Treatment technologies used for the removal of As, Cr, Cu, PCP and/or PCDD/F from contaminated soil: A review

Karima Guemiza[1], Lucie Coudert[2], Sabrine Metahni[3], Guy Mercier[4],
Simon Besner[5] and Jean-François Blais[6],*

[1] Ph.D. student, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone : (418) 654-2550, Fax : (418) 654-2600, email: karima.gmiza@ete.inrs.ca

[2] Research associate, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone : (418) 654-3793, Fax : (418) 654-2600, email: lucie.coudert@ete.inrs.ca

[3] Ph.D. student, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone : (418) 654-4677, Fax : (418) 654-2600, email: sabrine.metahni@ete.inrs.ca

[4] Professor, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone : (418) 654-2633, Fax : (418) 654-2600, email: guy_mercier@ete.inrs.ca

[5] Researcher, Institut de recherche d'Hydro–Québec (IREQ), IREQ, 1800, boul. Lionel–Boulet, Varennes, Qc, Canada, J3X 1S1, Phone: (450)–652–8318, Fax: (450)–652–8424, email: besner.simon@ireq.ca

[6] Professor, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone : (418) 654-2575, Fax : (418) 654-2600, email: blaisjf@ete.inrs.ca

* Corresponding author.

September 2016

detoxification or reductive transformation processes of chlorinated organic compounds such as PCP. The reduction of Fe(III) under abiotic conditions led to the generation of Fe(II) which acts as active reductants to stimulate the degradation of PCP [25]. The PCP adsorbed on soil particles can also be degraded by photolysis [26]. However, the biodegradation and the photolysis are natural degradation processes that required a long time (days to months) [19].

In many countries around the world, PCP has been classified as a major priority pollutant with potential risks to human health [27-29]. The presence of several impurities in the formulations of PCP is the main cause of the difficulty to conclude on the toxicological effects of PCP [19]. This compound is known to be teratogenic to the embryo and to be responsible of irreversible fetal malformations [30]. Exposure to high levels of PCP can cause harmful effects on the liver, kidneys and gastrointestinal tract. Contact with this compound can also cause reproductive problems, damage the immune system, and can even cause death (LD_{50} = 29 mg/kg for humans) [21,26,31].

The presence of PCP in soils is widespread and is mainly due to the emissions of industries, the disposal of hazardous waste, the accidental spills at industrial facilities, the land application of sewage sludge or the *in-situ* leaching of treated wood [19,21]. In the United States, among the 1,585 sites listed on the National Priority List (NPL) of intervention, 313 sites have a serious problem of contamination by PCP [19]. In Scandinavia, approximately 500 treated wood storage sites have a serious problem of contamination by PCP [8].

1.2 Dioxins and furans

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are two families of polycyclic chlorinated compounds with similar molecular structure and physico-chemical properties [32]. The PCDD/F belong to the chemical family of chlorinated polycyclic aromatic hydrocarbons (CPAHs) designated under the generic term of dioxins and furans. These halocarbons are made of two benzenic rings joined by a mono- or a di-oxygenated ring for PCDF and PCDD, respectively. In PCDD and PCDF compounds, the chlorine atoms may occupy one to eight different positions on the benzenic rings [33]. Depending on the number of chlorine atoms and their position, there are 75 different PCDD congeners and 135 PCDF congeners [34].

7

The PCDD/F compounds are very resistant to biological degradation and thus; they easily accumulate in the environment due to their long half-lives which is, in the atmosphere, in the order of 3.2 to 5.8 years [35]. In 1997, a study estimated that the half-life of 2,3,7,8-TCDD in soil is about 10 years [36]. The solubility in water of these compounds is very low, they are non-polar and hydrophobic compounds with high octanol/water partition coefficients (Kow) [37]. The hydrophobicity of the dioxins and furans is proportional to the number of chlorine atoms present in the molecule. According to CCME [34], in water at 25°C, the solubility of the 1,4-dibenzo-p-dioxin is equal to 0.87 mg/L whereas the solubility of the octachlorodibenzo-p-dioxin (OCDD) is equal to 0.74×10^{-7} mg/L. The solubility of PCDD and PCDF in chlorinated and non-chlorinated organic solvents is higher than in water. The solubility of PCDD/F in low polar solvents (aromatic hydrocarbons, fats, waxes) is very high.

These PCDD/F are semi-volatile compounds, making their gaseous dispersion in the environment negligible. The volatility of these compounds decreases as the number of chlorine atoms present on the molecule increases. In addition, PCDD/F are known for their high melting points, which increases with the number of chlorine atoms on the molecule. For example, the melting point of 1,4- dibenzo-p-dioxin is around 122-123°C, whereas the melting point of the octachlorodibenzo-p-dioxin is around 325-326°C. The PCDD/F are stable molecules at temperatures up to 800°C, their destruction is complete at temperatures higher than 1,300°C [33].

Due to their hydrophobic properties and densities, the PCDD/F are easily adsorbed by suspended particles in the water or can be deposited by sedimentation [38]. The PCDD/F adsorbed to soil particles will be mobilized in soil or transported by water (dissolved organic material or suspended soil particles) or by the air (fine soil particles) [39]. The adsorption of PCDD/F to the soil particles is favorable due to their hydrophobic properties and becomes stronger as the number of chlorine atoms increases; limiting the biodegradation process of highly substituted PCDD/F [33]. The low solubility and the high hydrophobicity of PCDD/F can both explain the persistence of these compounds in the environment. Moreover, desorption of PCDD/F from soil particles is difficult; explaining why these contaminants are persistent in soils [37].

The degradation of PCDD/F in the environment takes place by biodegradation processes in the presence of microorganisms (fungi, bacteria) or by photodechloration process [33]. However, in the soil, the photodegradation of PCDD/F is limited by the low penetration of ultraviolet rays and by the form in which the molecules are present. Also, the biodegradation of the molecules of PCDD/F is directly related to the biotic composition of the soil and to the climatic conditions [34].

PCDD/F are a group of dangerous chemicals known as persistent organic pollutants (POPs). Among the 210 congeners of PCDD/F, only 17 molecules (7 PCDD and 10 PCDF) are considered as toxic to humans. The toxicity of PCDD/F is directly related to the number of chlorine atoms substituted to the molecule and their position [37]. Beyond 5 chlorine atoms, toxicity drops sharply [33]. In order to define the degree of toxicity of each PCDD/F congener, a toxic equivalency factor (TEF) has been defined. This factor expressed the toxicity of dioxins and furans in terms of the most toxic dioxin (2,3,7,8-TCDD). The concentration of PCDD/F present in a matrix can be calculated from the different toxic equivalency factors following the Equation 1

where " Ci " represents the concentration of each dioxin or furan congener considered and " TEFi " represents the factor toxic equivalency of each toxic congener (7 PCDD and 10 PCDF).

The main sources of the contamination of soils by PCDD/F are the use of organochlorinated pesticides or herbicides and preservative agents, as well as, the production and the use of chlorinated compounds. PCDD/F are impurities present in the composition of chlorinated products, including the PCP-preservative agent. Due to their hydrophobic properties, these chlorinated compounds tend to easily penetrate and accumulate into the soil. Several sites polluted by PCDD/F are classified in the national list of priorities defined by the USEPA. In the USA, about 500,000 metric tons of soils are contaminated by PCDD/F [40]. Recently, Urban et

al. [41] showed that the concentrations of dioxins are higher and more variable in urban /suburban soils than in rural soils; indicating that, in the United States, the contamination of soils by PCDD/F is the result of industrial practices. Between 1960 and 1970, the annual emissions of PCDD/F measured on agricultural land in Japan were above 10 kg TEQ/year (International Toxic Equivalent) due to the intensive use of herbicides, pentachlorophenol and chloronitrofen (ether 2,4,6-trichloro-4'-nitrophenyl). In the years 1970-1980, several sites have been contaminated due to the production of pesticides (2,4,5-trichlorophenol or 2,4,5-trichlorophenoxyacetic acid) in Europe and in the United States [42]. According to this author, high levels of PCDD/F were measured in soils located near sources of industrial pollution, such as sawmills with concentrations higher than 224 ng TEQ/kg [42]. In the Netherlands, concentrations of PCDD/F above 200 ng TEQ/kg were measured near municipal waste incinerators [33]. In France, concentrations of PCDD/F higher than 40 ng TEQ/kg were reported in soils located near an urban waste incinerator [33]. In Finland, concentrations of PCDD/F around 90 ng TEQ/kg of soil were reported in soils near a plant of wood preservation [42].

1.3 Arsenic, Chromium and Copper

Chromated copper arsenate (CCA) is a mixture of metal oxides formed from As, Cr and Cu [43]. In CCA-treated wood, As is present in its pentavalent form and several studies highlighted that the As leached from treated wood in its pentavalent form [44]. The most common inorganic forms of arsenic usually found in the environment are arsenite (+III) and arsenate (+V) compounds [45]. The arsenite compounds are more mobile than the arsenate compounds, suggesting that the horizontal and vertical migration of As(III) into the soil is more favorable than for As(V). Even if arsenate compounds are more thermodynamically stable under normal environmental conditions, redox transformations between arsenate and arsenite compounds can occur under aerobic or anaerobic conditions in the presence of microorganisms or algae [46-48]. Iron redox cycle plays an important role on the oxidation state of As and therefore on the mobility of this contaminant through the soil. For example, the photolytic reduction of dissolved Fe(III) can enhance the oxidation of As(III) and therefore, the adsorption of As(V) to the intrinsic components of the soil [48]. According to several studies, As(V) is mainly fixed to the soil by adsorption onto the aluminum, manganese or iron oxides and hydroxides. Generally,

the various compounds of As(V) are preferentially adsorbed onto clay particles and residual fractions of the soil [44,49]. Recently, Reynier et al. [50] showed that As is mainly present in the residual fraction or is fixed to the organic matter contained into the studied soil. The fate of As in anoxic soil can be influenced by the microbial reduction of sulfates (SO_4^{2-}) to sulfide. Indeed, the sulfide produced can reduce Fe(III) and As(V), leading to the release of As into the aqueous phase. However, the sulfide can also immobilize As in the form of As_2S_3 [48]. Therefore, microbial and chemical processes occurring in soil can affect the mobility and the oxidation state of As and therefore the toxicity of this contaminants to humans and fauna. Some compounds of As have identified as hazardous substances to human health [49]. Several compounds of As are carcinogenic and may cause skin, liver, kidney or bladder cancers [51]. Some others effects are also reported in the literature, such as cardiovascular disease or diabetes [44], damage to the nervous or immune systems. Generally, the inorganic arsenite species of As are more toxic but more mobile in the environment that the inorganic species of As(V). According to the World Health Organization [52], the limit concentration of As recommended in potable water is 10 µg/L.

Chromium (Cr) is a transition metal, exhibits five oxidation states of which the most stable and the most prevalent in the environment and in the wood preservation industries are Cr(+III) and Cr(+VI). Chromium may be present as hydroxides ($CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3$, $Cr(OH)_4^-$) or oxide (Cr_2O_3) in groundwater, surface water or wastewater, depending on the pH and the redox potential of the solution. Moreover, the Cr (III) can also form stable complexes with sulfate ($CrSO_4^+$), ammonium ($Cr(NH_3)_6^{3+}$), cyanide, thiocyanate, chloride ($CrOHCl_2$) and fluoride [53]. For hexavalent chromium, the major forms found in the environment include $HCrO_4^-$, CrO_4^{2-}, H_2CrO_4, CrO_3, CrO_2Cl_2, $(NH_4)_2CrO_4$, Na_2CrO_4, $Na_2Cr_2O_7$. The chromium is less soluble and more stable in its trivalent form than the Cr(VI). Cr(III) can easily be precipitated as hydroxides ($Cr(OH)_3$) at pH between 7 and 11. Due to its high solubility, the hexavalent chromium is more bioavailable and more toxic to humans and animals than trivalent chromium [54]. According to several studies, Cr is leached from the wood in its trivalent oxidation state, but it may be present in its most oxidized form (Cr(+VI)) in small amounts in treated wood [55]. When penetrating into the soil, the hexavalent chromium is reduced to Cr(III) by the organic matter in

anaerobic conditions or by the Fe(II) or sulfides in anoxic conditions [48,53]. The mobility of Cr(III) in soil is very low, this contaminant can be quickly fixed to the intrinsic components of the soil by complexation with the organic matter (humic and fulvic acids). Reynier et al. [50] showed that Cr is mainly present in the residual fraction or complexed to the organic matter present in the soil when using sequential extraction technique [56]. Hexavalent chromium Cr(VI) is toxic for humans and fauna and is classified as carcinogenic compounds to human [57]. The USEPA indicates that the Cr(VI) causes damages to the liver and to the renal circulation or can cause irritation of the skin after long exposures. The inhalation of Cr(VI) can also cause damages to the nervous system [58] and the immune system [59]. According to the World Health Organization [52], the limit concentration of Cr acceptable in potable water is 50 μg/L.

Copper (Cu) is also a transition metalthat can be present in the environment under two oxidation states; which are (+I) and (+II), in addition to its metallic oxidation state (0). Cupric ions, Cu(II), are more stable in aqueous solutions than the cuprous ions, Cu(I). Copper is leached from treated wood in its cupric form, Cu(II). The mobility and the transport of the Cu(II) in the soil are reduced by the huge affinity of this contaminant for the intrinsic components of the soil. Indeed, copper is quickly complexed by the minerals, especially by iron hydroxides contained into the soil [53]. The fate of Cu into the soil mainly depends on iron redox cycle [48]. Dissolved organic matter also plays an important role on the biogeochemistry and bioavailability of Cu due to the high affinity of this contaminant to organic ligands. Therefore, the presence of huge amounts of dissolved organic matter has a strong impact on the solubility and transport of Cu through the soil [60]. According to several authors, oxidizing conditions are more favorable for the mobilization of Cu than reducing conditions. The sequential extraction of contaminated soils showed that 70% of Cu is present in the organic fraction [61]. Recently, Reynier et al. [50] showed that, in the studied soil, copper can be fixed to the carbonates (17-20%), the organic matter and sulfide (2-34%) and the metal oxides (16-29%) and also be found in the residual fraction (19-61%). Cu is known to be essential for many metabolic processes due to its presence in proteins and enzymes. This element regulates the transport of iron, cholesterol and glucose [62]. However, in excessive amounts, Cu can cause damages to the liver and kidneys [63]. In drinking water, the limit concentration of copper is fixed at 2 mg/L [52].

12

The contamination of soil by metals can be due to many natural or anthropogenic activities [64,65], such as domestic tasks, agricultural or industrial activities. Serious problems are encountered across the world due to the contamination of soil and groundwater by metals and especially As. For example, the contamination of soil and groundwater by As represents a serious problem in China, where the risk of cancers due to the high exposition of the population to this contaminant [66-67]. The industry of copper-based wood preservation represents an important source of soil contamination by metals (As, Cr, Cu). The leaching and the dispersion of metals from CCA-treated wood can cause many environmental issues including soil contamination. Concentrations of 500, 200 and 1,000 mg/kg of As, Cr and Cu, respectively, were measured in soil near CCA-treated poles [68]. Stilwell and Gorny [69] measured concentrations of metals of 350 mg As/kg, 150 mg Cr /kg and 350 to 500 mg Cu/kg in soils around CCA-treated poles. A study carried out in 2003 showed the presence of high levels of As, Cr and Cu in the top 10 cm of soil from different wood preservation sites. The concentration of metals measured on these sites ranged from 15 to 3,200 mg/kg for As, from 20 to 2,400 mg/kg for Cr and from 10 to 9,800 mg/kg for the Cu [53]. According to Chirenje et al. [70], the concentrations of As reached more than 23 mg As/kg in soil below treated wooden patios, whereas a concentration of 3 mg As/kg was measured in soil located at 1.5 m away from this treated structure. Solo-Gabriele et al. [71] found a similar behavior of soil contamination by CCA-treated wood with concentrations of 28.5 mg As/kg in soils near treated structures and concentration of 1.5 mg As/kg in soils located at 1.5 m away from the structures. The variation in the levels of Cu measured in soil near CCA-treated wood and in soil at 1.0-1.5 m away from the treated wood is more important than those observed for As [70-71]. Generally, the majority of Cr and Cu are immobilized in the soil to 15 cm and up to 15 and 30 cm for As, which is more mobile [70]. Unlike most of the organic contaminants, the degradation of metals is impossible and these compounds can easily be retained by the intrinsic components of the soil. Soil type (structure, pH, Eh, organic matter, presence of ferric or aluminum hydroxides, etc.) plays an important role in the distribution, the transport and the bioavailability of metals in soil [72]. However, significant amounts of metals may nevertheless migrate to the groundwater; leading to its contamination [53].

2 DECONTAMINATION TECHNIQUES

Due to the high levels of organic and inorganic contaminants measured in polluted soils and their toxicity to humans and the environment, several technologies have been developed over the past few years to manage polluted solid matrices including soils. The simplest and the most widely used method to manage contaminated soils is excavation followed by disposal in an appropriate secure landfill site. However, this solution becomes inappropriate in the context of the sustainable development due to the transfer of the contamination from a contaminated site to a secured landfill site, without any reduction of the amount of solid contaminated to be managed. In this context, several efforts have been made over the world to develop technologies to efficiently decontaminate sites contaminated by persistent contaminants. These decontamination techniques, presented in Table 1, can be classified into different groups (destructive or separative methods) according to the strategy used.

According to the literature, the destructive techniques including thermal treatments at high temperature or dechlorination methods are effective for the removal of organic contaminants such as PCP and PCDD/F [42]. Among the separative methods, the thermal desorption seemed to be highly efficient for the removal of PCP and PCDD/F from contaminated soils whereas soil washing with acidic or basic solutions seemed to be the most effective method for the removal of metals from contaminated [73-80].

For the determination of the most appropriate method of decontamination, a multitude of factors must be taken into account. Each contaminated site has different characteristics, especially if the geology and the hydrology of the contaminated site are different from one location to another one [81]. The area of the site to be rehabilitated and the intended use of the site should also be considered for the determination of the most appropriate method to manage the contaminated site [82]. The physico-chemical properties of the contaminants and their initial concentration in the soils play a very important role in the choice of the most efficient method of rehabilitation [81-83]. It is important to note that the treatment of sites contaminated by both inorganic and organic contaminants is more complex, which is mainly due to the different properties and behavior of inorganic and organic contaminants [84-88].

Usually, several successive stages (sequential extraction) must be performed to ensure an efficient decontamination of the site but the costs related to the rehabilitation of the site are very high [89].

2.1   Immobilization of contaminants

The techniques of immobilization of organic and/or inorganic contaminants are widely used in Canada for the rehabilitation of contaminated sites. These techniques can be applied in-situ or ex-situ. Usually, the in-situ techniques of immobilization consist on covering the contaminated sites by uncontaminated land. It is also possible to use a geomembrane (plastic), a composite clay barrier, a drainage layer, and a layer of vegetation or a hardened asphalt cap. These immobilization techniques are most frequently used for the control of inorganic contaminants, such as metal compounds used in the wood treatment industries. The stabilization of metals can be carried out by using plants that are able to bind these metals to the roots (phytostabilisation) [90-92]. Other substances that have a high ability to immobilize heavy metals can be used for the rehabilitation of contaminated soils. In addition, this method of treatment is applicable to certain contaminants localized at the surface [82].

Among the ex-situ techniques of immobilization, the predominant option to manage soils highly contaminated by organic and/or inorganic contaminants is the excavation followed by the stabilization/solidification (S/S) and a secure landfilling, due to the low costs related to soil landfilling. The stabilization consists on the reduction of the solubility and the mobility of the contaminants by the addition of binding materials [92]. These binding agents include phosphate compounds (e.g. apatite) [93,94], fly ash, lime and hydrated lime (CaO, Ca(OH)$_2$) [95,96], aluminosilicates, cementor minerals (clays, oxides/ hydroxides iron, zeolites) [97-98]. Kim et al. [99] used the iron to stabilize the As contained in tailings highly contaminated as iron oxy-hydroxides are known for their abilities to immobilize As. The precipitation of ferric arsenate (FeAsO$_4$.2H$_2$O) or the adsorption of As compounds onto the ferric hydroxides (Fe(OH)$_3$) are the main mechanisms responsible of As immobilization in the presence of iron [99-100]. A study carried out by Spuller et al. [101] revealed that an immobilization of heavy metals present in shooting range soil, with iron (hydro)oxides allows a reduction of the mobility of Cu, Pb and Sb of 95%, 97% and 78%, respectively. Moreover, the mobility of Pb was reduced by 45 to 99% in

the presence of phosphatic amendments. This physical isolation can be used for the rehabilitation of sites contaminated with low levels of PAHs and PCP. For example, the immobilization of PCP in contaminated soils was studied in the presence of carbonaceous material amendment, especially char amendment, which quickly and enduringly reduced the bioavailability of PCP initially present in soil [102]. Sukla and Lee [103] indicated that the immobilization mechanisms of PCP in cement are mainly due to the adsorption of this fairly weak acid on the surfaces containing Ca^{2+} or Al^{3+} around clinker particles. In Canada, the technique of S/S is also often used for the rehabilitation of urban and industrial sites; it has been successfully applied in several cases such as Project Sydney tar pond. Nowadays, this technology is commercially available in the North America to allow the rehabilitation of soils contaminated by metals and organic contaminants, if the total organic content did not exceed 30%.

The stabilisation/solidification or the physical isolation can be used after soil washing or bioremediation processes, which increases the costs of treatment. However, these treatments are not permanent, some contaminants remains accessible and these techniques require the monitoring and/or the maintenance of the secured systems. In short-term, this management option allows the reduction of the exposure of contaminants to humans, to surface water and groundwater by infiltration. Although S/S technologies are not considered as an ideal management option, they are still used for the treatment of contaminated sites in the United States and in Canada [104].

2.2   Methods of treatment of soils contaminated by organic compounds

Over the last years, several techniques based on thermal, biological, physical and chemical (action of a solvent, oxidation, etc.) principles have been developed for the decontamination of soils contaminated by organic compounds [7,42,50,86,89,94-114]. Table 2 presents a summary of several thermal, biological and chemical decontamination processes developed at laboratory scale to remove organic compounds such as PCP and PCDD/F from contaminated soils.

16

2.2.1   Thermal treatment

Thermal treatments are the most efficient and widely used techniques to simultaneously remove PCP and PCDD/F from highly contaminated soils. Among the ex-situ thermal processes, both thermal treatment and thermal desorption (pyrolysis) are applied at industrial scale in Canada and in the United States. The main differences between these techniques are the temperature imposed during the thermal treatment, the amount of oxygen required and the products obtained at the end of the thermal processes.

The incineration is based on the use of high temperatures (800-1,200°C) in the presence of oxygen, to convert the organic contaminants present in the soil such as PCP, PCDD/F and PAHs into simple and non-toxic molecules [115]. The main products of this total combustion are CO_2, H_2O and various other combustion residues [74]. According to INSERM [33], the destruction of the PCDD/F compounds is complete for temperature higher than 1,300°C and with a minimum contact time of 2 seconds. Therefore, the combustion of soils heavily contaminated by PCDD/F at temperatures above 1,000°C allows the removal of more than 99% of PCDD/F [42]. In addition, the high temperature of thermal treatments causes the decomposition of the organic matter present in soils which strongly limits the reuse of treated soil [66].

The pyrolysis processes are based on the decomposition of organic contaminants at low temperature (250-550°C) in the absence of oxygen. A recent study, carried out at laboratory scale, showed that the pyrolysis of soils contaminated by PCP at 250°C allows the removal of 70% of PCP. However, this pyrolysis process results in the formation of a significant amount of PCDD/F (1,436 ng/kg) [76]. According to Ken and Lo [73], desorption of PCP from contaminated soils increases with the increase of the temperature imposed to the system. In Florida (United States), soils contaminated by PCP and PCDD/F were efficiently treated by thermal desorption at 540°C on a pilot scale [111]. Speir et al. [116] have demonstrated, at a laboratory scale and then, at pilot scale, the effectiveness of a thermal desorption process (indirectly heated soil system) which allows the destruction of more than 99.99% of PCP and 98% of PCDD/F at a temperature fixed at 450°C. However, the thermal desorption at temperatures below 400°C may result in the formation of highly toxic dioxins [33,116]. The mechanisms of the formation

of PCDD/F during combustion or thermal desorption is not fully elucidated. However, two mechanisms responsible of the formation of PCDD/F have been identified: the formation of PCDD/F from precursors such as chorophenols (CPs) and chlorobenzenes and the Novo synthesis. The mechanisms of PCCD/F formation from the condensation of chlorhpenols and De novo synthesis are well described by Jansson [117]. Hung et al. [118] showed that inadequate retention time may lead to an increase of the TEQ-value due to an incomplete destruction of PCDDs and the formation of highly toxic congeners. Recent studies in the field of soil treatment (for sediment or sludge) showed interesting results for the destruction of some organochlorine contaminants including PCP and PCDD/F during thermal processes [7,114,115]. Usually, the thermal desorption of soils contaminated by PCP and PCDD/F is followed by the incineration of the gases generated. The conversion of PCDD/F compounds present in gases can reach 100% at temperature ranging between 500 and 950°C after a residence time of 3 secondes but several intermediary species were formed (benzofuran, polyaromatic hydrocarbons and other volatile organic compounds) [119]. Recently, Lundin et al. [120] showed that a reduction (> 90%) of the PCDD/F concentration was achieved by treating contaminated soil at 280°C and adding nanosized zerovalent iron (nZVI) to the soil; resulting in almost no detectable PCDD/F in the gas phase.

The temperature and the duration of the thermal treatment are fixed according to the type of contaminants present in soils and their concentration, to the humidity level and to the nature of the soil. In fact, the vapor pressure and the concentration of organic contaminants present in soils are the main properties of the contaminants that strongly affect the performances of the thermal desorption units. Furthermore, these thermal techniques applicable to clay and/or silty soils, which are usually too wet, require more fuel; thus increasing the cost of treatment. Thermal desorption is ineffective for inorganic contaminants such as arsenic, chromium and copper as these inorganic contaminants can't be decomposed; they are actually concentrated into the treated soil [7]. Moreover, there are some risks related to the formation of PCDD/F from precursors of chlorophenols via the novo synthesis during the incineration of chlorinated compounds which was observed to be 72-99 times higher than during the incineration of carbon at temperatures lower than 1,000°C [121]. The risks of PCDD/F formation and the high

costs of energy required for the combustion limited their applications to PCP and PCDD/F contaminated soils at temperature lower that 1,000°C.

Nowadays, thermal desorption is used at full-scale for the treatment of soils contaminated by organic compounds despite the high costs [119,120,122,123]. The first stage occurs in the primary combustion chamber and consists on the desorption and/or the gasification of the organic contaminants under temperatures in the range of 650 to 800°C for 20 min. Under the action of heat between 650 and 800°C, contaminated soils became inert and free of organic contaminants. The gases contaminated by organic pollutants are heated above 1,000°C in the secondary combustion chamber for 3 sec in order to break the carbon rings where the chlorine atoms are trapped [124]. This second step leads to the decomposition of the organic contaminants. Then, the gases are condensed, neutralized, oxidized and passed through activated carbon in order to remove pollutants. This technique produces two products: 1. Remediated soils, which once cooled and moistened, can be returned to the original site or to another site; 2. Treated gases are released into the atmosphere. This technology is allowing more than 99.99% of organic contaminant removals. Although these thermal processes are efficient to remove PCP and PCDD/F from contaminated soils, it is important to note that metals still remain in the soil or in vapors, requiring additional treatment, such as stabilization/solidification processes; increasing the costs of treatment.

2.2.2 Biological treatment

Bioremediation is an ancient and well-known technology used to treat soils contaminated by organic contaminants and sometimes by inorganic compounds. These decontamination processes are based on the complete or partial decomposition (or biodegradation) of these organic and/or inorganic contaminants using microorganism such as *Proteobacteria, Actinobacteria* and *Planctomyctes* [125], *Dehalococcoides* [126-128] or *Pseudomonas mendocina NSYSU* [129-130]. During bioremediation processes, the complex organic contaminants such as PCP or PCDD/F are broken down into simple elements, such as H_2O, CO_2, CH_4, H_2 and chloride or converted into microbial cellular material [110]. The rehabilitation of soils contaminated by organic compounds such as PCP, PAHs and/or PCDD/F, using

bioremediation processes, can be done in-situ or ex-situ. The in-situ bioremediation processes usually use the microorganisms existing in the soil and only require a supply of oxygen and nutrients to allow the development of the biomass. Therefore, it is usually necessary to combine the bioremediation with the treatment of wastewater to allow their release to the environment. Ex-situ bioremediation requires the excavation of the contaminated soils to be treated on-site or off-site; increasing the costs related to the bioremediation of contaminated sites. The main advantage of the bioremediation processes is the low cost of the raw materials, whereas the variable and long exposure times sometimes restrict the application of the bioremediation to remove contaminants from soils. According to Lecomte [131], the exposure time required to treat soils contaminated by PCP and/or PCDD/F ranged from few weeks to few months; depending on the size of the molecule to be degraded. To the best of our knowledge, these biological processes were performed at laboratory scale or pilot scale but none of them is actually used in full-scale application for the decontamination of soils contaminated by PCP and/or PCDD/F.

Several studies showed that the biological degradation of PCDD/F can be done using microorganisms by dechlorination under reducing and anaerobic conditions or by dioxygenation under aerobic conditions [125,127,132]. Moreover, the complete dechlorination of the molecule of dioxins and furans lead to the reduction of the toxicity of these molecules [120]. However, a recent study highlighted that the elimination of the lateral chlorides (chloride atoms in the position 2,3,7,8) decreases the toxicity of the molecule, whereas the peri-dechlorination (chloride atoms in the position 1,4,6,9) may lead to an increase of the toxicity of PCDD/F molecules producing the molecules 2,3,7,8-TCDD/F [133]. The formation of congeners during the dechlorination of PCDD/F depends on the nature of the microorganisms used, the exposure time and the temperature of incubation [128]. A study carried out by Bunge and Lechner [126] showed the efficiency of bacteria (*Dehalococcoides*) to transform the chlorinated dioxins into non-chlorinated dioxins or mono-chlorinated compounds under anaerobic conditions. Biological methods have been developed by the USEPA to biodegrade the PCP present in the soil; allowing the removal of 96-98% of the PCP initially bound to the intrinsic components of the soil. This technology, only tested at pilot-scale, may be applied *ex-situ* and

20

in-situ to near-surface soils [110,134]. Various studies showed that PCP and PCDD/F present in contaminated soil can be biodegraded by fungi (i.e. a lignocellulosic substrate, *Pleurotus ostreatus*, *Lentinulus edodes*, *Agaricus bisporus*, *Stropharia rugosoannulata*) [113,135]. According to Dien et al. [136], the reductive biodechlorination catalyzed by bimetallic nanoparticles Pd/Fe, studied at laboratory scale, is efficient for the removal of PCP (90%) from a sandy soil. However, many redox processes occurring in contaminated soils such as the reduction of nitrates or iron under the action of microorganisms may affect the efficiency of the dechlorination processes applied to organic chlorinated contaminants [137]. For the soils contaminated by both PCP and metals, the biodegradation processes became inefficient [134]. Bioremediation of soil contaminated by organic contaminants and heavy metals (arsenic, chromium, etc.) is often difficult because of the high toxicity of metals to microorganisms which inhibit the degradation of organic compounds by bacteria or fungi. The study carried out by Sahle-Demessie et al. [109] have shown that the bioremediation processes are not efficient to degrade contaminants (i.e. PCP, dioxins, PAHs) present in soil for a very long period; which can be due to the strong adsorption of the contaminants to the intrinsic components of soil. It appears that the strongly adsorbed molecules are not biodegradable because the adsorption of contaminants to clay results in a protection of contaminants from the microflora. In addition, heavy PAHs (containing four aromatic rings and more) and PCDD/F are very poorly biodegradable molecules, which represents a limitation to the application of the bioremediation technologies [81,138]. Moreover, the efficiency of the biological processes decreases as the initial concentration of PCP in contaminated soils increases [139]. According to Pittman and He [140], bioremediation processes can often be cost effective and can be used in-situ. However, bioremediation processes are very sensitive to the temperature, the moisture content, the geology/morphology of the site and the nature of the contaminants to be remediated [129].

2.2.3 Photodegradation

According to several studies, *in-situ* or *ex-situ* photodegradation of organic molecules is caused by the absorption of photons emitted by ultraviolet radiations (UV) coming from the sun (*in-situ*

techniques) or from UV lamps (*ex-situ* techniques). For in-situ treatments, the low penetration of UV rays into the soils limit the photodegration of the organic molecules to the surface (few centimeters). These processes become inefficient if the contamination has migrated deeper into the soil, which can occur for the PCP that can be found up to 60 cm from the surface. Moreover, the photodegradation of organic molecules seemed to be more efficient for soils with low levels of contamination. This method of treatment requires the addition of an organic solvent such as vegetable oils, which increases the solubility of organic compounds; improving their photodegradation. Isosaari et al. [42] used olive oil as an organic solvent to improve the photodegradation of PCDD/F under the action of solar UV or UV lamps. After one month of exposure, 48% of PCDD/F initially present in soil (a layer of 1 cm) were photodegraded by sun radiations (0,65 kJ/g). However, as the photodegradation is inefficient to remove inorganic compounds from contaminated soils, the treated soil requires further treatment for the removal of inorganic contaminants, if present. To the best of our knowledge, this process is not applied at industrial scale.

2.2.4 Leaching processes

Leaching processes consisted on the extraction or the solubilization of organic and/or inorganic components from contaminated soils using several leaching agents such as inorganic or organic acids, chelating agents, oxidizing agents or solvents. Nowadays, the leaching processes are less applied for the rehabilitation of soil contaminated by organic compounds than biological treatments. However, for soils highly contaminated or for soils contaminated by recalcitrant organic compounds, the leaching processes seemed to be more efficient and faster than biological treatments. Usually, the leaching processes can be applied in-situ (soil leaching) or ex-situ (most widely used option). Usually, the ex-situ treatments begin with a granulometric sorting in order to separate fine particles from coarser particles present in soil. Indeed, due to their high affinity for organic matter, the PCP and PCDD/F are usually adsorbed onto the fine particles of soil such as clay. Therefore, the granulometric sorting significantly reduces the volume of soil to be treated and, consequently, the rehabilitation costs. To the best of our knowledge, all the leaching processes, developed over the last decades and presented here,

22

were only studied at laboratory scale and none of them is currently applied at industrial scale due to the lack of organic contaminant removal efficiencies or high operating costs.

According to the USEPA [141], the ex-situ washing of contaminated soil with solvents is considered as a viable remediation technology. Over the last decades, many solvents have been studied, including polar solvents (methanol, ethanol, acetone, acetonitrile) or apolar solvents (hexane, dichloromethane). The choice of the solvent to be used strongly depends on its miscibility with water, the solubility of the organic pollutants in this solvent and its biodegrability. Also, the costs of the solvent used should be enough low for an industrial application. For example, ethanol, 2-propanol, acetone and 2-pentanol were tested, at laboratory scale, to remove PAHs compounds from contaminated soils [89,142]. According to the study carried out by [105], the extraction using solvent is particularly efficient for the removal of chlorinated organics but it seemed to be inefficient for metals [7]. The efficiency of PCP solubilization from contaminated soils using polar or apolar organic solvents has been demonstrated by several studies realized at laboratory scale [143-145]. Khodadoust et al. [105] studied the extraction of PCP present in soil with an aqueous solution of methanol (MeOH). The removal yields obtained achieved 50%, 88%, 81% and 52% with various mixtures made of 0%, 50%, 95% and 100% of MeOH, respectively. Jonsson et al. [146] extracted, at laboratory scale, between 80 and 98% of PCDD/F present in soil with a solution of ethanol (75%) after 10 washing steps of 30 min each carried out at 60°C with a solid/liquid ratio fixed at 1/3. This solvent seemed to be efficient for the removal of PAHs from contaminated soils [89]. In the same study, these authors showed that the cyclodextrins are efficient for the extraction of the PCP. According to Sahle-Demessie et al. [109], the solubilization of PCP and PCDD/F in the presence of dimethyl ether at 48°C is also efficient; allowing the removal, at laboratory scale, of more than 95% of PCP and PCDD/F initially present in the soils. Other compounds, such as rhamnolipids [147] and polymer solvents (poly-ethylene oxide and propylene oxide block copolymers) [148], can be used for the extraction of organic compounds such as PCP. Recently, Tomei et al. [149] evaluated the performances of the transfer of chlorophenols (4-chlorophenol, 2,4-dichlorophenol and pentachlorophenol) from the soil phase to the aqueous phase and then from the aqueous phase to the polymer phase using three commercial

23

polymers (Hytrel 8206, Tone P787 and Elvax 40W). Based on the partition coefficients (soil/water and polymer/water) obtained, these authors concluded that the polymer Hytrel 8206 showed the highest affinity for chlorophenols. Up to 87% of PCP was removed from synthetic contaminated soils during the extraction tests realized at laboratory scale with commercial polymer Hytrel 8206 24 h.

The addition of a surfactant (detergents) to the solution of extraction can be efficient for the removal of hydrophobic compounds such as PAHs [86, 138-152] or PCP and/or PCDD/F [50,107,108,153-155]. These agents are amphiphilic molecules consisting of a nonpolar and hydrophobic long chain and a polar and hydrophilic part. Due to their properties, these molecules are able to reduce the interfacial tension between two phases with different polarities such as water and the hydrophobic organic contaminants, which enhances their solubility. The formation of electrostatic interactions between the non polar contaminants and the hydrophobic long chain enhances the solubility of highly hydrophobic organic contaminants. This process allowed the extraction of organic materials (PAHs) and metals (Pb, Cu, Zn) by combining washing technologies in the presence of an anionic surfactant (Hustapur SAS 60) and physical techniques (Jig, spiral, fluidised bed classifier, gravity separator, flotation cells). During this process, the jig and the spiral were used for the sand fraction (0.106-6.4 mm) and flotation or multi gravimetric separator to the finer fractions (< 0.106 mm). The organic extraction was performed, in a separate attrition step, onto fractions contaminated by PAHs. This decontamination process allowed the removal of 90% of PAHs and 70% of Cu, Pb and Zn [156]. This process has not been studied for PCP or PCDD/F.

Over the last decades, several surfactants have been studied at lab scale for the extraction of PCP [50,157]. For example, Mulligan and Eftekhari [158] showed that 85% of the PCP present in sandy soils at an initial concentration of 1,000 mg/kg was removed when using Triton X-100. The use of the anionic surfactant sodium dodecyl sulfate (SDS) also enhanced the solubilization of the PCP present in the soil [159]. Park and Bielefeldt [154] have studied the ability of a nonionic surfactant, the Tergipol NP10, for the removal of PCP from contaminated soils. The authors revealed that more than 87% of the PCP present in soils containing initially 200 mg/kg was removed in the presence of Tergipol NP10. The nature and the form of the surfactant play

an important role in its ability to solubilize PCP or PCDD/F [158]. According to Mulligan [160], rhamnolipids, which are biosurfactants produced by the bacterium *Pseudomonas aeruginosa*, are able to extract 60-61% of PCP from soils initially containing 1,000 mg PCP/kg.

The solubilization of organic contaminants can also be performed by soil washing in the presence of acidic, neutral or basic solutions [81]. Nowadays, this type of treatment is more and more often studied for the rehabilitation of soils contaminated by both organic and inorganic contaminants. Ethylene diamine tetra-acetic acid (EDTA) and citric acid are two chelating agents known for their significant ability to complex metals and some organic compounds; allowing their removal from solid matrices [89]. Several studies, performed at laboratory scale, highlighted that the washing of soil under basic conditions (pH > 7) seemed to be highly efficient for the removal of PCP from contaminated soils [21,44]. According to these authors, highly basic solutions will allow the reduction of the hydrophobicity of this compound and therefore, the reduction of the adsorption of PCP to the intrinsinc components of the soil. According to World Health Organization [161], at pH higher than 13, more than 99% of PCP is present in its anionic form; enhancing its decomplexation from the organic matter of soil and therefore, its solubilization. For this reason, Xiao et al. [162] studied the extraction, at laboratory scale, of PCP in the presence of sodium hydroxide (NaOH) at pH higher than 12.5. After 20 min of agitation with a solid/liquid ratio fixed at 1/8 (g/mL), more than 90% of PCP was removed. Due to the low solubility of PCP in acidic solutions, few studies were carried out in the presence of organic or inorganic acids to remove PCP from contaminated soils. However, Subramanian [12] tested, at laboratory scale, the performances of lactic acid at different concentrations and at room temperature to remove PCP from contaminated soil. The results showed that approximately 85% of PCP can be removed after 24 h with a solution containing 25% of lactic acid.

To allow the decontamination or the reduction of the toxicity of contaminated sites, it might be interesting to focus the development of treatments based on the chemical dechlorination of chlorinated organic compounds such as PCP and PCDD/F. The principle of dechlorination processes consists on mixing the contaminated soil with chemical solutions that allow the elimination of chlorine atoms. According to Chen et al. [163], chemical dehalogenation

processes involved the addition of alkali or alkaline earth, metal carbonate, bicarbonate or hydroxide to the contaminated medium. Mitoma et al. [164] have studied, at laboratory scale, the detoxification of highly toxic polychlorinated aromatic compounds (PCDD/F, Polychlorinated biphenyls - PCB) using metallic calcium in ethanol. Concentration of each isomer of PCDD/F and PCB was reduced by 98-100% after a treatment in the presence of metallic calcium in ethanol at room temperature. According to INSERM [33], the chlorine atoms present in the position 1, 4, 6 or 9 are more easily removed from the molecules of PCDD/F. The mechanochemical dechlorination of PCP and PCDD/F present in contaminated soil in the presence of chemical products such as CaO and SiO_2, seemed to be efficient; allowing the decomposition of more than 98% of PCP [165] and more than 99% of OCDDF [166]. Moreover, Kim et al. [167] studied the dechlorination of PCDD in the presence of zerovalant iron (ZVI) and palladized nanosized ZVI (Pd/nFe). Pittman and He [128] used Na/NH_3 to allow the dechlorination of polychlorinated compounds (e.g. PCP) from contaminated soils or sludges. However, as the dechlorination is inefficient to remove metals from contaminated soils, the treated soil requires further treatment for the removal of inorganic contaminants, if present.

2.3 Treatment of inorganic contaminants

Over the last years, several techniques based on biological, physical and chemical principles have been developped for the decontamination of soils contaminated by inorganic compounds. Table 3 presents a summary of several physical and chemical decontamination processes developed at laboratory scale to remove inorganic compounds such as As, Cr and Cu from contaminated soils.

2.3.1 Phytoextraction

Among the extraction techniques developed over the last years to remove metals and metalloids from contaminated soils, the phytoextraction using tolerant and accumulating plants, such as *Ambrosia artemisiifilia, Brassica juncea* and *Alyssum lesbiacum,* seemed to be a promising *in-situ* method of decontamination for soils containing low concentrations of inorganic contaminants such as As, Cr and Cu [168-170]. However, this technique requires long periods to efficiently remove the contaminants from soils and it is only efficient for surface

contamination and for the most mobile metals present into the soil [171]. These metals present on the surface of the soil can also be extracted by another technique based on in-situ electrokinetic processes. These electrokinetic processes consist on the application of low intensity electric current between a cathode and an anode inserted into the contaminated soil. Due to the application of the electric current, the ions and the small charged particles are transported to the anode or to the cathode according to their charges. This strategy was used for the removal of Cu, As, Cr, and other metals from sediments [82].

2.3.2   Physical methods for metal removals

On the other hand, the metals can be removed from contaminated soils by physical and/or chemical processes usually used in mining industries. Generally, the physical separation methods can be used for the removal of metals present in a particulate form. However, the chemical processes developed for the decontamination of soils are efficient for the removal of metals adsorbed to the intrinsic components of soil under their ionic forms or salts [172].

As usually used in the mining industries, the physical techniques of separation can be applied to reduce the volume of soil to be managed by separating contaminants or contaminated particles from uncontaminated soil particles [173]. The performances of separation technologies strongly depend on various contaminants and soil characteristics such as particle size, particle shape, density, magnetic susceptibility, and surface hydrophobic properties of the contaminants. The applicability and the efficiency of these techniques also depend on soil moisture, clay content and soil heterogeneity [174]. Among the physical methods of separation applicable to the decontamination of soils, the density and the gravimetric separations including spirale, hydrocyclone, Jig or Shaking Table are the most oftently used. A physical separation using a spiral and a hydrocyclone followed by a chemical process allowed the removal of approximately 57% of the Pb present in a soil intially containing 2,200 mg/kg [70]. According to Laporte-Saumure et al. [175], the gravimetric techniques can be successfully applied to restore soils heavily contaminated by 16,000 to 38,000 mg Pb/kg and 11,500 mg Cu/kg. The application of the Jig and the shaking table to the fractions higher than 53 microns was highly efficient; allowing the removal of more than 92 and 90% Pb and Cu, respectively.

Rikers et al. [176] showed the importance of iron for the removal of heavy metals from contaminated soils such as Pb (85%), Cu (95%), Zn (85%), Cr (85%) and Cd (60%) using high intensity magnetic separation. However, this technique is less used than the gravimetric methods of separation.

Attrition is also a very simple and efficient mechanical technique of separation that is mainly used as a pre-treatment of a decontamination technology. According to Marino et al. [177], attrition allowed the removal of the thick films containing the contaminants around the particles soil by abrasion. In addition, the fragmentation of the agglomerated particles increases the release of the inorganic contaminants. The energy provided by attrition dislodges fine particles from coarse particles in order to concentrate the contaminant into small amounts of sludge containing fine contaminated particles [178]. Several parameters can influence the efficiency of the attrition processes such as the nature and the initial concentrations of contaminants, the pulp density, the temperature, the number of attrition steps, the concentration of a surfactant, the retention time and the stirring mode and speed [106, 178-180]. Williford et al. [181] showed that the preconditioning of contaminated soil using attrition decreased the chromium concentration in all fractions of soil, including a reduction from 41,000 to 30,000 mg/kg for the fine fraction (< 63 μm). Marino et al. [177] showed that the mechanical attrition, applied as a pre-treatment, can increase the Pb removal efficiency by 6.9% when using Wilfley table as a decontamination process. Bisone et al. [86] observed a significant increase of Cu and Zn removals in the range of 50% when using attrition upstream of a Wilfley table on soil contaminated by metallurgical slag. However, Mercier et al. [170] did not observed significant improvements on the removal of inorganic contaminants (Cu, Pb, Sn and Zn) when applying attrition (t = 5 min and total solids = 70%) as a pre-treatment followed by a separation with dense media (removal of 65%, 53%, 72% and 48% without attrition versus 84%, 50%, 62% and 55% with attrition as pre-treatement for Cu, Pb, Sn and Zn, respectively).

2.3.3 Leaching processes developed for the solubilization of metals

Several studies have shown that a chemical process applied downstream of physical separation processes can be successfully used to further reduce the concentrations of inorganic

28

contaminants from soils [173,175,183,184]. In fact, the chemical extraction technologies are frequently proposed to remove toxic metals attached to the fine particles of soil.

Over the last years, scientists have tried to optimize the extraction of heavy metals from contaminated soils by chemical leaching using different extractants. These chemical agents are used to transfer metal from contaminated soil to the aqueous solution. The efficiency of metals removal depends on the soil properties (texture, CEC, buffering capacity, organic matter content, presence of Fe, Ca and calcite), the forms in which the metals are present (adsorbed or particulate, oxidation state) and the operating conditions (pH, stirring speed, duration and number of washing steps, type and concentration of extractants) [61,185,186].

Over the last decades, chelating agents such as EDTA, EDDS or ADA have also been used to enhance the solubilization of metals from contaminated soils [187-191]. Wasay et al. [192] showed that EDTA, DTPA, citric acid and tartaric acid are very efficient for the removal of metals such as Cd, Cu, Pb and Zn present in contaminated soils, with removal yields ranging from 75 to 99.9% for experiments carried out at lab scale. Moreover, the weak organic acid salts (citrate, tartrate) allowed the removal of small amounts of macronutrients such as Ca, Mg and Fe, which are important for plants and microorganisms growth (less than 80% of the amounts of Ca, Mg and Fe are removed in the presence of EDTA and DTPA), and therefore, for the reuse of the soil. Lee et al. [193] showed that the use of EDTA (0.01 to 1 M), at laboratory scale, allowed the solubilization of As from contaminated soil with removal yields ranging from 65 to 80%. The use of biosurfactants has also been studied at laboratory scale for the extraction of metals from contaminated soils [82]. The application of lipoproteins, biosurfactant, allowed the extraction of 96.8% of the Cu initially present in contaminated soil [194]. Surfactants may also be succesfully used for the leaching of metals such as As from highly contaminated soils (initial concentration greater than 105 mg/kg) [195]. According to Mulligan et al. [196], a lipopeptide biosurfactant produced from *Bacillus subtilis* (0.25%), is also a good extractant for metals from contaminated soils with removal yields of 70% of the copper after a serie of five washing steps carried out at pH = 10 (1% NaOH) and with a pulp density fixed at 10% (w/w); study conducted at laboratory scale. Ehsan et al. [197] showed that during the extraction with EDTA (2 mM), the addition of a surfactant (Brij 98; 30 g/L) increases the removal efficiency of Pb

and Cu from 66% and 42% (without surfactant) to 73 and 49% (with surfactant), respectively. This study was performed at laboratory scale.

To improve the solubility of the metals such as As and Cr, the performances of the addition of oxidizing or reducing agents have been demonstrated [198]. For example, hexavalent chromium is more soluble than trivalent chromium whereas the arsenic is more soluble in its trivalent oxidation state than in its pentavalent oxidation state. The addition of potassium permanganate ($KMnO_4$), for example, can oxidized Cr in its hexavalent form that is more soluble, but also more toxic [172]. However, oxidizing chromium or reducing arsenic to improve the solubilization of metals is not favorable due to the high toxicities of Cr(VI) and As(III). The study conducted at a pilot scale by Ko et al. [199] showed that inorganic acids such as HCl, H_2SO_4 and H_3PO_4 are efficient to extract As from the fine particles (< 150 µm) of contaminated soils with removal yields reaching 63%, 70% and 75%, respectively. Bassi et al. [200] used citric acid (0.5 M) to remove the copper and other metals from contaminated soils. Citric acid is easy to handle and has a relatively low affinity for the alkaline earth metals (Ca, K and Mg). Therefore, it is a suitable agent for restoring soil using chemical leaching.

Several studies showed that high concentrations of chloride ions in the acid leaching solution resulted in the formation of chloro-complex, which increases the solubilization of some metals such as Pb and Cu [77,78, 201]. For example, a solution of H_2SO_4 (1.7 M) and NaCl (5.5 M) was used at laboratory scale by Laporte-Saumure et al. [175] to extract between 21 and 39% of the Cu present in the fine fraction (< 53 µm) of a soil initially containing between 1,800 and 3,800 mg Cu/kg. Lafond et al. [78] evaluated at laboratory scale the performances of various agents (CH_3COOH, HCl, H_2SO_4 + NaCl, H_2SO_4, H_2SO_4 + H_2O_2, EDTA) to solubilize heavy metals (Pb, Sb, Cu and Zn) present in in the fine fraction (< 125 µm) of contaminated soils. The results showed that the use of H_2SO_4 (1 M) and NaCl (4 M) is the best combination to remove metals from contaminated soils; allowing the removal of approximately 83% of Cu initially present in contaminated soils. Sulfuric acid is also an interesting leaching agent for economic reasons, since this chemical product costs about US$ 80-100/t and allowed the formation of stable and soluble complexes (metal-sulfate). Recently, Guemiza et al. [77] studied at pilot scale the use of 0.125 M H_2SO_4 and 4 M NaCl to treat soils initially containing between 418 and 1,015 mg

Cu/kg. After three 1 hour-leaching steps carried out at 25°C, with a pulp density fixed at 10% followed by one rinsing step, approximately 85 to 93% of Cu were removed from contaminated soils; with overall process costs of US$ 287/t treated soil. These results showed that larger amounts of Cu were solubilized in the presence of 0.25 M of H_2SO_4 and 4 M of NaCl (92% Cu removal) than with only 0.25 M of H_2SO_4 (78% of Cu removal) [77]. According to Bisone et al. [85], the solubilization of Cu in the presence of H_2SO_4 (pH = 1.5) allowed the removal of 88% of the Cu initially present ($[Cu]_i$ = 3,350 mg/kg) in the fine fraction (< 125 µm) of contaminated soils. According to the study carried out by Moutsatsou et al. [202], removal yields of 73% for As and 46% for Cu were obtained after 1 h of reaction (solid/liquid ratio = 30 g/L) in the presence of HCl (6 M). However, in the presence of H_2SO_4 at the same concentration (6 M), the removal of As increased to 80%, while for Cu, the removal yield decreased to 30% [202].

These studies and the experiments carried out by Lee et al. [193] showed that the performances of As solubilization are directly dependent of the pH of the washing solution. According to the study realized by Reynier et al. [50], the solubilization of As and Cu is favorable in alkaline solutions. After three 2 h-leaching steps carried out at 80°C in the presence of NaOH (1 M), more than 77%, 32% and 60% of As, Cr and Cu were removed from contaminated soils, respectively. Elgh-Dalgren et al. [195] showed that the solubilization of As is more efficient in alkaline solutions (NaOH, pH = 12) than in acidic solutions (HNO_3, pH = 3) with removal yields of 35% and 1%, respectively. Similarly, the solubilization of As is more effective in the presence of sodium hydroxide than in the presence of hydrochloric acid at a concentration fixed at 1 M [203]. The higher pH prevents the re-adsorption of As to the intrinsic components of soil particles [203]. According to these authors, more than 99% of As were removed from contaminated soils at high concentrations of NaOH (1 to 2 M) after 6 h (in a shaker at 300 rpm) and a pulp density fixed at 20%. Chromium is also more soluble in alkaline environments and is mainly present in the form of chromate in alkaline leaching solutions [204], while the Cu is mainly found in alkaline solutions in the form of hydroxycuprate [205].

2.4 Treatment of soils contaminated by both organic and inorganic compounds

The presence of both inorganic and organic contaminants in soils make their rehabilitation more difficult and expensive [84,110]. Over the last years, few researchers focused their studies

on the development of efficient and economically viable technologies able to simultaneously remove organic and inorganic contaminants from soils or solid matrix. Usually, several successive stages are required for the removal of both organic and inorganic contaminants from soils. Some decontamination processes have been developed recently and seemed to be efficient for the removal of both organic contaminants (PAHs, PCP, etc.) and inorganic contaminants (As, Cr, Cu, Zn, Pb) [50,86,88,89,206]. However, few of these decontamination processes are applicable to soils contaminated by PCP, PCDD/F, As, Cr and Cu [50, 106, 206]. Table 4 and Table 5 summarize the different technologies developed to remove As, Cr, Cu, PCP and PCDD/F from contaminated soils at laboratory and at pilot scale, respectively whereas Table 6 presents some technologies applied at full-scale to treat soils contaminated by organic or inorganic contaminants in Canada and in the USA but as our best knowledge, none of them is able to simultaneously treat soils contaminated by both organic and inorganic compounds, except stabilization/solidification used by various companies [114,207-213].

A study was conducted at laboratory scale to simultaneously remove Phenanthrene (a neutral organic compound) (PAHs) and nickel (Ni) from contaminated soils (Kaolin soil, low permeability soil) with electrokinetic techniques using cyclodextrins (1 and 10%) and NaOH (0.01 M) to maintain neutral pH conditions at the anode (periodic voltage gradient of 2 VDC/cm during 5 days on followed by 2 days off). The results showed that most of the Ni was precipitated as Ni(OH)$_2$ at neutral pH within the soil and that approximately 50% of the phenantrene was removed in the presence of high concentration (10%) of cyclodextrins [214].

Several successive stages of physical and/or chemical treatments may be beneficial to enhance the performances of contaminant removals without significantly affecting the costs of rehabilitation [86,89]. Among the physical treatments, attrition is the technique the most commonly used for the rehabilitation of soils contaminated by both organic and inorganic contaminants. The technique of attrition may be used with or without a surfactant to remove hydrophobic organic compounds from contaminated soils. Bisone et al. [86] removed more than 90% of PAHs from contaminated soil by attrition in the presence of a surfactant ([CAS] = 0.2 g/L). Bayley and Biggs [179] successfully extracted organic compounds of high molecular weight (mineral oils (Catenex S341)) present in contaminated soils using attrition

(approximately 96.7% of organic contaminant removals). Veetil et al. [215] studied the treatment of sediments contaminated with PAHs and metals (Pb, Cu, Zn) using physical separation techniques. The decontamination process developed by these authors consisted on froth flotation (fractions < 250 μm) (PD = 10% (w/w); [KAX] = 1.2 g/kg; [MIBC] = 0.24 g/kg; 1,050 rpm; air flow rate = 4 m³/hr and number of flotation steps = 3), Wilfley table (0.250-2 mm) (PD = 20% (w/w) and a feed rate of 200 g/L.min) and physical separation column preceeded by attrition as a pre-treatment step (> 2 mm) (10 min, PD = 20% (w/w), 2,000 rpm). This decontamination process allowed the removal of 71-80% of PAHs, 61-65% of Cu, 27-33% of Zn and 36-40% of Pb. Metahni [106] studied attrition, at pilot scale, without surfactant, to treat the coarse fractions (> 125 μm) of soils contaminated by As, Cr, Cu, PCP and PCDD/F. These fractions represented between 81% and 96% of the soil. After the treatment by attrition of the coarse fractions (> 0.125 mm), the removal yields obtained ranged from 22% to 43% for As, from 0% to 13% for Cr, from 23% to 46% for Cu, from 0% to 85% fo PCP and from 17% to 64% for PCDD/F. Recently, Jobin et al. [216] applied attrition (PD = 30%, t = 10 min, T = 25°C) to treat the 0.250-4 mm fraction of a soil contaminated by organic and inorganic compounds. This step was followed by a gravity separation with a Jig or a Shaking table to remove inorganic contaminants. Alternatively the elutriation column (PD = 7%, water flow = 120 L.min⁻¹) served to remove PAHs. This process allowed the removal of 50% of Cu, 64% of Pb and 40% of PAHs. According to these authors the effect of attrition was positively correlated with the size of soil particles [180].

For soil contaminated by both organic and inorganic compounds, the soil washing in the presence of surfactants is also highly efficient for the simultaneous removal of metals and organic contaminants [43]. The use of different solvents in a single washing unit for the extraction of organic compounds and metals has also been studied [50,89,108,217]. Maturi and Reddy [217] tested at laboratory scale the simultaneous extraction of PAHs (phenanthrene) and metals (Ni, Zn and Pb) in the presence of various agents of extraction (two surfactants, two co-solvents, two cyclodextrins, two chelating agents, six organic acids and one inorganic acid). The results of this study showed that the extraction using surfactants allowed the removal of phenantherene with removal yields varying from 5% to 100% depending on the nature of the

studied soil. The use of phosphoric acid (1 M) or citric acid (1 M) seemed to be effective for the removal of the heavy metals from all soils studied. Moreover, the combination of surfactant (Tween 80 at a concentration of 5%) and chelating agents (0.2 M EDTA) or citric acid (1 M) showed maximum removal of PAHs (81-98%) and heavy metals (50-68% for Ni, 69-88% for Zn and 47-89% for Pb). A study carried out at laboratory scale by Reynier et al. [50] showed that strong inorganic acids (HCl, H_2SO_4) are very efficient for the solubilization of metals and that they can even degrade organic compounds but they are inefficient for the solubilization or the degradation of pentachlorophenol that is resistant to most of these inorganic acids and whose solubility in acidic solutions is very low. According to Khodadoust et al. [89], EDTA (0.2 M) in combination with a nonionic surfactant (Tween 80 at a concentration of 5%) was efficient to simultaneously remove phenanthrene (> 90%) and zinc (> 99%) from contaminated soils. Surfactants are often used to solubilize both organic contaminants and metals [156,218]. Through their amphoteric properties, surfactants are useful for removing organic compounds such as PCP [107,153], and metals [89]. Over the last years, several researchers looked at the application of flotation using surfactant to simultaneously remove metals and organic contaminants from soils or solid matrix (sediments, etc.). These researchers observed that electrostatistical interactions (Van der Waals interaction) occurred between the particles carrying hydrophobic surfaces (e.g. organic pollutants) and the air bubbles during the conditioned flotation processes; allowing the removal of organic contaminants, while the hydrophilic particles (e.g. metals) remained in the pulp. Therefore, the organic contaminants attached to the air bubbles are present in the foam formed on the surface of the reactor and can be collected by skimming the froth. The treatment of soil contaminated by PAHs and Pb using flotation with hydroxysultaine cocamidopropyl (CAS) coupled to an acid and saline leaching solution was studied by Mouton et al. [87]. This process using sodium chloride ([NaCl] = 5 M) and a surfactant ([CAS] = 0.5%) at pH = 3 showed good results with removal yields reaching 55% for both contaminants PAHs and Pb [151]. This method has been successfully tested at pilot scale; allowing the removal of 86%-99.9% of PAHs and 78% of Pb from contaminated soils [219]. In the literature, various surfactants such as Triton X-100, sodium dodecyl succinate (SDS), Igepal CA-720, Tergipol NP10, etc. were tested to solubilize

PCP, PCDD/F or metals from contaminated soils [109, 154, 158, 159, 195, 220]. The process developped by Rivero-Huguet and Marshall [206] in the presence of a biodegradable complexing agent ([S,S]-EDDS) and a non-ionic surfactant (Brij 98) seemed to be efficient for the simultaneous removal of As, Cr and Cu, as well as, organic contaminants (PCP, PCDD/F). This combination allowed the removal of 70%, 75%, 80%, 90% and 79% of As, Cr, Cu, PCP and PCCDF, respectively. However, the chemical agents used are very expensive and the decontamination costs are estimated at US$ 137,000 per ton of dry soil [206], which is prohibitive. Recently, the performances of a flotation process in acidic conditions (t = 1 h, T = 60°C, three flotation steps, [BW] = 1%, [H$_2$SO$_4$] = 1 N) were studied for the treatment of soils containing large amounts of inorganic and organic compounds. This process allowed the removal of 82-93%, 30-80%, 79-90% and 36-78% of the As, Cr, Cu and PCP, respectively [50]. These authors have also developed at laboratory scale an alkaline leaching process to treat soils contaminated by PCP, PCDD/F, As, Cr and Cu. After three 1 h-leaching steps carried out at 60°C in the presence of a surfactant ([BW] = 1%) and NaOH (1 M), more than 60% of As, 32% of Cr, 77% of Cu and 87% of PCP were removed from contaminated soils. Under optimal conditions, the removal yields obtained for PCDD/F can reached 74% [108]. This leaching process was studied at pilot scale by Metahni [106] on the fine particles (< 125 μm) of soils contaminated by As, Cr, Cu, PCP and PCDD/F in presence of different concentrations of NaOH (1.0 to 1.5 M) and a surfactant ([BW] = 0.5-3.0% (w/v)). This process is highly efficient for the decontamination of soils containing organic (PCP and PCDD/F) and inorganic (As, Cr, Cu) contaminants; allowing the removal of 87-95% of As, 50-72% of Cr, 73- 84% of Cu, 52-99.9% of PCP and 26-74% of PCDD/F, with overall process costs of US$ 425/t of treated soil [106].

CONCLUSION

Industrial activities, especially the industrial wood preservation activities, led to the contamination of several sites by both organic (PCP, PCDD/F) and inorganic compounds (As, Cr, Cu) around the world. The management of soils contaminated by both PCP, PCDD/F, As, Cr and Cu is becoming a global and political challenge due to the amounts of PCP- and CCA-treated wood products reaching their end-of-life. Over the last years, several researchers focused their attention on the development of reliable effective and economical decontamination techniques based on physical, thermal, biological and/or chemical processes. Some technologies are applied at full-scale to treat soils contaminated by organic or inorganic contaminants in Canada and in the USA but as our best knowledge, none of them is able to simultaneously treat soils contaminated by both organic and inorganic compounds, except stabilization/solidification used by the various companies. However, this solution does not fit anymore into the framework of the sustainable development.

As discussed below, considerable advancements have been made in the development of decontamination processes over the past few years to remove organic and/or inorganic contaminants from soils. Among the ex-situ thermal processes, both thermal treatments and thermal desorption (pyrolysis) are effective for the removal of more than 99.99% of organic contaminants such as PCP and PCDD/F. However, these techniques are very expensive and led to the release of contaminants in gases, resulting in severe air pollution problems. In addition, metals still remain in the soil or in vapors, requiring additional treatment, such as stabilization/solidification processes, increasing the costs of treatment. Bioremediation is an ancient and well-known technology used to treat soils contaminated by organic contaminants and sometimes by inorganic compounds. The performances of biological processes are very low for recalcitrant organic compounds such as PCP and PCDD/F. However, bioremediation processes are very sensitive to the nature and the initial concentrations of contaminants to be remediated and many other parameters such as the temperature, the moisture content and the geology/morphology of the site. Researchers have to resolve these problems and reduce duration of biological treatments that may cause high operational costs.

The soil washing in the presence of acids or bases and surfactants is also highly efficient for the simultaneous removal of metals and organic contaminants. However, this technique seemed to be expensive when applied to all the soil fractions. Several successive stages of physical and/or chemical treatments may be beneficial to enhance the performances of contaminant removals without significantly increasing the costs of rehabilitation. Among the physical treatments, attrition is the most commonly used and promising technique for increasing the efficiency and decreasing the cost of the rehabilitation of soils contaminated by both organic and inorganic contaminants. Moreover, these processes are based on the transfer of the contaminant from the soil to another solid phase (fine particles of soil or sludge), that should properly be disposed of. The main advantage is the significant amounts of solid that should be properly disposed of. The mechanisms related to the solubilization of organic and inorganic contaminants using soil washing and/or physical treatments have to be better understood. Some researchers recently highlighted that the nature of the soil or the initial contaminants levels can affect the performances of both physical and chemical processes. Further efforts should be done to better understand this phenomenon in order to be able to predict the behavior of the contaminants during the decontamination process.

REFERENCES

[1]   Y.K. Wang, L. Tao, M.J. Chen, F.B. Li, Effect of the FeII/CuII interaction on copper aging enhancement and pentachlorophenol reductive transformation in paddy soil, Journal of Agricultural and Food Chemistry, 60 (2002) 630-638.

[2]   W.P. Canada, Certification des usines. Autorisation Canadienne de Certification de la Préservation du Bois (ACCPB) - Installations certifies. 202-2141 Thuston Drive, Ottawa, Ontario, Canada, 2016.

[3]   PNUE, Aspects environnementaux de la préservation industrielle du bois, Technical report No. 20, Programme des Nations-Unies pour l'Environnement, Geneva, Swiss, 1994.

[4]   P.I. Morris, J. Wang, Wood preservation in Canada. Canadian Wood Council, Vancouver, British Colombia, Canada, 2006.

[5]   M.H. Freeman, T.F. Shupe, R.P. Vlosky, H. Barnes, Past, present, and future of the wood preservation industry: Wood is a renewable natural resource that typically is preservative treated to ensure structural integrity in many exterior applications, Forest Products Journal, 53 (2003) 8-16.

[6]   H. Barnes, Wood preservation trends in North America forest products laboratory, Forest and Wildlife Research Center, Mississippi State University, Starkville, Mississippi, USA, 2008.

[7]   U.S. Congress, Cleaning up contaminated wood-treating sites, OTA-BP-ENV-164, Office of Technology Assessment, U.S. Government Printing Office, Washington, DC, USA, 1995, pp. 45.

[8]   L.M. Ottosen, A.B. Ribeiro, E. Melcher, Polluted wood preservation sites, Federal Research Centre for Forestry and Forest Products, Institute of Wood Biology and Wood Protection, Hamburg, Germany, 2002, pp. 10.

[9]   C.T. Darling, V.G. Thomas, The distribution of outdoor shooting ranges in Ontario and the potential for lead pollution of soil and water, Science of the Total Environment, 313 (2003) 235-243.

[10]   L.Q. Ma, D.W. Hardison Jr, W.G. Harris, X. Cao, Q. Zhou, Effects of soil property and soil amendment on weathering of abraded metallic Pb in shooting ranges, Water, Air, & Soil Pollution, 178 (2007) 297-307.

[11]   R. Charlatchka, P. Cambier, Influence of reducing conditions on solubility of trace metals in contaminated soils, Water, Air, & Soil Pollution, 118 (2000) 143-168.

[12]   B. Subramanian, Exploring neoteric solvent extractants: Applications in the removal of sorbates from solid surfaces and regeneration of automotive catalytic converters, Division of Research and Advanced Studies, University of Cincinnati, Cincinnati, Ohio, USA, 2007, pp. 82.

[13]   E.C.A.H. Canada, Document d'orientation à l'intention des utilisations de bois traités industriel. Version 1, Environnement Canada, Ontario, Canada, 2004, pp. 95.

[14]   B. Fisher, Pentachlorophenol: Toxicology and environmental fate, Journal of Pesticide Reform: A publication of the Northwest Coalition for Alternatives to Pesticides,USA, 1991.

[15]   M. Altarawneh, B.Z. Dlugogorski, E.M. Kennedy, J.C. Mackie, Mechanisms for formation, chlorination, dechlorination and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), Progress in Energy and Combustion Science, 35 (2009) 245-274.

[16]   W.H. Organization, Pentachlorophenol in drinking-water background fir development of WHO guidelines for drinking water quality, WHO/SDE/WSH/03.04/62, Geneva, Swiss, 2003, pp. 18.

[17]   B. Fabre, J. Ayele, M. Mazet, P. Lafrance, Removal of pentachlorophenol by adsorption onto various materials. The effect of organic co-adsorbates (humic substances and lindane), Revue des Sciences de l'Eau, 3 (1990) 277-292.

[18]   R.P. Schwarzenbach, P.M. Gschwend, D.M. Imboden, Environmental Organic Chemistry, 2nd Edition, Wiley-Interscience, A John Wiley & Sons, Inc., Hoboken, New Jersey, USA, 1327 p.

[19] ATSDR, (Agency for Toxic Substances and Disease Registry), Toxicological profile for chlorinated pentachlorophenol, U.S. Department of Health and Human Services, Atlanta, Georgia, USA, 2001, pp. 316.

[20] C. Tissier, C. Morvan, G. Bocquené, H. Grossel, A. James, M. Marchand, Les substances prioritaires de la Directive Cadre sur l'Eau (DCE). Fiches de synthèse, IFREMER, Issy-les-Moulineaux, France, 2005.

[21] CCME, Recommandations canadiennes pour la qualité des sols concernant le PCP: Environnement et santé humaine, Report prepared by the Conseil Canadien des Ministres de l'Environnement, Winnipeg, Manitoba, Canada, 1997, pp. 61.

[22] INERIS, Données technico-économiques sur les substances chimiques en France: PCP, INERIS, Paris, France, 2005, pp. 14.

[23] S.K. Banerji, S. Wei, R.K. Bajpai, Pentachlorophenol interactions with soil, Water, Air, & Soil Pollution, 69 (1993) 149-163.

[24] P. Augustijn-Beckers, A. Hornsby, R. Wauchope, The SCS/ARS/CES pesticide properties database for environmental decision-making. II. Additional compounds, Reviews of Environmental Contamination and Toxicology, Springer, Berlin, Germany, 1994, pp. 1-82.

[25] M. Chen, L. Tao, L. Fangbai, Q. Lan, Reductions of Fe(III) and pentachlorophenol linked with geochemical properties of soils from Pearl River Delta, Geoderma, 217-218 (2014) 201-211.

[26] INERIS, Données toxicologiques et environnementales des substances chimiques. Pentachlorophénol, INERIS, France, 2011, pp. 62.

[27] UE, Directives 2000/60/EC of the European Parliament and the Council of 23 October 2000 establishing a framework for Community action in the field of water policy, CELEX-EUR Official Journal L 327, 22, 2000, pp. 72.

[28] USEPA, 40 CFR part 423. Steam electric power generating point source category - Appendix A - 126 Priority pollutants, Report EPA 821-R-06-015, United States Environmental Protection Agency, Washington, DC, USA, 2003, pp. 128.

[29] W. Zheng, X. Wang, H. Yu, X. Tao, Y. Zhou, W. Qu, Global trends and diversity in pentachlorophenol levels in the environment and in humans: a meta-analysis, Environmental Science & Technology, 45 (2011) 4668-4675.

[30] INRS-Géoressources, CRM, Protocole d'évaluation de la trabilité des sédiments, des sols et des boues à l'aide des technologies minéralurgiques. Technical report, Environnement Canada, Institut National de la Recherche Scientifique, Centre de Recherches Minérales, Québec, Québec, Canada, 1997.

[31] H. Canada, Les chlorophénols. Santé de l'environnement et du milieu de travail. Qualité de l'eau, Santé Canada, Ottawa, Ontario, Canada, 1987, pp. 6.

[32] G.F. Fries, A review of the significance of animal food products as potential pathways of human exposures to dioxins, Journal of Animal Science, 73 (1995) 1639-1650.

[33] INSERM, Dioxines dans l'environnement: Quels risques pour la santé, Institut National de la Santé et de la Recherche Médicale, Paris, France, 2000, pp. 400.

[34] CCME, Recommandations canadiennes pour la qualité des sols: Environnement et santé humaine: les dibenzo-p-dioxines polychlorées et les dibenzofurannes polychlorés (PCDD/F), Rapport rédigé par le Conseil Canadien des Ministres de l'Environnement, Winnipeg, Manitoba, Canada, 2002, pp. 16.

[35] L.Y. Wang, P. Wang, L. Ding, X. Li, Y. Wang, Q. Zhang, A. Li, G. Jiang, Reduction of atmospheric polychlorinated dibenzo-p-dioxins ans dibenfurans (PCDD/Fs) during the 2008 Beijing Olympic Games, Environmental Science and Technology, 45 (2011) 3304-3309.

[36] K.C. Jones, A. Sewart, Dioxins and furans in sewage sludges: A review of their occurrence and sources in sludge and of their environmental fate, behavior, and significance in sludge amended agricultural systems, Critical Reviews in Environmental Science and Technology, 27 (1997) 1-86.

[37] ATSDR (Agency for Toxic Substances and Disease Registry), Toxicological profile for chlorinated dibenzo-p-dioxins (update), U.S. Department of Health and Human Services, Atlanta, Georgia, USA, 1998, pp. 721

[38] K.S. Kim, S.C. Lee, K.H. Kim, W.J. Shim, S.H. Hong, K.H. Choi, J.H. Yoon, J.G. Kim, Survey on organochlorine pesticides, PCDD/Fs, dioxin-like PCBs and HCB in sediments from the Han river, Korea, Chemosphere, 75 (2009) 580-587.

[39] U.E. Agency, Soil guideline values for dioxins, furans and dioxin like PCBs in soil, Science Report SC050021/Dioxins SGV, United Kingdom Environment Agency, Bristol, England, 2009, pp. 22.

[40] USEPA, Dioxin treatment technologies, Report OTA-BP-O-93, Order No. PB92–152511, 1991, pp. 68.

[41] J.D. Urban, D.S. Wikoff, A.T. Bunch, M.A. Harris, L.C. Haws, A review of background dioxin concentrations in urban/suburban and rural soils across the United States: Implications for site assessments and the establishment of soil cleanup levels, Science of the Total Environment, 466 (2014) 586-597.

[42] P. Isosaari, Polychlorinated dibenzo-p-dioxin and dibenzofuran contamination of sediments and photochemical decontamination of soils, University of Kuopio, Kuopio, Finland, 2004, pp. 95.

[43] N. Reynier, Décontamination des sols pollués par des métaux, Ph.D. thesis, INRS-ETE, Université du Québec, Québec, Québec, Canada, 2012, pp. 284.

[44] K.R. Henke, Arsenic: Environment chemistry, health threats and waste treatment, John Wiley and Sons Ltd, New York, New York, USA, 2009, pp. 569.

[45] LCPE, Liste des substances d'intérêt prioritaire. Rapport d'évaluation. L'arsenic et ses composés, Loi canadienne sur la protection de l'environnement, Santé Canada et Environnement Canada, Ottawa, Ontario, Canada, 1993, pp. 60.

[46] G. Liu, Y. Cai, Chapter 31: Arsenic speciation in soils: An analytical challenge for understanding arsenic biogeochemistry, Developments in Environmental Science, 5 (2007), 685-708.

[47] C. Gilmour, G. Riedel, Biogeochemistry of Trace Metals and Metalloids, in: Encyclopedia of Inland Waters, Oxford, Elsevier, (2013) 7-15 p.

[48] H.F Yu, F.B. Li, C.S. Liu, W. Huang, T.X. Liu, W.M. Yu, Chapter 5: Iron redox cycling coupled to transformation and immobilization of heavy metals: Implications for paddy rice safety in red soil of South China, in: Advances in Agronomy, 137 (2016) 279-317.

[49] ATSDR (Agency for Toxic Substances and Disease Registry), Toxicological profile for arsenic, U.S. Department of Health and Human Services, Atlanta, Georgia, USA, 2007, pp. 559

[50] N. Reynier, J.F. Blais, G. Mercier, S. Besner, Treatment of arsenic-, chromium-, copper-and pentachlorophenol-polluted soil using flotation, Water, Air, & Soil Pollution, 224 (2013) 1-12.

[51] K.G. Brown, G.L. Ross, Arsenic, drinking water, and health: A position paper of the American Council on Science and Health, Regulatory Toxicology and Pharmacology, 36 (2002) 162-174.

[52] W.H. Organization, Guidelines for drinking-water quality: Incorporating 1st and 2nd addenda. Vol. 1, Recommendations. Third Edition, World Health Organization Geneva, Swiss, 2008, pp. 668.

[53] G. Lespagnol, Lixiviation du chrome, du cuivre et de l'arsenic (CCA) à partir de sols contaminés sur des sites de traitement du bois, Ph.D. thesis, École Nationale Supérieure des Mines de Saint-Étienne et de l'Université Jean Monnet, Saint-Étienne, France, 2003, pp. 212.

[54] J. Kotaś, Z. Stasicka, Chromium occurrence in the environment and methods of its speciation, Environmental Pollution, 107 (2000) 263-283.

[55]   L. Coudert, J.F. Blais, G. Mercier, P. Cooper, A. Janin, L. Gastonguay, Demonstration of the efficiency and robustness of an acid leaching process to remove metals from various CCA-treated wood samples, Journal of Environmental Management, 132 (2014) 197-206.

[56]   A. Tessier, P.G. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, Analytical Chemistry, 51 (1979) 844-851.

[57]   E.C.A.H. Canada, Liste des substances d'intérêts prioritaires – Rapport d'évaluation – Le chrome et ses composés, Ottawa, Ontario, Canada, 1994.

[58]   A. Baral, R.D. Engelken, Chromium-based regulations and greening in metal finishing industries in the USA, Environmental Science & Policy, 5 (2002) 121-133.

[59]   W. Dang, J. Chen, A probabilistic risk assessment for children who contact CCA-treated playsets and decks, United States Environmental Protection Agency, Washington, DC, USA, 2003, pp. 325.

[60]   S.M. Shaheen, T. Frohne, J.R. White, R.D. DeLaune, J. Rinklebe, Redox-induced mobilization of copper, selenium, and zinc in deltaic soils originating from Mississipi (U.S.A.) and Nile (Egypt) River Deltas: A better understanding of biogeochemical processes for safe environmental management, Journal of Environmental Management, (2016) 1-10.

[61]   C. Mulligan, R. Yong, B. Gibbs, Remediation technologies for metal-contaminated soils and groundwater: an evaluation, Engineering Geology, 60 (2001) 193-207.

[62]   S.B. Goldhaber, Trace element risk assessment: essentiality vs. toxicity, Regulatory Toxicology and Pharmacology, 38 (2003) 232-242.

[63]   USEPA, Consumer factsheet on copper, United States Environmental Protection Agency, Washington, DC, USA, 2006.

[64]   M.V. Coronas, J.A.V. Rocha, D.M.F. Salvadori, V.M.F. Vargas, Evaluation of area contaminated by wood treatment activities: Genetic markers in the environment and in the child population, Chemosphere, 144 (2016) 1207-1215.

[65]   F.X. Han, A. Banin, Y. Su, D.L. Monts, J.M. Plodinec, W.L. Kingery, G.E. Triplett, Industrial age anthropogenic inputs of heavy metals into the pedosphere, Naturwissenschaften, 89 (2002) 497-504.

[66]   L. Chai, Z. Wang, Y. Wang, Z. Yang, H. Wang, X. Wu, Ingestion risks of metals in groundwater based on TIN model and dose-response assessment - A case study in the Xiangjiang watershed, central-south China, Science of the Total Environment, 408 (2010) 3118-3124.

[67]   Z. Wang, L. Chai, Z. Yang, Y. Wang, H. Wang, Identifying sources and assessing potential risk of heavy metals in soils from direct exposure to children in a mine-impacted city, Changsha, China, Technical reports: Heavy metals in the environment, Madison, Winconsin, USA, 1616-1623.

[68]   P.A. Cooper, Y.T. Ung, Effect of water repellents on leaching of CCA from treated fence and deck units - An update, IRG/WP 97-50086, International Research Group on Wood Protection, Stockholm, Sweden, 1997.

[69]   D. Stilwell, K. Gorny, Contamination of soil with copper, chromium, and arsenic under decks built from pressure treated wood, Bulletin of Environmental Contamination and Toxicology, 58 (1997) 22-29.

[70]   T. Chirenje, L. Ma, C. Clark, M. Reeves, Cu, Cr and As distribution in soils adjacent to pressure-treated decks, fences and poles, Environmental Pollution, 124 (2003) 407-417.

[71]   H.M. Solo-Gabriele, T.G. Townsend, J.D. Schert, Environmental impact of CCA-treated wood: A summary from seven years of study focusing on the U.S. Florida environment, International Research Group on Wood Protection Annual Meeting, Brisbane, Australia, 2003.

[72]   H. Cheng, Y. Hu, J. Luo, B. Xu, J. Zhao, Geochemical processes controlling fate and transport of arsenic in acid mine drainage (AMD) and natural systems, Journal of Hazardous Materials, 165 (2009) 13-26.

[73] K. Ken, S.L. Lo, Desorption kinetics of PCP-contaminated soil: effect of temperature, Water Research, 36 (2002) 284-290.

[74] J.H. Li, X.F. Sun, Z.T. Yao, X.Y. Zhao, Remediation of 1,2,3-trichlorobenzene contaminated soil using a combined thermal desorption–molten salt oxidation reactor system, Chemosphere, 97 (2014) 125-129.

[75] N.T. Thuan, M.B. Chang, Investigation of the degradation of pentachlorophenol in sandy soil via low-temperature pyrolysis, Journal of Hazardous Materials, 229 (2012) 411-418.

[76] N.T. Thuan, N.T. Dien, M.B. Chang, PCDD/PCDF behavior in low-temperature pyrolysis of PCP-contaminated sandy soil, Science of the Total Environment, 443 (2013) 590-596.

[77] K. Guemiza, G. Mercier, J.F. Blais, Pilot-scale decontamination of small-arms shooting range soil polluted with copper, lead, antimony, and zinc by acid and saline leaching, Journal of Environmental Engineering, 141 (2014) 04014054.

[78] S. Lafond, J.F. Blais, R. Martel, G. Mercier, Chemical leaching of antimony and other metals from small arms shooting range soil, Water, Air, & Soil Pollution, 224 (2013) 1-15.

[79] G. Mercier, J.F. Blais, M. Chartier, Décontamination à l'échelle pilote de sols pollués en métaux toxiques par des procédés miniers et lixiviation chimique, Journal of Environmental Engineering and Science, 6 (2007) 53-64.

[80] K. Guemiza, G. Mercier, J.F. Blais, Pilot-scale counter-current acid leaching process for Cu, Pb, Sb, and Zn from small-arms shooting range soil, Journal of Soils and Sediments, 14 (2014) 1359-1369.

[81] A. Duchesne, Recommandation pour la réhabilitation des sols contaminés d'un ancien site de traitement du bois, Université de Sherbrooke, Québec, Québec, Canada, 2013, pp. 87.

[82] C.N. Mulligan, R.N. Yong, B.F. Gibbs, Heavy metal removal from sediments by biosurfactants, Journal of Hazardous Materials, 85 (2001) 111-125.

[83] W. Xing, C. Hendriks, Decontamination of granular wastes by mining separation techniques, Journal of Cleaner Production, 14 (2006) 748-753.

[84] USEPA, Cleaning up the Nation's waste sites markets and technology trends, 4th Edition, United States Environmental Protection Agency, Washington, DC, USA, 2004, pp. 50.

[85] S. Bisone, J.F. Blais, P. Drogui, G. Mercier, Toxic metal removal from polluted soil by acid extraction, Water, Air, & Soil Pollution, 223 (2012) 3739-3755.

[86] S. Bisone, G. Mercier, J.F. Blais, Decontamination of metals and polycyclic aromatic hydrocarbons from slag-polluted soil, Environmental Technology, 34 (2013) 2633-2648.

[87] J. Mouton, G. Mercier, J.F. Blais, Laboratory-scale flotation process for treatment of soils contaminated with both PAH and lead, Journal of Environmental Engineering, 136 (2010) 1063-1074.

[88] J. Mouton, G. Mercier, P. Drogui, J.F. Blais, Experimental assessment of an innovative process for simultaneous PAHs and Pb removal from polluted soils, Science of the Total Environment, 407 (2009) 5402-5410.

[89] A.P. Khodadoust, K.R. Reddy, K. Maturi, Effect of different extraction agents on metal and organic contaminant removal from a field soil, Journal of Hazardous Materials, 117 (2005) 15-24.

[90] E.L. Arthur, P.J. Rice, P.J. Rice, T.A. Anderson, S.M. Baladi, K.L. Henderson, J.R. Coats, Phytoremediation—an overview, Critical Reviews in Plant Sciences, 24 (2005) 109-122.

[91] I. Brunner, J. Luster, M.S. Günthardt-Goerg, B. Frey, Heavy metal accumulation and phytostabilisation potential of tree fine roots in a contaminated soil, Environmental Pollution, 152 (2008) 559-568.

[92] FRTR, Remediation technologies screening matrix and references guide. Version 4.0, Federal Remediation Technologies Roundtable, Website: https://frtr.gov/matrix2/top_page.html, 2012.

[93] S. Chen, Y. Zhu, Y. Ma, The effect of grain size of rock phosphate amendment on metal immobilization in contaminated soils, Journal of Hazardous Materials, 134 (2006) 74-79.

[94] R.A. Wuana, F.E. Okieimen, Heavy metals in contaminated soils: A review of sources, chemistry, risks and best available strategies for remediation, ISRN Ecology, 2011 (2011) Article ID 402647, pp. 20.

[95] R. Bade, S. Oh, W.S. Shin, Assessment of metal bioavailability in smelter-contaminated soil before and after lime amendment, Ecotoxicology and Environmental Safety, 80 (2012) 299-307.

[96] S.R. Mallampati, Y. Mitoma, T. Okuda, S. Sakita, M. Kakeda, Enhanced heavy metal immobilization in soil by grinding with addition of nanometallic Ca/CaO dispersion mixture, Chemosphere, 89 (2012) 717-723.

[97] C.C. Association, Remediation on contaminated site, Canadian Cement Association, 2012.

[98] A. Garcıa-Sánchez, A. Alastuey, X. Querol, Heavy metal adsorption by different minerals: Application to the remediation of polluted soils, Science of the Total Environment, 242 (1999) 179-188.

[99] J.Y. Kim, A.P. Davis, K.W. Kim, Stabilization of available arsenic in highly contaminated mine tailings using iron, Environmental Science & Technology, 37 (2003) 189-195.

[100] A. Janin, J.F. Blais, G. Mercier, P. Drogui, Selective recovery of metals in leachate from chromated copper arsenate treated wood using ion exchange resins and chemical precipitation, Journal of Hazardous Materials, 169 (2009) 1099-1105.

[101] C. Spuller, H. Weigand, C. Marb, Trace metal stabilisation in a shooting range soil: Mobility and phytotoxicity, Journal of Hazardous Materials, 141 (2007) 378-387.

[102] B. Wen, R.J. Li, S. Zhang, X.Q. Shan, J. Fang, K. Xiao, S.U. Khan, Immobilization of pentachlorophenol in soil using carbonaceous material amendments, Environmental Pollution, 157 (2009) 968-974.

[103] S.S Sukkla, A.S. Sukkla, K.C. Lee, Solidification/stabilization study for the disposal of pentachlorophenol, Journal of Hazardous Materials, 30 (1992) 317-331.

[104] USEPA, Treatment technologies for site cleanup: Annual status report, 12th Edition, Soil Waste and Emergency Response, United States Environmental Protection Agency, Washington, DC, USA, 2007, pp. 66

[105] A.P. Khodadoust, M.T. Suidan, C.M. Acheson, R.C. Brenner, Solvent extraction of pentachlorophenol from contaminated soils using water-ethanol mixtures, Chemosphere, 38 (1999) 2681-2693.

[106] S. Metahni, Décontamination à l'échelle pilote des sols pollués par des métaux, du pentachlorophénol et des dioxines et furanes, M.Sc. thesis, INRS-ETE, Université du Québec, Québec, Québec, Canada, 2014, pp. 188.

[107] I.F. Paterson, B.Z. Chowdhry, S.A. Leharne, Polycyclic aromatic hydrocarbon extraction from a coal tar-contaminated soil using aqueous solutions of nonionic surfactants, Chemosphere, 38 (1999) 3095-3107.

[108] N. Reynier, J.F. Blais, G. Mercier, S. Besner, Decontamination of metals, pentachlorophenol, and polychlorined dibenzo-p-dioxins and dibenzofurans polluted soil in alkaline conditions using an amphoteric biosurfactant, Environmental Technology, 35 (2014) 177-186.

[109] E. Sahle-Demessie, D.W. Grosse, E.R. Bates, Solvent extraction and soil washing treatment of contaminated soils from wood preserving sites: Bench-scale studies. United States Environmental Protection Agency, Cincinnati, Ohio, USA, 2000, pp. 25.

[110] USEPA, Bio Trol soil washing system for treatment of wood preserving site, applications analysis report, Report EPA 540/A5-91/003, United States Environmental Protection Agency, Cincinnati, Ohio, USA, 1992, pp. 76.

[111] C.A. Young, R.F. Weston, H. Hatch, J. Leibbert, On-site thermal desorption of PCP- and dioxin-contaminated soil at the Coleman-Evans wood preservative site, Whitehouse, Florida, USA, 2000, pp. 11

[112]   M. Walter, K.S. Boyd-Wilson, D. McNaughton, G. Northcott, Laboratory trials on the bioremediation of aged pentachlorophenol residues, International Biodeterioration & Biodegradation, 55 (2005) 121-130.

[113]   L. Valentín, H. Oesch-Kuisma, K.T. Steffen, M.A. Kähkönen, A. Hatakka, M. Tuomela, Mycoremediation of wood and soil from an old sawmill area contaminated for decades, Journal of Hazardous Materials, 260 (2013) 668-675.

[114]   Récupère-Sol, Récupère-Sol., Website: http://www.recuperesol.com/, 2015.

[115]   M.T. Smith, F. Berruti, A.K. Mehrotra, Thermal desorption treatment of contaminated soils in a novel batch thermal reactor, Industrial & Engineering Chemistry Research, 40 (2001) 5421-5430.

[116]   T. Speir, D. Hannah, B. Kathiravelu, R. Smart, Remediation of dioxin, pentachlorophenol and organochlorine pesticide contaminated soils, Symposium No. 38- Scientific registration: 1882, 1997, pp. 7.

[117]   S. Jansson, Thermal formation and chlorination of dioxins and dioxin-like compounds, Ph.D. Thesis, Umea University, Umea, Sweden, 88 p.

[118]   P.C. Hung, S.H. Chang, C.C. Ou-Yang, M.B. Chang, Simultaneous removal of PCDD/Fs, pentachlorophenol and mercury from contaminated soil, Chemosphere, 144 (2016) 50-58.

[119]   A. Tritz, I. Ziegler-Devin, C. Perrin, P.M. Marquaire, Experimental study of the oxidation and pyrolysis of dibenzofuran at very low concentration, Journal of Environmental Chemical Engineering, 2 (2014) 143-153.

[120]   L. Lundin, J. Moltó, A. Fullana, Low temperature thermal degradation of PCDD/Fs in soil using nanosized particles of zerovalent iron and CaO, Chemosphere, 91 (2013) 740-744.

[121]   B. Stanmore, Modeling the formation of PCDD/F in solid waste incinerators, Chemosphere, 47 (2002) 565-573.

[122]   Q. Dai, X. Jiang, F. Wang, Y. Chi, J. Yan, PCDD/Fs in wet sewage sludge pyrolysis using conventional and microwave heating, Journal of Analytical and Applied Pyrolysis, 104 (2013) 280-286.

[123]   L. Zhao, H. Hou, K. Iwasaki, A. Terada, M. Hosomi, Removal of PCDD/Fs from contaminated sediment and released effluent gas by charcoal in a proposed cost-effective thermal treatment process, Chemosphere, 93 (2013) 1456-1463.

[124]   W.J. Lee, S.I. Shih, C.Y. Chang, Y.C. Lai, L.C. Wang, G.P. Chang-Chien, Thermal treatment of polychlorinated dibenzo-p-dioxins and dibenzofurans from contaminated soils, Journal of Hazardous Materials, 160 (2008) 220-227.

[125]   W.Y. Chen, J.H. Wu, Y.Y. Lin, H.J. Huang, J.E. Chang, Bioremediation potential of soil contaminated with highly substituted polychlorinated dibenzo-p-dioxins and dibenzofurans: Microcosm study and microbial community analysis, Journal of Hazardous Materials, 261 (2013) 351-361.

[126]   M. Bunge, U. Lechner, Anaerobic reductive dehalogenation of polychlorinated dioxins, Applied Microbiology and Biotechnology, 84 (2009) 429-444.

[127]   H. Liu, J.W. Park, M.M. Häggblom, Enriching for microbial reductive dechlorination of polychlorinated dibenzo-p-dioxins and dibenzofurans, Environmental Pollution, 184 (2014) 222-230.

[128]   H. Zhen, S. Du, L.A. Rodenburg, G. Mainelis, D.E. Fennell, Reductive dechlorination of 1,2,3,7,8-pentachlorodibenzo-p-dioxin and Aroclor 1260, 1254 and 1242 by a mixed culture containing Dehalococcoides mccartyi strain 195, Water Research, 52 (2014) 51-62.

[129]   C. Kao, J. Liu, Y. Chen, C. Chai, S. Chen, Factors affecting the biodegradation of PCP by *Pseudomonas mendocina* NSYSU, Journal of Hazardous Materials, 124 (2005) 68-73.

[130]   Y. Tu, J. Liu, W. Lin, J. Lin, C. Kao, Enhanced anaerobic biodegradation of OCDD-contaminated soils by Pseudomonas mendocina NSYSU: Microcosm, pilot-scale, and gene studies, Journal of Hazardous Materials, 278 (2014) 433-443.

[131]   P. Lecomte, Les sites pollués: Traitement des sols et des eaux souterraines, Lavoisier TEC & DOC, Paris, France, 1995, pp. 198.

[132]   T. Johnson, Bioremediation and detoxification of polychlorinated dioxin contaminated environments, Warning: get_class expects parameter 1 to be object, array given in/home/vhosts/ejournal/user-dir/htdocs/classes/cache/GenericCache. inc. php on line 63 MMG 445, Basic Biotechnology eJournal, 4 (2008) 1-9.

[133]   S. Kuokka, A.L. Rantalainen, M. Häggblom, Anaerobic reductive dechlorination of 1,2,3,4-tetrachlorodibenzofuran in polychlorinated dibenzo-p-dioxin-and dibenzofuran-contaminated sediments of the Kymijoki River, Finland, Chemosphere, 98 (2014) 58-65.

[134]   USEPA, Site technology capsule GRACE bioremadiation technologies DARAMEND TM bioremediation technology, Report EPA 540/R-95/536a, United States Environmental Protection Agency, Cincinnati, Ohio, USA, 1997, pp. 6.

[135]   J.M. Thwaites, R.L. Farrell, S.D. Duncan, R.T. Lamar, R.B. White, Fungal-based remediation: Treatment of PCP contaminated soil in New Zealand. In: Environmental Bioremediation Technologies, Springer-Verlag, Berlin, Germany, 2007, pp. 465-479.

[136]   N.T. Dien, W. De Windt, A. Buekens, M.B. Chang, Application of bimetallic iron (BioCAT slurry) for pentachlorophenol removal from sandy soil, Journal of Hazardous Materials, 252 (2013) 83-90.

[137]   H.Y. Yu, Y.K. Wang, P.C. Chen, F.B. Li, M.J. Chen, M. Hu, X. Ouyang, Effect of nitrate addition on reductive transformation of pentachlorophenol in paddy soil in relation to iron (III) reduction, Journal of Environmental Management, 132 (2014) 42-48.

[138]   E. Winquist, K. Björklöf, E. Schultz, M. Räsänen, K. Salonen, F. Anasonye, T. Cajthaml, K.T. Steffen, K.S. Jørgensen, M. Tuomela, Bioremediation of PAH-contaminated soil with fungi – From laboratory to field scale, International Biodeterioration & Biodegradation, 86 (2014) 238-247.

[139]   K. Dercová, Z. Sejáková, M. Skokanová, G. Barančíková, J. Makovníková, Bioremediation of soil contaminated with pentachlorophenol (PCP) using humic acids bound on zeolite, Chemosphere, 66 (2007) 783-790.

[140]   C.U. Pittman, J. He, Dechlorination of PCBs, CAHs, herbicides and pesticides neat and in soils at 25 C using Na/NH 3, Journal of Hazardous Materials, 92 (2002) 51-62.

[141]   USEPA, Soil washing treatment. Engineering Bulletin, Report EPA 540/2-90/017, United States Environmental Protection Agency, Washington, DC, USA, 1990.

[142]   A.P. Khodadoust, R. Bagchi, M.T. Suidan, R.C. Brenner, N.G. Sellers, Removal of PAHs from highly contaminated soils found at prior manufactured gas operations, Journal of Hazardous Mmaterials, 80 (2000) 159-174.

[143]   A. Di Corcia, Analysis of phenols by gas—liquid—solid chromatography, Journal of Chromatography A, 80 (1973) 69-74.

[144]   M.R. Lee, Y.C. Yeh, W.S. Hsiang, B.H. Hwang, Solid-phase microextraction and gas chromatography–mass spectrometry for determining chlorophenols from landfill leaches and soil, Journal of Chromatography A, 806 (1998) 317-324.

[145]   T. Tsuda, A. Takino, M. Kojima, H. Harada, K. Muraki, Gas chromatographic–mass spectrometric determination of 4-nonylphenols and 4-tert-octylphenol in biological samples, Journal of Chromatography B: Biomedical Sciences and Applications, 723 (1999) 273-279.

[146]   S. Jonsson, H. Lind, S. Lundstedt, P. Haglund, M. Tysklind, Dioxin removal from contaminated soils by ethanol washing, Journal of Hazardous Materials, 179 (2010) 393-399.

[147] S. Berselli, G. Milone, P. Canepa, D. Di Gioia, F. Fava, Effects of cyclodextrins, humic substances, and rhamnolipids on the washing of a historically contaminated soil and on the aerobic bioremediation of the resulting effluents, Biotechnology and Bioengineering, 88 (2004) 111-120.

[148] P.N. Hurter, T.A. Hatton, Solubilization of polycyclic aromatic hydrocarbons by poly (ethylene oxide-propylene oxide) block copolymer micelles: Effects of polymer structure, Langmuir, 8 (1992) 1291-1299.

[149] M.C. Tomei, D.M. Angelucci, N. Ademollo, A.J. Daugulis, Rapid and effective decontamination of chlorophenol-contaminated soil by sorption into commercial polymers: Concept demonstration and process modeling, Journal of Environmental Management, 150 (2015) 81-91.

[150] J.F. Blais, N. Reynier, G. Mercier, Process for decontamination of soils polluted with metals, pentachlorophenol, dioxins and furans and contaminants removal from leachates. Patent pending No. CA 2,762,060, PCT/2012/050904, 2011.

[151] J. Mouton, G. Mercier, J.F. Blais, Amphoteric surfactants for PAH and lead polluted-soil treatment using flotation, Water, Air, & Soil Pollution, 197 (2009) 381-393.

[152] D.J.L. Prak, P.H. Pritchard, Solubilization of polycyclic aromatic hydrocarbon mixtures in micellar nonionic surfactant solutions, Water Research, 36 (2002) 3463-3472.

[153] A.F. Olea, C. Gamboa, Solubilization of phenols in surfactant/polyelectrolyte systems, Journal of Colloid and Interface Science, 268 (2003) 63-67.

[154] S.K. Park, A.R. Bielefeldt, Aqueous chemistry and interactive effects on non-ionic surfactant and pentachlorophenol sorption to soil, Water Research, 37 (2003) 4663-4672.

[155] V.J. Schacht, S.C. Grant, B.I. Escher, D.W. Hawker, C. Gaus, Solubility enhancement of dioxins and PCBs by surfactant monomers and micelles quantified with polymer depletion techniques, Chemosphere, 152 (2016) 99-106.

[156] M. Bergeron, Method of decontaminating soil. Canadian patent No. CA 6,915,908, 2009.

[157] L.C. Seronero, M.E.F. Laespada, J.L.P. Pavon, B.M. Cordero, Cloud point preconcentration of rather polar compounds: Application to the high-performance liquid chromatographic determination of priority pollutant chlorophenols, Journal of Chromatography A, 897 (2000) 171-176.

[158] C.N. Mulligan, F. Eftekhari, Remediation with surfactant foam of PCP-contaminated soil, Engineering Geology, 70 (2003) 269-279.

[159] C. You, J. Liu, Desorptive behavior of chlorophenols in contaminated soils, Water Science and Technology, 33 (1996) 263-270.

[160] C.N. Mulligan, Environmental applications for biosurfactants, Environmental Pollution, 133 (2005) 183-198.

[161] W.H. Organization, Pentachlorophenol health and safety guide. Health and Safety Guide No. 19, IPCS international programme on chemical safety, Geneva, Swiss, 1989, pp. 46.

[162] Y.F. Xiao, G.M. Liu, Y.L. Dong, L.L. Yin, Rapid Determination of pentachlorophenol in soil samples [J], Rock and Mineral Analysis, 2 (2008) 012.

[163] A.S. Chen, A.R. Gavaskar, B.C. Alleman, A. Massa, D. Timberlake, E.H. Drescher, Treating contaminated sediment with a two-stage base-catalyzed decomposition (BCD) process: bench-scale evaluation, Journal of Hazardous Materials, 56 (1997) 287-306.

[164] Y. Mitoma, T. Uda, N. Egashira, C. Simion, H. Tashiro, M. Tashiro, X. Fan, Approach to highly efficient dechlorination of PCDDs, PCDFs, and coplanar PCBs using metallic calcium in ethanol under atmospheric pressure at room temperature, Environmental Science & Technology, 38 (2004) 1216-1220.

[165] Y. Wei, J. Yan, L. S., X. Li, Mechanochemical decomposition of pentachlorophenol by ball milling, Journal of Environmental Sciences, 21 (2009) 1761-1768.

[166] Y. Nomura, S. Nakai, M. Hosomi, Elucidation of degradation mechanism of dioxins during mechanochemical treatment, Environmental Science & Technology, 39 (2005) 3799-3804.

[167] J.H. Kim, P.G. Tratnyek, Y.S. Chang, Rapid dechlorination of polychlorinated dibenzo-p-dioxins by bimetallic and nanosized zerovalent iron, Environmental Science & Technology, 42 (2008) 4106-4112.

[168] E. Cooper, J. Sims, S. Cunningham, J. Huang, W. Berti, Chelate-assisted phytoextraction of lead from contaminated soils, Journal of Environmental Quality, 28 (1999) 1709-1719.

[169] P.K. Padmavathiamma, L.Y. Li, Phytoremediation technology: Hyper-accumulation metals in plants, Water, Air, & Soil Pollution, 184 (2007) 105-126.

[170] I. Raskin, R.D. Smith, D.E. Salt, Phytoremediation of metals using plants to remove pollutants from the environment, Current Opinion in Biotechnology, 8 (1997) 221-226.

[171] P. Lens, T. Grotenhuis, G. Malina, H. Tabak, Soil and sediment remediation: Mechanisms, technologies and applications, IWA Publishing, England, 2005, pp. 523.

[172] G. Dermont, M. Bergeron, G. Mercier, M. Richer-Laflèche, Soil washing for metal removal: A review of physical/chemical technologies and field applications, Journal of Hazardous Materials, 152 (2008) 1-31.

[173] G. Mercier, Disponibilité des métaux dans les sols et prévision du rendement d'enlèvement par des techniques minéralurgiques, Ph.D. thesis, Université Laval, Québec, Québec, Canada, 2000.

[174] G. Dermont, M. Bergeron, G. Mercier, M. Richer-Laflèche, Metal-contaminated soils: Remediation practices and treatment technologies, Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management, 12 (2008) 188-209.

[175] M. Laporte-Saumure, R. Martel, G. Mercier, Evaluation of physicochemical methods for treatment of Cu, Pb, Sb, and Zn in Canadian small arm firing ranges backstop soils, Water, Air, & Soil Pollution, 213 (2010) 171-189.

[176] R. Rikers, P. Rem, W. Dalmijn, Improved method for prediction of heavy metal recoveries from soil using high intensity magnetic separation (HIMS), International Journal of Mineral Processing, 54 (1998) 165-182.

[177] M.A. Marino, R.M. Brica, C.N. Neale, Heavy metal soil remediation: The effects of attrition scrubbing on a wet gravity concentration process, Environmental Progress, 16 (1997) 208-214.

[178] J. Stražišar, A. Sešelj, Attrition as a process of comminution and separation, Powder Technology, 105 (1999) 205-209.

[179] R. Bayley, C. Biggs, Characterisation of an attrition scrubber for the removal of high molecular weight contaminants in sand, Chemical Engineering Journal, 111 (2005) 71-79.

[180] P. Jobin, G. Mercier, J.-F. Blais, V. Taillard, Understanding the effect of attrition scrubbing on the efficiency of gravity separation of six inorganic contaminants, Water, Air, & Soil Pollution, 226 (2015) 1-13.

[181] C.W. Williford, Z. Li, Z. Wang, R.M. Bricka, Vertical column hydroclassification of metal-contaminated soils, Journal of Hazardous Materials, 66 (1999) 15-30.

[182] G. Mercier, J. Duchesne, D. Blackburn, Prediction of metal removal efficiency from contaminated soils by physical methods, Journal of Environmental Engineering, 127 (2001) 348-358.

[183] H. Lin, X. Man, D. Walsh, Lead removal via soil washing and leaching, JOM, 53 (2001) 22-25.

[184] G. Mercier, J. Duchesne, D. Blackburn, Removal of metals from contaminated soils by mineral processing techniques followed by chemical leaching, Water, Air, & Soil Pollution, 135 (2002) 105-130.

[185] X. Cao, L.Q. Ma, M. Chen, D.W. Hardison, W.G. Harris, Weathering of lead bullets and their environmental effects at outdoor shooting ranges, Journal of Environmental Quality, 32 (2003) 526-534.

[186] P. Masscheleyn, F. Tack, M. Verloo, A model for evaluating the feasibility of an extraction procedure for heavy metal removal from contaminated soils, Water, Air, & Soil Pollution, 113 (1999) 63-76.

[187]   L. Di Palma, P. Ferrantelli, Copper leaching from a sandy soil: mechanism and parameters affecting EDTA extraction, Journal of Hazardous Materials, 122 (2005) 85-90.

[188]   L. Di Palma, R. Mecozzi, Heavy metals mobilization from harbour sediments using EDTA and citric acid as chelating agents, Journal of Hazardous Materials, 147 (2007) 768-775.

[189]   N. Finzgar, B. Kos, D. Lestan, Heap leaching of lead contaminated soil using biodegradable chelator [S, S]-ethylenediamine disuccinate, Environmental Technology, 26 (2005) 553-560.

[190]   R.W. Peters, Chelant extraction of heavy metals from contaminated soils, Journal of Hazardous Materials, 66 (1999) 151-210.

[191]   K. Vaxevanidou, N. Papassiopi, I. Paspaliaris, Removal of heavy metals and arsenic from contaminated soils using bioremediation and chelant extraction techniques, Chemosphere, 70 (2008) 1329-1337.

[192]   S. Wasay, S. Barrington, S. Tokunaga, Remediation of soils polluted by heavy metals using salts of organic acids and chelating agents, Environmental Technology, 19 (1998) 369-379.

[193]   S.W. Lee, J.Y. Kim, J.U. Lee, I. Ko, K.W. Kim, Removal of arsenic in tailings by soil flushing and the remediation process monitoring, Environmental Geochemistry and Health, 26 (2004) 403-409.

[194]   R.D. Rufino, J.M. Luna, G.M. Campos-Takaki, S.R. Ferreira, L.A. Sarubbo, Application of the biosurfactant produced by *Candida lipolytica* in the remediation of heavy metals, Chemical Engineering, 27 (2012) 61-66.

[195]   K. Elgh-Dalgren, Z. Arwidsson, A. Camdzija, R. Sjöberg, V. Ribé, S. Waara, B. Allard, T. von Kronhelm, P.A. van Hees, Laboratory and pilot scale soil washing of PAH and arsenic from a wood preservation site: changes in concentration and toxicity, Journal of Hazardous Materials, 172 (2009) 1033-1040.

[196]   C.N. Mulligan, R.N. Yong, B.F. Gibbs, Removal of heavy metals from contaminated soil and sediments using the biosurfactant surfactin, Journal of Soil Contamination, 8 (1999) 231-254.

[197]   S. Ehsan, S.O. Prasher, W.D. Marshall, A washing procedure to mobilize mixed contaminants from soil, Journal of Environmental Quality, 35 (2006) 2084-2091.

[198]   K.R. Reddy, S. Chinthamreddy, Comparison of extractants for removing heavy metals from contaminated clayey soils, Soil and Sediment Contamination, 9 (2000) 449-462.

[199]   I. Ko, Y.-Y. Chang, C.-H. Lee, K.-W. Kim, Assessment of pilot-scale acid washing of soil contaminated with As, Zn and Ni using the BCR three-step sequential extraction, Journal of Hazardous Materials, 127 (2005) 1-13.

[200]   R. Bassi, S.O. Prasher, B. Simpson, Extraction of metals from a contaminated sandy soil using citric acid, Environmental Progress, 19 (2000) 275-282.

[201]   G. Mercier, M. Chartier, D. Couillard, Strategies to maximize the microbial leaching of lead from metal-contaminated aquatic sediments, Water Research, 30 (1996) 2452-2464.

[202]   A. Moutsatsou, M. Gregou, D. Matsas, V. Protonotarios, Washing as a remediation technology applicable in soils heavily polluted by mining–metallurgical activities, Chemosphere, 63 (2006) 1632-1640.

[203]   M. Jang, J.S. Hwang, S.I. Choi, Sequential soil washing techniques using hydrochloric acid and sodium hydroxide for remediating arsenic-contaminated soils in abandoned iron-ore mines, Chemosphere, 66 (2007) 8-17.

[204]   C.N. Neale, R. Bricka, A.C. Chao, Evaluating acids and chelating agents for removing heavy metals from contaminated soils, Environmental Progress, 16 (1997) 274-280.

[205]   S. McGrath, J. Cegarra, Chemical extractability of heavy metals during and after long-term applications of sewage sludge to soil, Journal of Soil Science, 43 (1992) 313-321.

[206]   M. Rivero-Huguet, W.D. Marshall, Scaling up a treatment to simultaneously remove persistent organic pollutants and heavy metals from contaminated soils, Chemosphere, 83 (2011) 668-673.

[207]   Cleanearth, Cleanearth Technologies Inc., http://www.cleanearthtechnologies.ca/, 2015.

[208]   DEC, DEME Environmental Contractore, http://www.deme-group.com/dec/node/594, 2015.

[209]   ETG, Environmental Technologies Group, http://www.etgroupinc.com/, 2015.

[210]   J.H. Lehr, Wiley's remediation technologies handbook – Major contaminant chemicals and chemical groups. John Wiley & Sons Inc., New Jersey, USA, 2004, pp. 1288.

[211]   Tecosol, Tecosol. http://tecosol.com/, 2015.

[212]   Biogenesis, Demonstration testing and full-scale operation of the Biogenesis TM sediment decontamination process, In: Biogenesis Washing BGW, LLC, New-Jersey, USA, 2008, pp. 1019

[213]   H. Environnement, Horizon Environnnement, http://www.horizonenviro.com/home, 2015.

[214]   K. Maturi, K.R. Reddy, Simultaneous removal of organic compounds and heavy metals from soils by electrokinetic remediation with a modified cyclodextrin, Chemosphere, 63 (2006) 1022-1031.

[215]   D.P. Veetil, G. Mercier, J.-F. Blais, M. Chartier, L.H. Tran, V. Taillard, Remediation of contaminated dredged sediments using physical separation techniques, Soil and Sediment Contamination: An International Journal, 23 (2014) 932-953.

[216]   P. Jobin, L. Coudert, V. Taillard, J.-F. Blais, G. Mercier, Remediation of inorganic contaminants and polycyclic aromatic hydrocarbons from soils polluted by municipal solid waste incineration residues, Environmental Technology, 37 (2016) 1983-1995.

[217]   K. Maturi, K.R. Reddy, Extractants for the removal of mixed contaminants from soils, Soil & Sediment Contamination, 17 (2008) 586-608.

[218]   , Éditions Le Griffon d'Argile, Sainte-Foy, Québec, Canada, 2001.

[219]   V. Taillard, Démonstration à l'échelle pilote d'un procédé d'extraction simultanée des HAP et du plomb, M.Sc. thesis, INRS-ETE, Université du Québec, Québec, Québec, Canada, 2010, pp. 273.

[220]   Y. Kumar, K. Popat, H. Brahmbhatt, B. Ganguly, A. Bhattacharya, Pentachlorophenol removal from water using surfactant-enhanced filtration through low-pressure thin film composite membranes, Journal of Hazardous Materials, 154 (2008) 426-431.

[221]   C.M. Santana, S.F. Zoraida, J.J.S. Rodriguez, An environmentally friendly method for the extraction and determination of priority phenols in soils using microwave-assisted micellar extraction, Anal. Bioanal. Chem., 382 (2005) 125–133.

[222]   Stablex, Website: http://www.stablex.com/en/index.html, Consulted on May 2015.

Table 1   **Methods of treatment developed to improve the rehabilitation of sites contaminated by inorganic and/or organic contaminants [Adapted from 7]**

Contaminants	Destructive methods			Separative methods		
	Thermal treatment	Bioremediation	Dechlorination	Thermal desorption	Washing	Solvent extraction
As, Cr, Cu	x	±	x	x	√	x
PCP	√	±	±	√	±	±
PCDD/F	√	x	√	√	±	±

√ : highly efficient (more than 70% removal)

± : more or less efficient (45 to 70% removal)

x : inefficient (less than 45% removal)

Table 2 **Effective removals of PCP and PCDD/F from different types of soil using thermal, biological and chemical treatments developed at laboratory scale**

Treatment technology and operating conditions	Initial contents	Extraction yields (%)	References
Thermal desorption			
Presence of nanosized zerovalent iron particles (1%) or CaO (10%), T = 200 -280°C, t = 60 min	$[PCDD/F]_0$ = 1,800 µg/kg	PCDD/F : >90	[118]
In a nitrogen atmosphere, T = 200 - 400°C, t = 30 min	$[PCP]_0$ = 90 mg/kg	PCP : > 70	[76]
T = 350°C, t = 40 min	$[PCP]_0$ = 90 ± 5.7 mg/kg	PCP : > 90	[75]
40 g of soil, Primary furnace : T = 750 - 850°C, t = 1 h Secondary furnace: T = 1,200°C, t = 3 sec	$[PCDD/F]_0$ = 36,000 µg I-TEQ/kg	PCDD/F : >99.99	[122]
Biological treatment			
0.5 g of biomass (*Micrococcus various, Comamonas testoteroni*) per kg of soil, T = 28°C, t = 7 d	$[PCP]_0$ = 10 mg/kg	PCP : 10-20	[138]
0.5 g of biomass (*Micrococcus various, Comamonas testoteroni*) per kg of soil, T = 28°C, t = 14 d		PCP : 20-65	
0.5 g of biomass (*Micrococcus various, Comamonas testoteroni*) per kg de soil, T = 28°C, t = 28 d		PCP : 40-65	
0.5 g of biomass (*Micrococcus various, Comamonas testoteroni*) per kg of soil, T = 28°C, t = 7 d	$[PCP]_0$ = 100 mg/kg	PCP : 5-20	
0.5 g of biomass (*Micrococcus various, Comamonas testoteroni*) per kg of soil, T = 28°C, t = 14 d		PCP : 5-10	
0.5 g of biomass (*Micrococcus various, Comamonas testoteroni*) per kg of soil, T = 28°C, t = 28 d		PCP : 20-40	
20 g of soil, 1 mL of mineral medium, 5 mL of *P.*	$[OCDD]_0$ = 20 – 200 ng/kg	OCDD: 71	[128]

mendocina NSYSU strain solution, pH = 7.5 ([NaOH] = 1 N), anaerobic bioreactor (20% H_2 and 80 % CO_2), in dark, T = 20°C, t = 65 d, with addition of lecithin		OCDD: 75	
5 kg of soil, 20 L of mineral medium, 1 L of *P. mendocina* NSYSU strain solution, pH = 7 ([NaOH] = 1 N), anaerobic bioreactor (20% H_2 and 80 % CO_2), in dark, T = 20°C, t = 75 d, with addition of lecithin			
20 mL of a minimal medium (*Proteobacteria, Actinobacteria* and *Planctomyctes*) per 10 g of soil, T = 28°C in the dark, t = 6 weeks	$[OCDD]_0$ = 1,570 - 1,654 µmol/kg $[OCDF]_0$ = 683 – 913 µmol/kg $[1,2,3,4,6,7,8\text{-}HpCD/F]_0$ = 80 -88 µmol/kg	OCDD : < 1% OCDF : 99.9 HpCD/F : 95.8-99.7	[125]
Biomass : *Trametes versicolor*, t = 175 weeks	$[PCP]_0$ = 1,000 mg/kg	PCP : 75	[112]
Incubation : T = 25°C, 15 weeks, 30 g biomass (*Stropharia rugosoannulata*) per 40 g of soil	$[PCP]_0$ = 300 mg/kg $[PCDD/F]_0$ = 24,000 ng/kg	PCP : 73 PCDD/F : 13	[113]
600 mg of bimetallic iron nanoparticles (BioCAT) slurry per 2 g of soil, T = 25 ± 1°C, t = 21 d	$[PCP]_0$ = 85±6 mg/kg	PCP : 90	[135]
Chemical or mechano-chemical dechlorination			
7 g of soil mixture, ratio Cl (PCP of soil)/CaO = 1/4, stainless steel balls or of Al_2O_3, in presence of SiO_2, t = 1 h, 400 rpm, room temperature	n.c.	PCP : 98.4	[164]
3 treatments mecano-chemical in presence of CaO (ratio soil: CaO = 1 : 20), 700 rpm, t = 15 min	n.c.	OCDD : > 99 OCDF : > 99	[165]
Extraction with solvents			
Soil/dimethylether ratio = 1/1, T = 48°C, t = 25 min, P = 150-350 psi	$[PCP]_0$ = 1,490 mg/kg $[PCDD/F]_0$ = 15,600 µg/kg	PCP : 95.1 PCDD/F : 95.2	[109]
Chemical washing			
Water / MeOH = 100/0, T = 25°C Water / MeOH = 50/50, T = 25°C	$[PCP]_0$ = 99 mg/kg	PCP : 50 PCP : 88	[106]

Conditions	Initial conc.	Yield (%)	Ref.
Water / MeOH = 5/95, T = 25°C Water / MeOH = 0/100, T = 25°C		PCP : 81 PCP : 52	
Soil/solution ratio = 1/20, [lactic acid] = 25 %, T = 25°C, 24 h	$[PCP]_0$ = 100 mg/kg	PCP : 85	[12]
Soil/solution ratio = 1/8, NaOH, pH = 12.5, T = 25°C, t = 20 min		PCP : >90	[162]
Soil/solution ratio = 1/6, T = 49°C, pH = 9, Surfactant Makon 12 = 3% (w/w) Soil/solution ratio = 1/6, T = 49°C, pH = 9, Surfactant Ipegal CA 720 = 3% (w/w) Soil/solution ratio = 1/6, T = 49°C, pH = 9, Without surfactant	$[PCP]_0$ = 1,206 mg/kg $[PCDD/F]_0$ = 29 µg/kg	PCP : 82.6 PCDD/F : 10.3 PCP : 63.5 PCDD/F : 17.2 PCP : 70.1 PCDD/F : 20.7	[109]
Soil/solution ratio = 1/3, 10 washing cycles with 75% ethanol, T = 60°C, t = 30 min	$[PCDD/F]_0$ = 29 µg/kg	PCDD/F : 80-98	[146]
5 g of soil, 0.25 g of polymer (Hytrel 8206), 5 mL tap water, T = 25°C, 320 rpm, t = 24 h	$[PCP]_0$ = 639 mg/kg $[PCP]_0$ = 2,522 mg/kg	PCP : 87 PCP : 77	[149]
10 g of soil, 1 L of aq. solution : anionic surf. SDS (0.5 – 1.0 CMC), $NaClO_4$ = 0.01 N, T = 24°C, t = 6 h	$[PCP]_0$ = 452 mg/kg $[PCP]_0$ = 460 mg/kg	PCP : 80 - 84 PCP : 72 - 92	[159]
Soil/water ratio = 0.14-1.02 g/mL, nonionic surf. Tergipol NP10 (50 g/L), T = 23°C, t = 7-26 d	$[PCP]_0$ = 200 mg/kg	PCP : 87	[154]
Triton X-100 (non ionique) 1 % JBR 425 (anionique) 1%	$[PCP]_0$ = 1,000 mg/kg	PCP : 85 PCP : 60	[158]
T = 30°C, pH = 6.5, [SDS] = 0.0012 M T = 30°C, pH = 6.5, [SDS] = 0.0015 M T = 30°C, pH = 6.5, [SDS] = 0.0030 M	$[PCP]_0$ = 332 mg/kg $[PCP]_0$ = 224 mg/kg	PCP : 74.7 PCP : 30.4 PCP : 89.7	[23]
Extraction with a non-surfactant 5% (Polyoxyethylene 10 Lauryl ether) assisted by microwave, t = 3 min, P = 700 W	n.c.	PCP : 100	[221]

n.c. : not communicated.

Table 3 Performances of arsenic, chromium and copper removals from different types of soil using physical and chemical treatments

Treatment technology and operating conditions	Initial contents (mg/kg)	Costs ($/t)	Extraction yield (%)	References
Physical techniques				
Pretreatment by attrition (t = 10 min, 2,000 rpm), followed by:				[175]
Fraction 53-500 µm : shaking table (PD = 70%)	$[Pb]_0$ = 5,647	n.c.	Pb : 92	
	$[Cu]_0$ = 366		Cu : 84	
Fraction 500-2,000 µm: Jig (density barriers Si_3N_4; ρ = 3.2 g/cm^3)	$[Pb]_0$ = 45,478		Pb : 94	
	$[Cu]_0$ = 13,531		Cu : 98	
Fraction 63-850 µm : shaking table	$[Pb]_0$ = 3,500	n.c.	Pb : 61	[184]
	$[Cu]_0$ = 6,090		Cu : 52	
Fraction 850-2,000 µm : Jig	$[Pb]_0$ = 2,900		Pb : 70	
	$[Cu]_0$ = 11,100		Cu : 89	
Fraction 63-2,000 µm : shaking table (PD = 20%)	$[Cu]_0$ = 904	n.c.	Cu : 88.7	[177]
Fraction 63-2,000 µm : pretreatment by attrition (PD = 75-80%, t = 15 min, 1,100 rpm), shaking table (PD = 20%)			Cu : 95.6	
High intensity magnetic separation : intensity = 0.1A	$[Cu]_0$ = 121	n.c.	Cu : >95	[176]

	$[Cr]_0 = 598$		Cr : >85	
Fraction 63 - 2,000 µm : Attrition (PD = 70%, t = 5 min, 2,100 rpm) as a pretreatment followed by separation with dense media (d = 1.9-2.9)	$[Cu]_0 = 7,458$	n.c.	Cu : 64.8 Cu : 83.8	[182]
Fraction 125 – 10,000 µm : Attrition (ratio soil/water = 3:2, t = 20 min, 1,500 rpm) upstream of a Wilfley table	$[Cu]_0 = 3,030$	116	Cu : 63	[86]
Fraction <250 µm: Froth flotation (3 flotation stages, PD = 10%, [potassium xanthate]=1.2 g/kg, [methyl isobutyl carbinol]=0.24 g/kg, t = 4-6 min, 1,050 rpm, air flow rate = 4 m^3/hr)	$[Cu]_0 = 1,280-1,360$	n.c.	Cu : 61-70	[208]
Fraction : 250 – 2,000 µm : Wilfley table (PD = 20%, 200 g/L.min)			Cu : 27-33	
Fraction >2,000 µm : pretreatment by attrition (PD = 20% (w/w), t = 10 min, 2,000 rpm), physical separation column			Cu : not effective	
Soil washing				
Soil/Liquid ratio = 30 g/L, t = 1 h, [HCl] = 1 to 6 M	$[As]_0 = 8$ $[Cu]_0 = 4$	n.c.	As : 64-92 Cu : 41-51	[202]
Soil/Liquid ratio = 30 g/L, t = 1 h, [EDTA] = 0.1 M			As : 13 Cu : 41	
Soil/Liquid ratio = 30 g/L, t = 1 h, $[H_2SO_4]$ = 6 M			As : 80 Cu : 30	

300 g of soil, ratio S/L = 1:1, oxalic acid (0.47 M), t = 10 min, pH = 3.4	$[As]_0 = 105$	n.c.	As : 74	[195]
Soil/Liquid ratio = 1/1, t = 1 h, HNO_3			As : 1	
Soil/Liquid ratio = 1/1, t = 1 h, NaOH			As : 35	
Soil/Liquid ratio = 1/1, t = 1 h, MGDA			As : 3	
2 g of soil, 25 mL of citric acid solution, NaOH (1 N) pH = 5.5, t = 24 h, 200 rpm	$[Cu]_0 = 40$	n.c.	Cu : 50	[200]
50 g of soil, PD = 20%, t = 6 h, [HCl] = 2 M, 300 rpm	$[As]_0 = 1,710$	n.c.	As > 99	[203]
50 g of soil, PD = 20%, t = 6 h, [NaOH] = 2 M, 300 rpm			As > 99	
40 kg of soil, Soil/Liquid ratio = 1/10, pH 2-3, H_2SO_4	$[As]_0 = 41$	n.c.	As : 70	[129]
40 kg of soil, Soil/Liquid ratio = 1/10, pH 2-3, H_3PO_4			As : 75	
40 kg of soil, Soil/Liquid ratio = 1/10, pH 2-3, HCl			As : 63	
Fraction <53 µm : 250 g of soil, 1 L of solution of H_2SO_4 (1,7 M) and NaCl (5.5 M), t = 25 min	$[Cu]_0 = 1,800 - 3,800$	n.c.	Cu : 21-39	[175]
20 g of soil (fraction <125 µm)/200 mL of solution of H_2SO_4 (1 M) and NaCl (4 M), three leaching steps, t = 1 h, T=20°C	$[Cu]_0 = 1,800 - 3,800$	n.c.	Cu : 83	[78]
2 kg of soil, 18 L of washing solution (PD=10%, NaCl (4 M), three leaching steps, t = 1 h, T = 20°C)	$[Cu]_0 = 418 - 1,015$	287		[77]
$[H_2SO_4] = 0.125$ M			Cu : 96-97	

[H$_2$SO$_4$] = 0.25 M			Cu : 86-92	
[H$_2$SO$_4$] = 0.5 M			Cu : 91-92	
2 g of soil in 40 mL of washing solution, T = 25°C, t = 24 h, [EDTA] = 0.01 to 1 M	[As]$_0$ = 4,120 – 4,590	n.c.	As : 65-80	[193]
EDTA, DTPA, citric acid and tartaric acid, t =24 h, pH = 2.1 – 9	[Cu]$_0$ = 926	n.c.	Cu : 75-99.9	[192]
Lipopeptide biosurfactant (8 g/L) (CMC = 0.03%)	[Cu]$_0$ = 133	n.c.	Cu : 96.8	[194]
300 g of soil, L/S ratio = 1:1, chelating agent MGDA (0.213 M), non-ionic surfactant AG (3.2×CMC), Ca(OH)$_2$, T = 50°C, t = 10 min	[As]$_0$ = 105	n.c.	As : 86	[195]
3 g of soil, 20 mL EDTA (2 mM), Brij 98 at 30 g/L	[Cr]$_0$ = 534	n.c.	Cr : 42	[197]
	[Cu]$_0$ = 2,732		Cu : 49	
L/S ratio= 10:1 (w/w), five washing steps, lipopepted biosurfactant (0.25%), [NaOH] = 1% (pH = 10), t = 24 h	[Cu]$_0$ = 420	n.c.	Cu : 70	[196]

n.c. : not communicated.

Table 4   Performances of chemical treatments developed and applied at laboratory scale to simultaneously remove inorganic and organic contaminants from different types of soil

Treatment technologies and operating conditions	Initial contents	Cost ($/t)	Extraction yields (%)	References
Soil washing				
5 g of soil, 25 mL of extracting solution (combination of Tween 80 (nonionic) 5% and EDTA (0.2 M) or citric acid (1 M), T = 25°C, t = 24 h, 250 rpm	$[Ni]_0 = 14$-18.6 mg/kg $[Zn]_0 = 84$-776 mg/kg $[Pb]_0 = 51$-$1,478$ mg/kg $[Phe^1]_0 = 193$-260 mg/kg		Ni : 50-68 Zn : 69-88 Pb : 47-89 Phe : 81-98	[210]
5 g of soil, 25 mL of extracting solution, T = 25°C, t = 24 h 5% Non-ionic surfactant (Igepal CA 720) 5% Non-ionic surfactant (Tween 80), 0.2 M EDTA 1 M Citric acid	$[Zn]_0 = 84.4$ mg/kg $[Pb]_0 = 50.6$ mg/kg $[Phe]_0 = 260$ mg/kg		Phe: 76 Phe: 100 Zn : 100 Pb : 100	[89]
100 g of soil in 200 mL of washing solution ([S,S]-EDDS 0.1 M, Brij 98 à 2%), pH = 9, t = 20 min	$[As]_0 = 230$ mg/kg $[Cr]_0 = 190$ mg/kg $[Cu]_0 = 290$ mg/kg $[PCP]_0 = 5$ mg/kg	137,000	As : 70 Cr : 75 Cu : 80 PCP : 90	[206]

10 g of soil in 100 mL of washing solution (PD = 10% (w/v), 1,200 rpm, t = 60 min, T = 60°C, three flotation steps, BW = 1% (w/w), $[H_2SO_4]$ = 1 N)	$[As]_0$ = 50-250 mg/kg		As : 82-93	[50]
	$[Cr]_0$ = 35-220 mg/kg		Cr : 30-80	
	$[Cu]_0$ = 80-350 mg/kg		Cu : 79-90	
	$[PCP]_0$ =2.5-30 mg/kg		PCP : 36-78	
100 g of soil in 100 mL of washing solution (PD= 10% (w/v), t = 2 h, T = 80°C, three leaching steps, [BW] = 1% (w/w), [NaOH] = 1 N, pH >13)	$[As]_0$ = 50-250 mg/kg	600	As : 60	[108]
	$[Cr]_0$ = 35-220 mg/kg		Cr : 32	
	$[Cu]_0$ = 80-350 mg/kg		Cu : 77	
	$[PCP]_0$ =2.5-30 mg/kg		PCP : 87	
	$[PCDD/F]_0$ =1,375-6,289 ng/kg		PCDD/F : 25-74	

[1] Phe : Phenanthrene.

Table 5   **Performances of biological, thermal, physical and chemical treatments developed and applied at pilot scale to remove As, Cr, Cu, PCP and PCDD/F from different types of soil**

Treatment technologies and operating conditions	Initial contents	Costs ($/t)	Extraction yields (%)	References
Biological treatment				
Pretreatment by washing with flocculant + Process Biotrol®			PCP : 96-98	[110]
On site treatment of 65,000 dry tons of PCP and dioxin-contaminated soil , T >540°C, 17-25 t/h	$[PCP]_0$ = 500 mg/kg $[PCDD/F]_0$ = 15 µg/kg	370	n.c.	[111]
Thermal treatment				
CaO (10%), soil rate = 40-80 kg/h, T = 400°C	$[PCP]_0$ = 2,900 mg/kg $[PCDD/F]_0$ = 74.9 µg/kg		PCP : >99.9% PCDD/F : 97.9%	[115]
CaO (10%), soil rate = 40-80 kg/h, T = 450°C			PCP : >99.9% PCDD/F : 99.9%	
On site treatment of 65,000 dry tons of PCP and dioxin-contaminated soil , T > 540°C, 17-25 tons of soil per hour	$[PCP]_0$ = 500 mg/kg $[PCDD/F]_0$ = 15 µg/kg	370	PCP :	[111]
First combustion chamber, soil treatment, T = 650-800°C, t = 20 min, secondary combustion chamber, gases treatment, T = 1000°C, condensation,	High levels of PCP and PCDD/F	400-800	PCP : >99.99% PCDD/F : 99.99%	[114]

neutralization, oxidation of gases and passed through
activated carbon, 3 sec

Physical and chemical treatments

2 kg of soil (<125 μm), three leaching steps (PD = 10%, t = 2 h, T = 80°C, [BW] = 0.5-3.0% (w/w), [NaOH] = 1.0-1.5 M)	$[As]_0$ = 65-142 mg/kg	425	As : 87-95%	[106]
	$[Cr]_0$ = 156-188 mg/kg		Cr : 50-72%	
	$[Cu]_0$ = 90-215 mg/kg		Cu : 73-84%	
	$[PCP]_0$ = 11-35 mg/kg		PCP : 52-99.9%	
	$[PCDD/F]_0$ =1,210-13,100 ng/kg		PCDD/F : 26-74%	
[NaCl] = 5 M, [CAS] = 0.5%, pH = 3			HAP : 86-99.9%	[212]
			Pb : 78%	

n.c.: non communicated.

Table 6 **Performances of biological, thermal, physical and chemical treatments developed and applied at industrial scale to remove As, Cr, Cu, PCP and PCDD/F from different types of soil**

Company	Country	Contaminant	Technology	Efficiency (%)	Capacity (t/yr)	Costs ($/t)	References
Arcadis Geroaghty and Miller	UK	PCDD/F, PCBs, Hg, Pb	STRATEX Process: *ex-situ* technology (thermal desorption followed by steam stripping (PCDD/F, PCBs, Hg) and solidification/stabilization (non-volatile metals)). **Technology no longer available**	n.c.	50,000	125-150	[210]
BioGenesis Enterprises Inc.	USA	PCDD/F, PCBs, Heavy metals	Cleansing and enhanced biodegradation in a two-stage process followed by an oxidation step	85% PCDD/F, low efficient for As	n.c.	40-200	[210,212]
Horizon Environnement Inc.	Canada	PCP	Thermal desorption at high temperature	99.99%	n.c.	n.c.	[213]
		As, Cr, Cu	Secured landfilling in containment cells	n.a.	n.c.	n.c.	

Stablex	Canada	PCP, PCDD/F	Secured landfilling in containment cells if organic contaminants is lower than 30% (w/w)	n.a.	100,000	n.c.	[222]
		As, Cr, Cu	Secured landfilling in containment cells	n.a.	100,000	n.c.	[222]
Récupère-Sol	Canada	PCP, PCDD/F	Thermal desorption at 600-850°C followed by gases treatment at 1,000°C	99.99%	100,000	n.c.	[114]
DEC	Belgium	PCP, PCDD/F, Metals	Thermal treatment or solidification/stabilization	65-90%	400,000	n.c.	[208]
CleanEarth Technologies	Canada	Heavy metals	Chemical treatment	n.c.	n.c.	n.c.	[207]
Tecosol	Canada	Heavy metals, HAP, BPC	Metox Process - Flottation in acidic solution in the presence of a surfactant	n.c.	n.c.	n.c.	[211]
ETG Environmental Technologies	USA/Canada	PCDD/F, PCP, PCB	*In-situ* or *ex-situ* soil vapor extraction	n.c.	n.c.	n.c.	[209]
Bennett Environmental Inc.	Canada	PCDD/F, PCP, PCB, creosote	Thermal treatment	99.999%	200,000	n.c.	[210]

Supporting Table 1   Physical and chemical properties of pentachlorophenol

Melting temperature	188 to 191 °C
Boiling point	310°C [20]
Odor	Very pungent when heated [19]
Density	1.978 g/cm^3 at 22 - 24°C [19]
Vapor Pressure	41.10^{-4} to 51.10^{-4} Pa at 20°C [20]
Octanol / water (Log K_{ow})	5.17 (pH = 2.00)
	3.00 (pH = 7.00) [18]
Adsorption coefficient (Log K_{oc})	6 - 11 (high) [20]
pKa	4.75 at 25°C [16]
Solubility in water (at 20 °C)	14 mg/L (pH = 5) [16]
	330 g/L (pH >13)