Protocol for Hazardous Waste Combustion Facilities. EPA530-R-05-006. U.S.
EPA, Office of solid waste.

539

540 Vandecasteele, B., Samyna, J., De Vosa, B., Muysc, B. 2008. Effect of tree species choice

and mineral capping in a woodland phytostabilisation system: A case-study for calcareous

542 dredged sediment landfills with an oxidised topsoil. *Ecological Engineering* 32, 263–273.

543

- 544 Vroblesky, D.A., Nietch, C.T., Morris, J.T. 1999. Chlorinated ethenes from groundwater in
- 545 tree trunks. *Environ. Sci. Technol.* 33, 510-515.

547 <u>Tables and Figures</u>

Table 1. Total concentration in soil (mg/kg) measured at Møringa (Amundsen et al. 2005).

Sample	As	Cd	Cr	Cu	Ni	Zn
Ø1-2	61	14	200	1500	130	7300
Ø1-1+2	69	20	170	1700	120	5100
Ø2-1+2+3	75	16	170	3700	190	9800
Ø2-4+5	15	2.2	49	860	42	3900
Ø3-1+3	44	8	130	2500	120	6000
Ø3-2+4	28	9.5	76	1400	120	3000
V4 bottom	5	1.3	81	3700	160	540
V4 sand	5	0.2	71	76	560	450
V5 bottom	21	3.9	100	4000	63	3900
V5 top	15	3	99	1100	88	11000
V6-1+2+3	5	1.4	58	280	410	1000
V6-4+5	5	0.2	110	18	2300	320
V 7 1+2	5	0.9	92	140	460	790
V 7 4+5	5	1.8	150	940	260	1400

- 553 **Table 2.** Description of the the wood samples from Møringa, first campaign (n = 71) and second
- 554 campaign (n = 68). Concentrations in mg/kg dry weight; std = standard deviation; min = minimum;
- 555 max = maximum; DL = detection limit (mg/kg dw); <DL =number of samples below DL.

Element	Campaign	mean	std	min	max	DL	<dl< th=""></dl<>
As	1	0.32	0.24	0.23	1.64	0.45	57
Cd	1	0.18	0.26	0.015	1.01	0.03	30
Cd	2	0.66	0.31	0.15	1.49	0.03	0
Cr	1	0.23	0.26	0.06	1.94	0.04	0
Cr	2	0.40	0.26	0.06	1.17	0.11	3
Cu	2	2.17	1.06	0.49	5.28	0.97	1
Ni	2	0.29	0.17	0.12	0.75	0.24	23
Zn	1	28.6	18.0	4.1	92.6	8.1	6
Zn	2	33.1	13.5	14.2	96.9	0.48	0

556

558 **Table 3a.** Mean of measured concentrations (mg/kg dw) of elements in wood samples from Møringa,

559 first campaign; R is reference site (nominally low polluted) and T is test site (high polluted). Significant

560 differences in bold ($\alpha = 5\%$).

	all trees		bir	ch	willow	
	n =	71	n = 34		n = 16	
	R	Т	R	Т	R	Т
As	0.23	0.39	0.23	0.32	0.23	0.47
Cd	0.14	0.18	0.015	0.035	0.33	0.71
Cr	0.19	0.26	0.13	0.15	0.24	0.41
Zn	25.4	30.0	33.1	39.8	15.0	24.7

561

562

563 **Table 3b.** Mean of measured concentrations (mg/kg dw) of elements in wood samples from Møringa,

564 second campaign; R is reference site (nominally low polluted) and T is test site (high polluted).

565 Significant differences in bold ($\alpha = 5\%$) or italic ($\alpha = 10\%$).

	will	ow	poplar		
	n =	44	n = 24		
	R	Т	R	Т	
Cd	0.69	0.76	0.62	0.51	
Cr	0.34	0.35	0.48	0.49	
Cu	1.95	3.05	1.33	1.66	
Ni	0.29	0.34	0.14	0.29	
Zn	32.0	36.4	27.0	32.5	

566

567

569 <u>Figure legends</u>

570

- 571 **Figure 1.** Map of the Møringa peninsula with risk zones and soil sampling points (Amundsen et al.
- 572 2005) and areas of tree core sampling, July 2009 and March 2010.

573

Figure 2. Example results from the tree core analysis (mg/kg dw); top: Cr in willow wood (1st campaign); below: Cu in willow wood (2nd campaign). x-axis indicates location of trees (Fig. 1): Ref refers to reference site; Ø refers to eastern part of the site, V to western part. Results from individual replicates are shown.

578

580 <u>Figures</u>

581



582

583 **Figure 1**



585





