

28 **1. Introduction**

29

30 The contamination of soils with toxic metals has become a major environmental concern
31 in many parts of the world due to rapid industrialization, increased urbanization, modern
32 agricultural practices and inappropriate waste disposal methods. In Europe, the polluted
33 agricultural lands likely encompass several million hectares (Flathman and Lanza, 1998). In
34 China, the degraded land associated with mining activities reached about 3.2 Mha by the end
35 of 2004, and the figure is increasing at an alarming rate of 46,700 ha per year (Bai et al., 1999;
36 Li, 2006).

37 In soils, toxic metals are present in various chemical forms and generally exhibit different
38 physical and chemical behaviors in terms of chemical interactions, mobility, biological
39 availability and potential toxicity (Bohn et al., 1979). Chemical speciation plays a vital role in
40 the solubility and potential bioavailability of metals in soils (Tandy et al., 2004). Unlike
41 organic compounds, toxic metals are not degradable in the environment, and can persist in
42 soils for decades or even centuries. The contamination of soils by metals can have long-term
43 environmental and health implications.

44 It is highly desirable to apply suitable remedial approaches to polluted soil, which can
45 reduce the risk of metal contamination. The excavation and disposal of soil is no longer
46 considered to be a permanent solution. The demand for soil treatment techniques is
47 consequently growing and the development of new low-cost, efficient and environmentally
48 friendly remediation technologies has generally become one of the key research activities in
49 environmental science and technology. In selecting the most appropriate soil remediation
50 methods for a particular polluted site, it is of paramount importance to consider the
51 characteristics of the soil and the contaminants. At present, various approaches have been
52 suggested for the remediation of metal-contaminated sites. Some of these technologies, like

53 soil washing using particle size separation and chemical extraction with aqueous solutions of
54 surfactants and mineral acids are in full-scale use (Kuhlman and Greenfield, 1999; Mann,
55 1999), while technologies addressed in this review, chelant-assisted soil washing and
56 enhanced phytoextraction, are still largely in the development phase.

57 Toxic metals and other contaminants can be isolated and contained to prevent their further
58 movement, *i.e.* by leaching through soil or by soil erosion. This can be achieved by capping
59 the site with asphalt or other impermeable materials to prevent the infiltration of water, by
60 planting permanent plant cover (*e.g.*, phyto-stabilization) or by covering the site with
61 unpolluted soil (Guo et al., 2006).

62 Smaller, but usually more polluted, soil particles can be removed from the rest of the soil
63 by various separation techniques developed and used in the mining industry. These include
64 the use of hydrocyclones, which separate larger particles from smaller ones using centrifugal
65 force; and solid-liquid separation techniques, such as gravimetric settling and flotation, which
66 are based on the different surface characteristics of particles (Mulligan et al., 2001; Vanthuyne
67 and Maes, 2002).

68 Stabilization involves fixing up the contaminants in stable sites by mixing or injecting
69 inorganic or organic soil amending agents (*e.g.*, liming agents, organic materials,
70 aluminosilicates, phosphates, iron and manganese oxides, coal fly ashes, *etc.*). Due to the
71 effects of a change in pH, such agents are effective at decreasing the bioavailability of metals
72 by introducing additional binding sites for toxic metals. Stabilized metals then become less
73 available for plants, and their bioconcentration through the food chain is reduced (Guo et al.,
74 2006). However, the toxic metals remain in the soil and can be harmful when soil dust is
75 ingested or inhaled. Many of the amendments used in soil stabilization are by-products of
76 industrial activities, and are therefore inexpensive and available in large amounts. Overviews

77 on previously successfully applied amending agents and their effectiveness for different
78 metals have been given by Knox et al. (2001) and Puschenreiter et al. (2005).

79 Another immobilization method is vitrification by heating the contaminated soil to up to
80 2000°C. Vitrification usually involves imposing an electrical current between electrodes
81 inserted into the contaminated soil. Due to its low electrical conductivity, the soil begins to
82 heat and produces a melt that hardens into a blocks of glasslike material. Vitrification is
83 expensive but applicable to soils with mixed organic and metallic contamination, for which
84 few technologies are available (Buelte and Farnsworth, 1991).

85 Electrokinetic extraction has been proposed as an *in situ* method for the remediation of
86 blocks of contaminated soil. Electrokinetic extraction involves the electrokinetic movement of
87 charged particles suspended in a soil solution, initiated by an electric gradient. The target
88 metals can be removed by precipitation at the electrodes (Hicks and Tondorf, 1994).

89 Phytoextraction is a publicly appealing (green) remediation technology. However,
90 phytoextraction can be effectively applied only for soils contaminated with specific (and less
91 problematic) potentially toxic metals and metalloids, *e.g.* Ni, Zn and As, which are readily
92 bioavailable for plants and for which appropriate hyper-accumulating plants with a high
93 enough biomass are known. Common crop plants with a high biomass can be triggered to
94 accumulate large amounts of low bioavailability metals (*e.g.* Pb, Cr, U, Hg) when the mobility
95 of these metals in the soil is enhanced by the addition of mobilizing agents (Huang et al.,
96 1997; Wu et al., 1999; Shen et al., 2002; Luo et al., 2005). In such chemically enhanced
97 phytoextraction, chelating agents are used almost exclusively as the mobilizing agents.

98 This paper reviews the current remediation technologies for metal-contaminated soils,
99 which use chelating agents. Chelants desorb toxic metals from soil solid phases by forming
100 strong water-soluble complexes, which can be removed from the soil by plants through
101 enhanced phytoextraction or by using soil washing techniques. The latter currently consist of

102 soil flushing, the extraction of soil slurry in reactors, and soil heap/column leaching. Another
103 innovative remediation method that uses chelating agents for mobilizing metals is enhanced
104 electrokinetic extraction.

105

106 **2. Chelant assisted phytoextraction**

107

108 The idea of using plants to remediate metal-contaminated soil has attracted a great deal of
109 research in the last two decades. But due to the limited plant species with a high capacity to
110 accumulate metals, especially metals with low bioavailability in soil, such as Pb, and to
111 produce a large amount of biomass, one alternative approach using chelants to improve the
112 uptake of metals by high biomass plants has been proposed, inspired by studies on plant
113 nutrition (Marschner, 1995).

114 Careful assessment and evaluation is required to determine the biodegradation and
115 toxicity of the chelating agents and their metal complexes in soils (Means et al., 1980;
116 Borgmann and Norwood, 1995; Nörtemann, 1999; Grčman et al., 2001; Römkens et al.,
117 2002). Although EDTA (ethylenediaminetetraacetic acid) was recognized as the most efficient
118 chelant to increase metal uptake by plants, especially for the uptake of Pb, the low
119 biodegradability of the chemical does not make it a good choice for large-scale field
120 applications (Kos and Leštan, 2004; Tandy et al., 2004; Luo et al., 2005). In recent years, the
121 focus of research has shifted to some more biodegradable chelants, such as NTA
122 (nitrilotriacetate), [S,S]-EDDS (S,S-ethylenediaminedisuccinic acid), and others. The use of
123 these biodegradable chelants in improving the uptake of metals by plants and in limiting the
124 leaching of metals from soil has become an attractive field of research. Most of this kind of
125 research has been carried out in the form of studies comparing the previous EDTA results in
126 metal uptake efficiencies with additional data on the biodegradability of chelants and the

127 metal leaching potential from the application of the chemicals (Grčman et al., 2003; Kos and
128 Leštan, 2004; Luo et al., 2005; Meers et al., 2005; Luo et al., 2006b). The optimization and
129 application of this technology should be based on the full understanding of important
130 processes involved, such as metal solubilization from the application of chelants, the uptake
131 of metals by the roots of plants, and their transport upwards to the shoots of the plants. To
132 prevent the possible movement of metal-chelants into groundwater and to reduce the impact
133 of the remaining chelant on soil microorganisms, the selection of chelants and the amount and
134 process of their application are important, as well as irrigation techniques and the time of the
135 chelant application (Blaylock et al., 1997; Evangelou et al., 2007; Luo et al., 2007). The
136 following section reviews the research progresses on the phytoextraction of metals using
137 chelants in recent literature, and highlights some potential research area for future
138 devolvement.

139

140 ***2.1. Theoretical considerations***

141

142 In the process of chelant-assisted phytoextraction, chelant is applied to the soils. First,
143 chelant can desorb metals from the soil matrix, and the mobilized metals move to the
144 rhizosphere for uptake by plant roots. The amounts of bioavailable metals in soil solution are
145 mainly determined by the properties of the soil and the chelant which is applied (Huang et al.,
146 1997; Kos and Leštan, 2004; Tandy et al., 2004; Luo et al., 2005).

147 The efficacy of a chelant in the extraction of metals is usually rated with the stability
148 constants K_s of the chelant-metal complexes. According to Elliott et al. (1989), the order of
149 magnitude of the K_s can be used to rank different chelants according to their general efficacy,
150 but not to rank the efficacies of a specific chelant toward different metals because the latter is
151 also influenced by the metal speciation in a given soil matrix. Huang et al. (1997) indicated

152 that a variety of synthetic chelants have the potential to induce Pb desorption from soil. Their
153 effectiveness, in decreasing order, was EDTA > HEDTA (N-hydroxyethylenediaminetriacetic
154 acid) > DTPA (diethylenetriaminepentaacetic acid) > EGTA [ethyleneglycol -bis (β -
155 aminoethyl ether), N, N, N', N-tetraacetic acid] > EDDHA [ethylenediamine-di (*o*-
156 hydroxyphenylacetic acid)]. EGTA has been shown to have a high affinity for Cd^{2+} , but not
157 for Zn^{2+} . Luo et al. (2005) found that EDTA is more efficient than [S,S]-EDDS in the
158 extraction of Pb and Cd, but that [S,S]-EDDS is more effective in the extraction of Cu and Zn.

159 The predominant theory for metal-chelant uptake is the split-uptake mechanism, by which
160 only free metal ions can be absorbed by plant roots (Chaney et al., 1972; Marschner et al.,
161 1986). Fe-EDTA is known to dissociate before plant uptake (Marschner et al., 1986; Sarret et
162 al., 2001). Another important theory suggests that some of the purportedly intact metal-
163 chelant complexes are taken up by plants (Wallace, 1983; Bell et al., 1991; Laurie et al., 1991;
164 Salt et al., 1995; Nowack et al., 2006). A schematic display of this process is shown in Figure
165 1.

166 As a typical soil metal contaminant, Pb has been extensively studied. The metal can be
167 absorbed by plant roots and transferred as a Pb-EDTA complex (Vassil et al., 1998; Epstein et
168 al., 1999). In the leaves of *Phaseolus vulgaris*, Sarret et al. (2001) detected that some of the
169 Pb was complexed to EDTA. The complexes of Pb-EDTA cannot be split through the
170 reduction or oxidation of Pb. It is also unlikely that Pb-EDTA or EDTA can diffuse across the
171 plasma membrane at any significant rate, as they are too large and polar to move the
172 plasmalemma lipid bilayer. It has been concluded that the uptake of Pb-EDTA by plants can
173 take place in the location where suberization of the root cell walls has not yet occurred and at
174 breaks in the root endodermis and the Casparian strip (Tanton and Crowdy, 1972; Bell et al.,
175 1991). Therefore, some damage to the root may be helpful for the indiscriminate uptake of Pb-

176 EDTA by plant roots. The damage could be caused by the toxicity of metals, chelants and
177 other artificial means (Vassil et al., 1998; Luo et al., 2006a).

178

179 ***2.2. Application of chelants***

180

181 For a given chelant, different methods of application can produce different levels of
182 phytoextraction efficiency. Exploring effective strategies for the application of chelants is
183 useful in optimizing the technology. It has been reported that placing chelant at some depth
184 near the roots of plants instead of mixing this agent into the entire soil area will lead to a
185 significantly higher accumulation of trace metals by plants (Kayser et al., 1999). Applying
186 chelant in several smaller dosages (versus in one application) can result in the enhanced
187 phytoextraction of Pb (Grčman et al., 2001; Puschenreiter et al., 2001; Shen et al., 2002). The
188 combined application of different chemicals can also greatly improve the metal
189 phytoextraction efficiency. One type of combination is the use of two chelants/chemicals,
190 which can increase the solubility of metals by lowering the pH of the soil. Blaylock et al.
191 (1997) demonstrated that the application of EDTA and acetic acid led to a two-fold
192 accumulation of Pb in Indian mustard shoots compared with the application of EDTA alone.
193 This result was explained by the lower cell wall retention of Pb as lead carbonate at a lower
194 rhizosphere pH. The second type of combination is based on the interactions between metals
195 and different chelants, in which the solubility of metals by a chelant can be increased by
196 another chelant through the reduction of competition from other metals in soil. Luo et al.
197 (2006c) found that the combined application of EDTA and [S,S]-EDDS led to a higher level
198 of efficiency (*i.e.*, a synergy effect) in the phytoextraction of Cu, Pb, Zn and Cd than could be
199 obtained by the application of either chelant alone. There are two reasons for the result: the
200 fact that EDTA and [S,S]-EDDS have different levels of efficiency in extracting metals from

201 soils; and a decrease in the competitive cations for trace metals with EDTA, such as soil-
202 soluble Ca, due to the addition of [S,S]-EDDS (Tandy et al., 2004). The third type of
203 combination is the utilization of one chemical to destroy the plant root structure to facilitate
204 the direct uptake of metal-chelants and their translocation into the shoots. In several
205 experiments, it was found that the application of glyphosate enhanced the Pb accumulation of
206 the tested crops (Kayser et al., 1999; Mathis and Kayser, 2001). The mechanism of enhanced
207 metal accumulation after the application of glyphosate was explained by a disruption of the
208 plant's metabolism, leading to the enhanced transport of trace metals from roots to shoots
209 (Ensley et al., 1999).

210 Some artificially physiological damage to roots, such as that resulting from pretreatments
211 with MC (methanol: trichloromethane), HCl and hot water, and from treatment with DNP (2,
212 4-dinitrophenol, an uncoupler of oxidative phosphorylation), dramatically increased the
213 concentrations of Pb in shoots with the EDTA treatment (Luo et al., 2006a). Applying similar
214 treatments in a pot experiment, Luo et al. (2006d) found that when chelants were applied as
215 hot solutions at the rate of 1 mmol kg^{-1} , the concentrations and total phytoextraction of Cu, Zn
216 and Cd by plant shoots exceeded or at least approximated those in the shoots of plants treated
217 with normal chelants at a rate of 5 mmol kg^{-1} (Luo et al., 2006d). This result indicated that the
218 amount of chelant applied could be greatly decreased for the given effectiveness of chelants in
219 enhancing the phytoextraction of trace metals from contaminated soils. The soil leaching
220 study demonstrated that there was no significant difference in the soluble metals between the
221 hot and normal chelant applications when the chelant was applied at the same dosage. The
222 decreased dosage of chelant resulted in decreased concentrations of soluble metals in soils,
223 which meant that the hot chelant application did not increase metal leaching compared with
224 the normal chelant application. Similarly, some environmental stresses, such as excessive
225 toxic metals, high temperatures, and drought, may also result in a breakdown of the root

226 exclusion mechanisms, subsequently influencing the chelant-enhanced accumulation of trace
227 metals in plant shoots. This result may be one of the reasons behind the different
228 phytoextraction efficiencies in using EDTA treatments reported by various researchers even
229 for the same plant species (Blaylock et al., 1997; Huang et al., 1997; Wu et al., 1999; Salido et
230 al., 2003; Walker et al., 2003; Lim et al., 2004; Meers et al., 2004).

231

232 ***2.3. Optimizing the phytoextraction process***

233

234 Environmental and economic concerns require that the addition of chelants should be kept
235 to a minimum. This suggests that further improvements in the process of selecting and
236 applying chelants should be made in parallel with the selection of plant species. As for plants,
237 first, the species should be one that is able to tolerate some degree metal contamination.
238 Screening for more sensitive species/cultivars and optimizing plant growth conditions would
239 help to reduce the dosage of chelants for a given phytoextraction efficiency (Kumar et al.,
240 1995; Li et al., 2005; Luo et al., 2006b,d). Desirable plant species are those that are fast-
241 growing, have a high biomass and are easily harvested. Native plant species are better than
242 exotic species, as using the former increases the probability of success and reduces the
243 potential risk of plant invasion. Research on an easily biodegradable chelant to replace those
244 with low levels of biodegradability has led to some exciting new results. A typical example is
245 the recent reports about the use of [S,S]-EDDS in the phytoextraction application (Grčman et
246 al., 2003; Kos and Leštan, 2004; Luo et al., 2005; Meers et al., 2005; Tandy et al., 2006).
247 Different chelant application methods will also have a significant impact on the efficiency of
248 metal phytoextraction.

249 In addition, there are several new areas of development that are worthy further research to
250 reduce potential metal leaching in chelant-enhanced phytoextraction.

251 First, a new slow-releasing chelating agent can be developed by coating solid EDTA (or
252 other chelants) with a layer of silicate to slow down the mobilization of metals in soil in order
253 to match plant uptake, and thus prevent excessive mobilization (Li et al., 2005). The results
254 have indicated that the slow release of CCA (coated chelating agent) improved the
255 bioavailability of metals in soil to match the plant uptake of these metals, and that this could
256 reduce the risk of metals leaching from the soil.

257 Second, some agronomic practices should be adapted to increase the efficiency of metal
258 phytoextraction. The efficiency of phytoremediation depends on large plant yields and high
259 metal concentrations in plant shoots. Therefore, increasing plant dry biomass yields can be
260 helpful in increasing the total metal uptake by plants. It has been suggested that the use of
261 foliar-applied P to plants grown in Pb-contaminated soils can overcome P deficiencies and
262 avoid the necessity of adding P fertilizer to soils. Huang and Cunningham (1996) reported that
263 foliar P application not only increased plant biomass four-fold in goldenrod, but also
264 increased total plant Pb uptake by 115%.

265 A significant increase in the uptake and translocation of Pb has been reported for corn
266 transplanted into soil, then treated with EDTA, in comparison with the plants that were
267 germinated and grown in Pb-contaminated soil to which EDTA was subsequently applied
268 (Wu et al., 1999). Transplanting seedlings rather than planting seeds resulted in an increased
269 uptake of chelates, probably through breaks in the Casparian strip due to possible mechanical
270 damage to the roots (Wallace and Hale, 1962).

271 Using deep-rooted, higher water-use plants or trees to reduce metal leaching may be
272 another good approach. Chen et al. (2004) found that 98, 54, 41 and 88% of the initially
273 applied Pb, Cu, Zn and Cd could re-adsorbed in the soil due to the effects of vetiver grass.
274 Although the deep-rooted plants of vetiver grass could not accumulate high concentrations of
275 metals, the plant may reduce the risk of metals migrating downwards and contaminating the

276 groundwater through the evaporation of water by the roots of vetiver grass. Therefore, if other
277 high metal-tolerant plants, such as Indian mustard, are intercropped with vetivar grass, on the
278 one hand the metals will be accumulated by the shoots of mustard, and on the other hand the
279 leached metals would be reduced by their readsorption in deep soil layers due to the root
280 effect of vitiver grass.

281 Third, different phytoremediation technologies can be combined in field applications.
282 Electrodeic and electrokinetic remediation is another alternative for removing trace metals and
283 radionuclides from contaminated soil and ground water (Li and Li, 2000; Yong, 2001). Lim et
284 al. (2004) reported that the addition of an electric field around the plants in combination with
285 the application of EDTA did more to enhance the uptake of Pb by Indian mustard than the
286 addition of EDTA only. The accumulation of Pb in the shoots of Indian mustard increased 2-
287 to 4-fold when 0.5 mmmol kg⁻¹ of EDTA was applied with the parallel application of
288 electrodiacs.

289

290 **3. Soil washing using chelating agents**

291

292 Soil washing involves the separation of toxic metals from soil solid phases by solubilizing
293 the metals in a washing solution. Acids and chelating agents are the most prevalent removal
294 agents used in soil washing (Peters, 1999). Acids dissolve carbonates and other metal-bearing
295 soil material and exchange trace metals from soil surfaces where H⁺ ions are attracted more
296 strongly than the cations of toxic metals. Chelating agents desorb trace metals from soil solid
297 phases by forming strong and water-soluble metal-chelant coordination compounds
298 (complexes). These complexes are very stable, prevent the precipitation and sorption of
299 metals, and do not release their metal ions unless there is a significant drop in soil pH. Since
300 acidic solutions can cause deterioration in the physico-chemical properties of the soil, using

301 chelating agents is considered to be environmentally less disruptive than using acids (Xu and
302 Zhao, 2005).

303 The important issues concerning the selection of chelants and the development of washing
304 solutions are summarized as follows (Peters and Shem, 1992; Hong and Jiang, 2005):

- 305 • Extraction strength. The chelant should be able to form strong, stable complexes with
306 toxic metals over a wide pH range.
- 307 • Extraction selectivity towards target toxic metals.
- 308 • The potential for recovering the spent chelant. If the chelant is to be recycled and reused in
309 the process several times, it should have low biodegradability in soil.
- 310 • The metal-chelant complexes should have low adsorption affinity towards solid soil
311 surfaces.
- 312 • The chelant should have low toxicity and a low potential to harm the environment.
- 313 • The chelant should be cost-effective.

314 Many different chelants (mostly aminopolycarboxylic acids) have been tested for soil
315 washing. In the literature, EDTA (Na_2EDTA) is the most frequently cited chelating agent for
316 extracting potentially toxic trace metals from soils, because of its efficiency, availability and
317 relatively low cost.

318 Since common soil constituents (e.g., Ca^{2+} , Fe^{2+} , Mg^{2+} , Al^{3+}) compete with toxic metals
319 for the binding sites of chelating agents, an excess amount of chelant is needed to ensure the
320 adequate removal of contaminants. Elliott and Brown (1989) reported that more than 95% of
321 the Pb that was present was removed when a 2:1 EDTA:Pb molar ratio was used. The removal
322 efficiency was lower when an equimolar ratio was used.

323 The stability constants of the formation of the metal-chelant complex and thus the
324 efficiency of chelant metal extraction are pH dependent. The removal of greater amounts of
325 toxic metals has most often been observed at lower pH levels (Van Benschoten and

326 Matsumoto, 1997). However, Vandevivere et al. (2001) reported that a slightly alkaline pH
327 was optimal for the removal of Pb, Zn and Cd with [S,S]-EDDS. The formation of complexes
328 in soils is controlled by the kinetic of all complexation reactions, adsorption in soil solid
329 phases, mineral dissolution and the possible degradation of the chelating agent or its metal
330 complexes (Nowack, 2002). These interactions are difficult to predict and depend on the
331 contaminants and soil conditions. Interestingly, applying chelant in several small dosages
332 often results in the extraction of considerably more toxic metals than when using one large
333 dose (Finžgar and Leštan, 2007). In practice, the choice of washing solution pH, the
334 concentration of the chelating agent and the application mode, the optimum soil/washing
335 solution ratio, the retention (reaction) time of the chelating agent solution in the soil and the
336 designated soil washing technique must therefore be selected individually for each case of
337 remediation. Technically, soil-washing techniques comprise soil flushing, extraction or
338 leaching.

339

340 ***3.1. In situ soil flushing***

341

342 Soil flushing is an *in situ* soil washing technique applicable to specific soil conditions, in
343 which the contaminated zone is underlain by non-permeable materials, which allows the
344 washing solution to be pumped and treated (Gracia-Delgado et al., 1998; Khan et al., 2004).
345 The method is suitable for sandy soil or sediment with high hydraulic conductivity. As shown
346 in Figure 2, the washing solution is forced through the in-place soil matrix via injection wells
347 or is infiltrated into the soil using surface sprinklers or similar devices. The washing solution
348 is pumped from the soil using a set of recovery wells installed down a gradient of the
349 contaminated area. The washing solution must be treated to remove toxic metals and the
350 process water reused in the flushing process. Treating the washing solution could prove to be

351 more difficult than the soil remediation itself (Mulligan et al., 2001). The disadvantage of *in*
352 *situ* soil flushing is the low degree of control over the movement of contaminants into
353 undesirable areas. The hydrology of the site must therefore be precisely understood.

354

355 **3.2. Extraction of soil slurry**

356

357 The extraction of soil slurry refers to the batch treatment of soil slurry in a reactor, as
358 shown in Figure 3. Following an initial screening of the excavated soil to remove the surface
359 debris, the soil is vigorously mixed with the chelating agent solution, separated by a second
360 screening step (filtration), and then returned to the ground (Vandevivere et al., 2001). The
361 washing of soil in reactors involves stringent physical treatments. It is harsh for the soil flora
362 and can cause the physical quality of the soil (its structure, water holding capacity and
363 hydraulic conductivity) to deteriorate (Finžgar and Leštan, 2006a).

364

365 **3.3. Soil heap/column leaching**

366

367 In soil leaching, the washing solution is gravitationally percolated through a soil heap or
368 column *ex situ* (Papassiopi et al., 1999; Sun et al., 2001). As shown in Figure 4, the soil which
369 is contaminated with toxic metals is excavated, screened and placed in a mound on a pad.
370 Metals are removed by passing washing solution through the soil using some type of liquid
371 distribution system. The extractant is collected in a pregnant solution pit and processed to
372 remove metals (Hanson et al., 1992). Soil leaching is operationally simple and holds the
373 potential for the economical treatment of large amounts of soil. The leaching efficiency is
374 higher for soils with higher hydraulic conductivity.

375

376 **3.4. Chelant enhanced electrokinetic extraction**

377

378 When a direct current electrical field is imposed across a wet mass of contaminated soil,
379 the pore fluid migrates by electroosmosis and the ions migrate by ionic migration towards the
380 electrodes. Combining these two removal mechanisms results in the electrokinetic extraction
381 of metal contaminants from soils.

382 During electrokinetic soil treatment, hydrogen ions (H^+) are generated at the anode due to
383 water electrolysis, and migrate into the bulk of the soil. A low pH develops through the soil
384 (except at the cathode where OH^- is generated), causing desorption of metallic contaminants
385 from the soil solid phases. The dissolved metallic ions are then removed from the soil solution
386 by ionic migration and precipitation at the cathode (Acar and Alshawabkeh, 1993). However,
387 a high soil buffer and ion exchange capacity can prevent soil acidification and thus decrease
388 the efficiency of the electrokinetic extraction of toxic metals. In such conditions, the addition
389 of a chelating agent to the soil can enhance electrokinetic extraction. EDTA has most often
390 been tested, since EDTA form strong water-soluble chelant complexes with most toxic metals
391 (Yeung et al., 1996). Chelant-enhanced electrokinetic extraction is promising for dealing with
392 contamination at moderate depths in fine-grained soils and soils with a high clay or organic
393 matter content, where the application of soil washing technologies is impractical.

394

395 **3.5. Treatment of soil washing solutions**

396

397 One of the main drawbacks of the soil washing methods is the vast consumption of water
398 required for making up the washing solution, and of clean water for the removal of the
399 mobilized metallic species that have been complexed with the chelating agent and that have
400 been retained in the soil after the remedial treatment. Another problem is that the washing

401 solution, now rich with metal-chelant complexes, must subsequently be treated before it can
402 be safely discharged. EDTA, the chelating agent that is most often used, is toxic, especially in
403 its free form (Sillanpaa and Oikari, 1996; Dirilgen, 1998), and is poorly photo-, chemo- and
404 biodegradable in the environment (Nörtemann, 1999). In the case of conventional treatments
405 such as settling, chemical precipitation or activated carbon, it is difficult to recover chelating
406 agents from spent extraction fluid or wastewater from other processes.

407 Several strategies have been proposed for the treatment of spent soil washing solutions.
408 For Pb-EDTA soil extractant, Kim and Ong (1999) proposed the replacement of the Pb in the
409 EDTA complex with Fe^{3+} ions at a low pH level, followed by the precipitation of Pb ions with
410 phosphate or sulfate ions. Ferric iron is then separated from the EDTA with precipitation at a
411 high pH level. The method allows chelates to be recycled and reused. Similarly, Ager and
412 Marshall (2003) investigated the possibility of substituting zero-valent Mg and Pd for metals
413 in EDTA complexes. Zeng et al. (2005) proposed that metals be precipitated from the soil
414 washing solution as insoluble sulphides after the addition of Na_2S . Di Palma et al. (2003a)
415 advocated the recovery of EDTA after washing soils “artificially” contaminated with Pb or Cu
416 in two steps: using an initial evaporation treatment that leads to a reduction of the extractant
417 volume by 75%, followed by acidification, which precipitates more than 90% of the EDTA
418 complexes. The feasibility of the evaporation of the extractant is probably constrained by the
419 high cost of water evaporation, an operation that consumes a great deal of energy. The same
420 research team (Di Palma et al., 2003b) also proposed reverse osmosis to reduce the volume of
421 the extractant. Allen and Chen (1993) suggested the electrolytic separation of metals and the
422 chelating agent in the soil washing solution. A two-chamber cell separated by a cation
423 exchange membrane to prevent migration to the anode and the oxidative destruction of
424 negatively charged metal-EDTA complexes was used for this. In electrolytic separation and
425 reverse osmosis, colloidal particles (clays and humic materials) and bacteria can clog the

426 membranes and thus diminish the performance and shorten the lifetime of the membranes.
427 Tejowulan and Hendershot (1998) used a simple procedure to remove negatively charged
428 metal-EDTA complexes from the soil washing solution using an anion exchange resin.
429 However, an effective method of recycling expensive resins still needs to be developed.

430 The cost of the chelating agent can be an important issue in soil remediation. Methods that
431 recycle not only the process water, but also the chelant may therefore be economically
432 feasible. However, at the current stage of development, the proposed EDTA recycling
433 methods involve the use of other expensive chemical materials or are technically demanding.
434 For example, the substitution procedure proposed by Kim and Ong (1999) can prove difficult
435 to apply if EDTA is complexed with more than one trace metal, especially with Zn. It is rare
436 for soil to be contaminated with a single metal; rather, several toxic metals are usually
437 simultaneously present in elevated concentrations. On the other hand, EDTA, the most
438 commonly used chelating agent, is relatively inexpensive (in Europe, it costs about 1.3 euros
439 per kg⁻¹ for the technical-grade chemical, according to a major European manufacturer)
440 compared to the cost of soil remediation, which can go up to 450 euros per m⁻³ for *in situ* soil
441 washing (Summerville and Scott, 2005). Chaney et al. (2000) reported that the price of
442 technical-grade EDTA in the U.S.A. was 4.3 US\$ per kg⁻¹. The efficient destruction of EDTA
443 complexes and the removal of toxic metals from the washing solution could provide a simple
444 and robust treatment, and the process water can be reused.

445 To treat decontaminated wastewater from the nuclear industry and other aqueous effluents
446 contaminated with EDTA, the chemical destruction of EDTA and its complexes using
447 advanced oxidation processes (AOP) has been proposed (Korhonen et al., 2000; Munoz and
448 von Sonntag, 2000). AOP involves the use of ozone, H₂O₂, ultrasonic waves, UV irradiation,
449 Fenton's reagent (Fe²⁺ and H₂O₂), alone or in combination, and electrochemical methods, to
450 generate free hydroxyl radicals that are powerful, effective and non-specific oxidizing agents.

451 Finžar and Leštan (2006b) introduced a novel EDTA-based soil leaching method that involves
452 treating and reusing the washing solution in a closed process loop (Figure 5). An AOP
453 combination of ozone and UV was used to generate hydroxyl radicals for the oxidative
454 decomposition of EDTA-metal complexes. The metals which were released were then
455 removed from the washing solution by absorption on a zeolite-based commercial metal
456 absorbent. The method was successfully tested for soils contaminated with Pb, Zn, Cd and Cu,
457 resulting in the removal of a substantial amount of metals and in a major reduction of the
458 mobility and bioaccessibility (toxicity) of metals left in the soil after remediation (Leštan and
459 Finžgar, 2007). The method produced a colorless discharge washing solution with a close to
460 neutral pH and fairly low concentrations of toxic metals and EDTA. Compared to
461 conventional soil washing methods, this method requires very little process water, and enables
462 potential emissions to be easily controlled – in short, it is environmentally and soil “friendly.”

463

464 **4. The fate of metals left after soil remediation**

465

466 Toxic metals in soil are usually not entirely accessible to chelating agents. Consequently,
467 only part of the total amount of metals in soil is removed by soil washing or enhanced
468 phytoextraction, especially from soils rich in organic matter or clay. Peters and Shem (1992),
469 for example, reported that a maximum of 64.2 and 19.1% of Pb (compared with the initial Pb
470 concentration) was washed with EDTA and NTA as chelants, respectively, from contaminated
471 soil with a high clay and silt content. Similarly, Pichtel et al. (2001) reported that various
472 concentrations of EDTA and PDA (pyridine-2,6-dicarboxylic acid) removed up to 58 and
473 56% of Pb, respectively, from soil material at a battery recycling/smelting site. Metal
474 speciation and fractionation are also crucial for extraction efficiency of chelating agents.
475 Barona and Romero (1996) extracted Pb-contaminated soil with EDTA and observed that the

476 amount of Pb that was removed correlated with the amount of Pb associated with the Fe and
477 Mn-oxide and organic matter soil fractions. Finzgar et al. (2005) reported that using 40 mmol
478 kg⁻¹ of [S,S]- EDDS extracted 31.1% of Pb from vegetable garden soil, which was rich in
479 organic matter. Lead was removed proportionally from the carbonate and organic matter soil
480 fractions. To evaluate the potential of EDTA, NTA, DTPA and [S,S]- EDDS to extract Pb,
481 Zn, Cd and Cu from soil, Nowack et al. (2006) compiled data from 28 publications. Except in
482 some reports for Pb, complete solubilization did not occur, even at a chelant-to-metal ratio of
483 greater than 10. The compiled data also indicated large variations in metal extraction among
484 soils for a given chelant-to-metal ratio.

485 Potentially toxic metals left in soil after remediation are likely to be present in chemically
486 stable mineral forms and bound to non-labile soil fractions. As such, they are less mobile and
487 bioavailable, and therefore less toxic in comparison with the original conditions before
488 remediation. However, the question is whether the reduced mobility and bioavailability of soil
489 residual metals is a permanent or only temporal achievement of soil remediation. Soil is a
490 dynamic natural body and, after remediation, various abiotic (i.e., climatic, hydrological) and
491 biotic soil (microorganisms and fauna) factors could presumably initiate the transition of
492 residual metals from less to more mobile/accessible forms, thus changing their toxicity status.
493 Of the biotic factors, earthworms are perhaps the most important soil organisms in terms of
494 their influence on soil properties. By ingesting organic debris, earthworms have been shown
495 to enhance the bioavailability of soil nutrients such as C, N and P, and also of trace metals.
496 For example, Udovic et al. (2007) reported that EDTA soil leaching removed 58.4% of initial
497 soil Pb and decreased Pb mobility by 83.7% (assessed by the toxicity characteristic leaching
498 procedure, TCLP). However, after the exposure of remediated soil to the earthworm species
499 *Eisenia fetid*, the Pb mobility in their casts increased by 6.2-times – back to the initial level
500 before remediation. In the process of phytoextraction, although the metals accumulated by the

501 shoots of plants are proposed to be recovered by incineration, this technology still needs
502 further research and development in the future.

503

504 **5. Conclusion**

505

506 The remediation of metal-contaminated soils using synthetic chelants for soil washing and
507 for enhancing phytoextraction by plants has become one of a number of well studied clean-up
508 techniques in the last two decades.

509 In soil washing, however, the strategies for developing chelant-washing solutions to
510 achieve optimal efficiency in the extraction of toxic metals and in the recovery of chelant and
511 process water need to be improved. Furthermore, the methods currently being proposed to
512 recycle chelating agents from spent washing solution are still encountering operational
513 difficulties and work well only within a narrow range of contamination and soil types. The
514 cost for soil washing and vitrification is estimated to be between US\$ 100,000 and 1,000,000
515 per ha (Russel et al., 1991). The development of more robust recycling methods would greatly
516 increase the economic value of soil washing technologies.

517 The operational cost of chelant-enhanced phytoremediation is much lower than the soil
518 washing operation. In combination with the possible recovery of extracted metals, this
519 technology can be more promising in the future. However, the potential leaching of metals
520 into surrounding environments is the most important concern in this process. It is therefore
521 essential to optimize this technology before it can be safely adopted in field applications.

522 Since toxic metals in soil cannot be entirely removed by chelants and plants, enhanced
523 phytoextraction and soil washing generally focus on stripping the bioavailable and mobile
524 metal fractions those interact with biological targets and poses a threat to the environment and
525 human health, instead of trying to reduce the total concentration of metals in soil below limits

526 set by legislation (Hamon and McLaughlin 1999). However, the potential effect of abiotic and
527 biotic soil factors on the availability and mobility of toxic metals left in soil after soil
528 remediation requires further investigation.

529

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536

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814 **Figure Captions**

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817 Figure 1. The schematic representation of the uptake of metal-chelant complexes by plant
818 roots, their translocation upward, and the potential leaching of metals into the
819 surrounding environment in the process of chelant-enhanced phytoextraction (the red
820 circle and yellow moon represent the metals and the applied chelant in the soil,
821 respectively)

822

823 Figure 2. Flow chart of *in situ* soil flushing via the injection (A), irrigation (B) and sprinkling
824 (C) of the soil washing solution.

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826 Figure 3. Flow chart of *ex situ* extraction of the soil slurry in the reactor.

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828 Figure 4. Flow chart of *ex situ* soil heap/column leaching.

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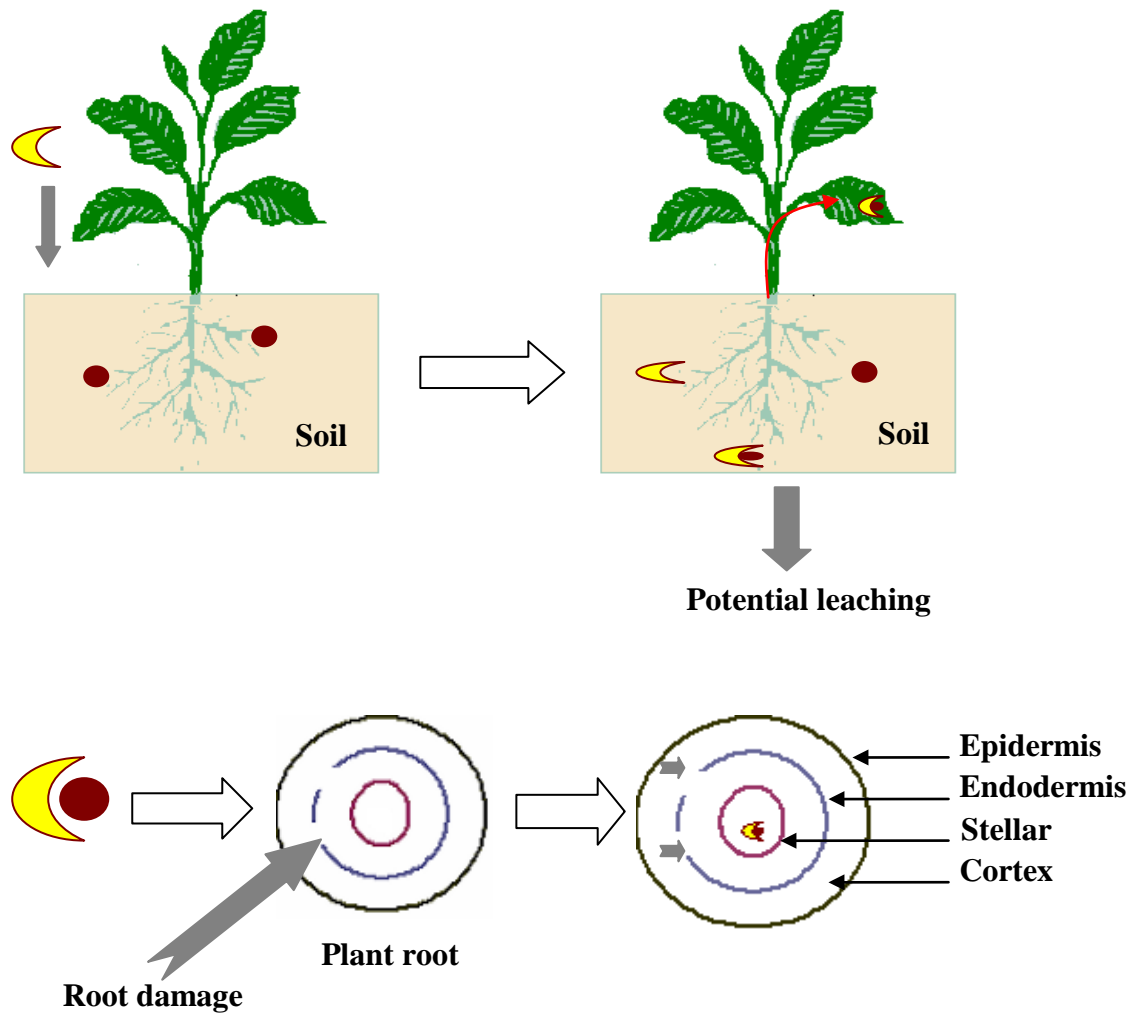
830 Figure 5. Flow chart of the chelant-based soil leaching method using AOP to treat and reuse
831 the washing solution in a closed process loop. The washing solution first circulates
832 solely through soil (A- washing step) until the optimal contact time for removing the
833 metals is reached, and afterwards also through the soil solution treatment units (B),
834 to remove all mobilized metal complexes from the soil.

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Figure 1

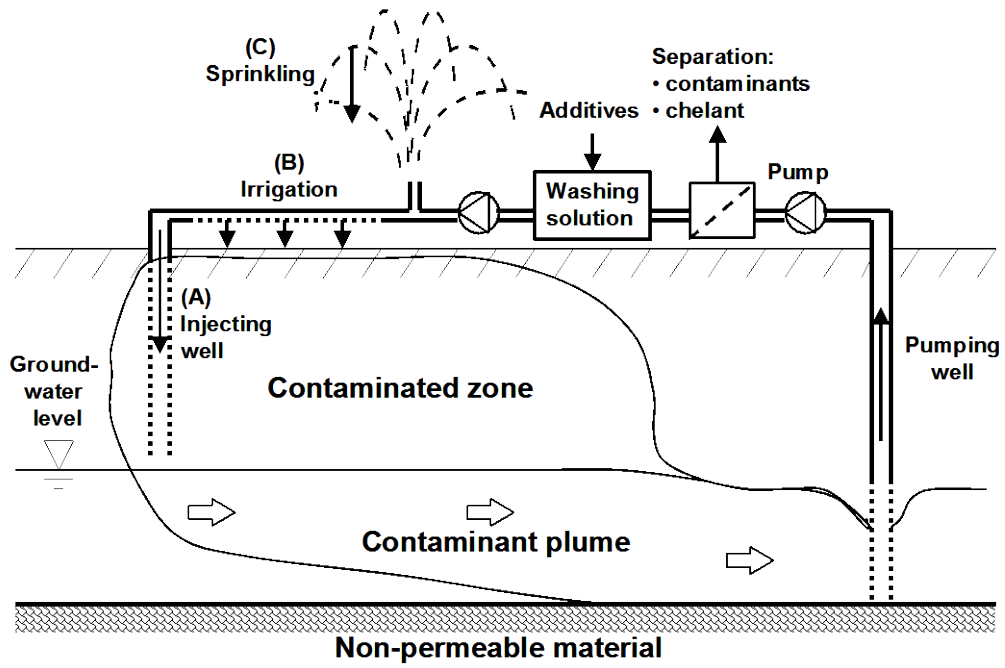


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Figure 2

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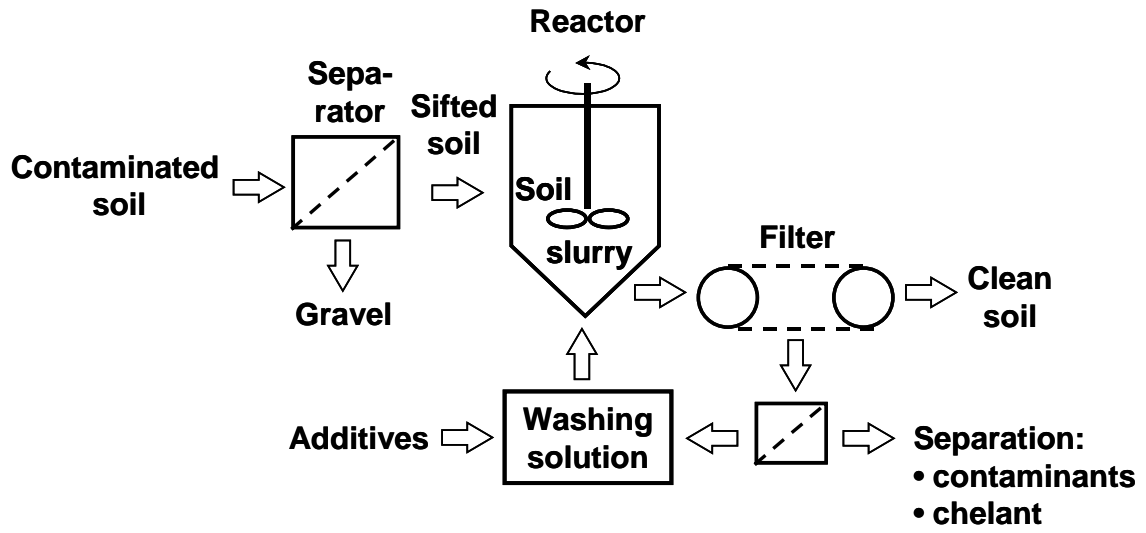
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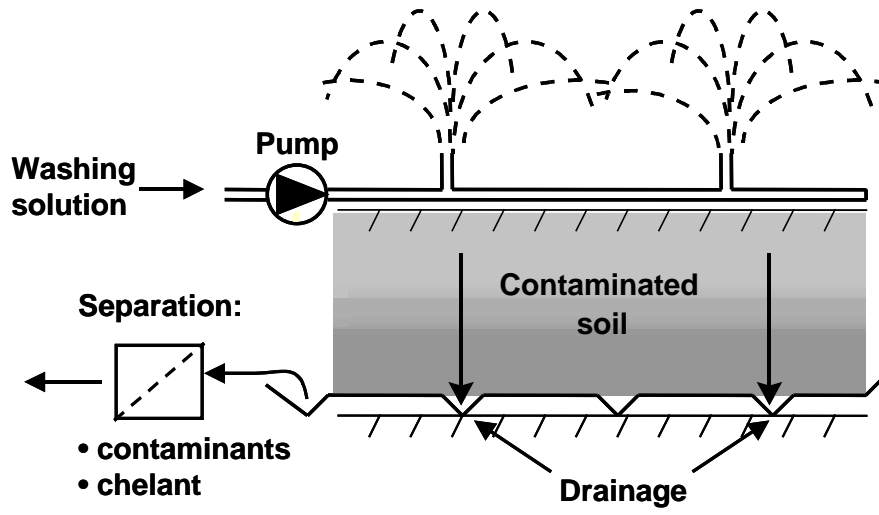
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Figure 3



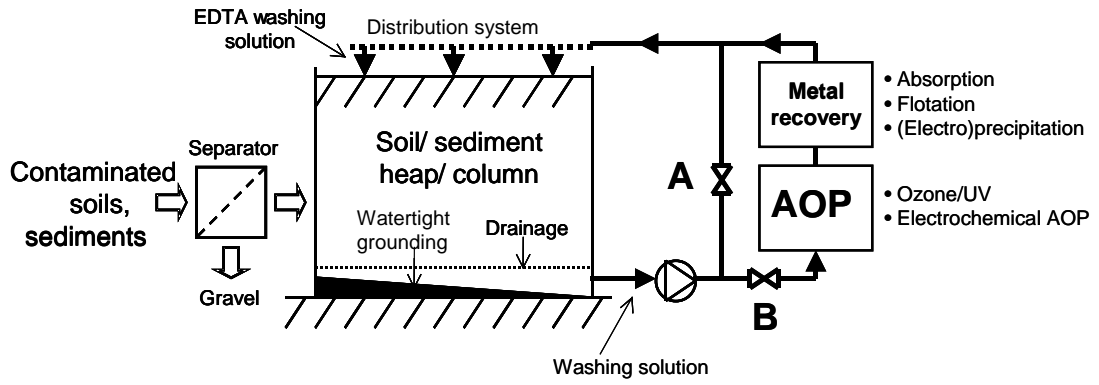
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Figure 4



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Figure 5



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