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REVIEW ARTICLE

In situ remediation technologies for mercury-contaminated soil

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Abstract Mercury from anthropogenic activities is a pollutant that poses significant risks to humans and the environment. In soils, mercury remediation can be technically challenging and costly, depending on the subsurface mercury distribution, the types of mercury species, and the regulatory requirements. This paper introduces the chemistry of mercury and its implications for in situ mercury remediation, which is followed by a detailed discussion of several in situ Hg remediation technologies in terms of applicability, cost, advantages, and disadvantages. The effect of Hg speciation on remediation performance, as well as Hg transformation during different remediation processes, was detailed. Thermal desorption, electrokinetic, and soil flushing/washing treatments are removal technologies that mobilize and capture insoluble Hg species, while containment, solidification/stabilization, and vitrification immobilize Hg by converting it to less soluble forms. Two emerging technologies, phytoremediation and nanotechnology, are also discussed in this review.

Keywords Mercury · Soil contamination · In situ remediation · Immobilization · Stabilization

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Introduction

Several hundred thousand tons of mercury (Hg) have been released into the environment due to anthropogenic activity over the past century (Bizily et al. 1999). According to the United Nations Environment Programme (UNEP) report (UNEP 2008), global mercury emission from anthropogenic sources in the year 2005 alone was estimated to be approximately 1930 metric tons. Mercury pollution is of significant global concern not only because of its increased level in the environment, but also due to its toxic effect on human health. The organomercuric form, such as methylmercury (CH_3Hg^+), impairs growing fetus and damages brain function and is of particular concern because it biomagnifies up the food chain.

In pristine environments, atmospheric deposition is the primary cause of Hg contamination. While mercury-bearing soil is also an important source of Hg to surface waters and biota through erosion and transport to rivers, lakes, and oceans, it is less than direct atmospheric inputs. Mercury deposited in terrestrial and aqueous environments can generate the more toxic species: methylmercury. Methylmercury can damage the central nervous system, causing symptoms such as blindness, deafness, speech difficulties, and impaired consciousness. It is lipid soluble and readily concentrates in the aquatic food chains: more than 80 % of all fish advisories issued in 2010 in the USA (USEPA 2011a) were attributed to methylmercury. Understanding the environmental mercury cycle, from the soil-bound form to methylmercury in fish, is of great importance and is being studied intensively globally (Avramescu et al. 2011; Hu et al. 2013; Morel et al. 1998; Parks et al. 2013; Ullrich et al. 2001).

Mercury contamination is widespread in soils and sediments and challenging to remediate. In the USA, 290 Superfund sites have been identified with mercury pollution, of which 173 involve mercury-contaminated soils or sediments (USEPA 2007a). Subsurface sediments and soils contaminated with mercury present unique challenges for remediation, not only because Hg is often heterogeneously distributed in these environments, but also due to the variety of chemical forms in which mercury can occur. Additionally, the low concentrations required by regulatory bodies or risk assessments often limit the choice of technologies. Both in situ and ex situ remediation technologies have been used at the Superfund sites (USEPA 1997b, 2000b). Ex situ technologies involve excavation and removal of contaminated soils and this is treated or buried off-site, while in situ treatments remediate contaminants in place and/or on site. Although less extensively, in situ technologies are often the preferred treatment options because they are practical, more cost-effective, and less disruptive to on-site operations. They are also generally less intrusive to the environment and can minimize contaminant exposure (Cabrejo and Phillips 2010; Hinton and Veiga 2001; USEPA 1997b).

Mercury, like many other heavy metals, cannot be degraded in the environment, and therefore, remediation must involve either removal or immobilization (Ochoa-Loza et al. 2001; Wang et al. 2012). In situ removal technologies aim to separate Hg from the contaminated solids, while the immobilization technologies stabilize Hg in the subsurface (Hempel and Thöeming 1999). Removal techniques mainly include thermal treatment, electrochemical/electrokinetic recovery, soil flushing, and phytoextraction and phytovolatilization. Immobilization techniques include containment, solidification/stabilization, vitrification, phytostabilization, and nanotechnology applications. Each technology has advantages and disadvantages, which will be reviewed and discussed in the following sections. We note that many abovementioned processes have been reviewed by Wang et al. (2012). However, the focus of this review is the in situ remediation technologies, and extra attention was paid to the physical/chemical fundamentals of the remediation processes, effect of Hg speciation on the remediation performance, the transformation of Hg during different remediation processes, and the engineering implementation of these technologies.

Chemistry of mercury and implications for soil-sediment remediation

Mercury is present in the natural environment in various inorganic and organic forms, including elemental (Hg^0), mercurous (Hg_2^{2+}), mercuric (Hg^{2+}), and alkylated compounds (methylmercury, ethyl mercury, etc.). Each species has its unique chemical characteristics, environmental behavior, and biotoxicity (Fig. 1). Metallic mercury may maintain its elemental state in bead or globule forms for decades after accidental spills (Bloom et al. 1997). We have recently demonstrated that coatings of oxidized mercuric species develop on beads of mercury in the subsurface environment (to be published), which stabilizes the species below the coating layer. Many factors affect mercury speciation and environmental transformation, including soil pH, redox potentials, physicochemical properties of the media, microbial activity, and presence of other ionic species (Boszke et al. 2003; Cabrejo and Phillips 2010; He et al. 2012b; Ullrich et al. 2001).

Besides Hg^0, other common Hg species found in contaminated soil-sediment include HgS, $HgCl_2$, Hg_2Cl_2, HgO, CH_3HgCl, and CH_3HgOH (USEPA 2007a). These mercury species have quite different solubility properties, where mineral cinnabar (HgS) has a solubility of 4.65×10^{-25} g L^{-1} at 25 °C, meta-cinnabar has increased solubility (1.04×10^{-24} g L^{-1} at 25 °C), followed by Hg^0 and Hg_2Cl_2 with low solubility (5.6×10^{-5} and 2.0×10^{-3} g L^{-1} at 25 °C, respectively). Both HgO and $HgCl_2$ are relatively soluble in water, with solubilities of 0.051 g L^{-1} at 25 °C and 69 g L^{-1} at 20 °C, respectively (Aurivillius and von Heidenstam 1961; Myers 1986; USEPA 2007a) (Table 1). Mercuric and mercurous salts can adsorb strongly to soil particles, particularly clay minerals and iron oxides within neutral pH ranges (Boszke et al. 2003; Liu et al. 2012). Organic matter can also interact with most ionic mercury species and immobilize mercury by association with soil matrix in acidic soils (Liu et al. 2012).

Because of the complex chemistry of Hg, it is hard to obtain speciation information—especially in a soil matrix. Sequential extractions are used to provide data that differentiates Hg compounds into behavioral classes. For example, Bloom et al. (2003) proposed a method to divide Hg in soil into five fractions including (a) water soluble (fraction 1 or F1), (b) "human stomach acid" soluble (F2), (c) organo-chelated (F3), (d) elemental Hg (F4), and (e) mercuric sulfide (F5), which were extracted using deionized water, 0.1 M CH_3COOH+0.01 M HCl (pH 2), 1 M KOH, 12 M HNO_3, or aqua regia, respectively. Toxic characteristic leaching procedure (TCLP) employs a solution of 0.5 M sodium acetate and 0.5 M glacial acetic acid (pH of 4.9±0.1) to simulate leachability of solids within a moderately acidic environment typical of a municipal landfill (USEPA 1992), which is used by EPA to determine whether the material is hazardous. The leachable Hg from the TCLP procedure is called "bioaccessible" Hg and the regulated level is 0.2 mg L^{-1}. The soluble Hg from Bloom's method (determined as the sum of F1 and F2) corresponds favorably with TCLP results.

We note that there is no consensually agreed sequential extraction procedure for a Hg-contaminated soil. In addition to Bloom's method (Miller et al. 2013), there are other procedures used to determine the fractions of Hg in soil and how these fractions changed as a result of a remediative process. For example, many studies separate soil-bound Hg into six fractions: water soluble (extraction with deionized water), exchangeable (extraction with 1 M CH_3COONH_4), elemental mercury (by heating in an oven for 48 h at 373 K), fulvic and humic acids (extraction with 1 M KOH and acidification to pH 2), organic and sulfide (extraction with 0.1 M HNO_3

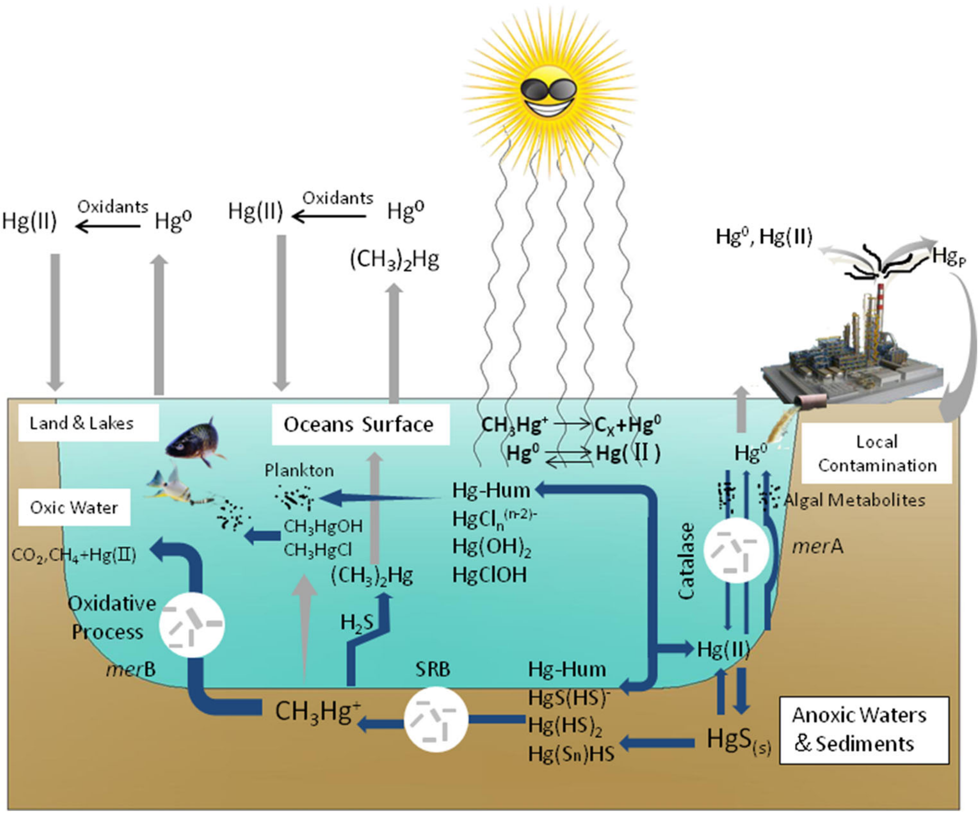

Fig. 1 Mercury biogeochemical cycle in the environment (adapted from Barkay et al. 2003)

and H_2O_2), and the residual (extraction with aqua regia) (Biester and Scholz 1997; Di Giulio and Ryan 1987; Kucharski et al. 2005). A sequential extraction procedure proposed by the Community Bureau of Reference (BCR) (Ure et al. 1993) was also adopted by researchers for Hg fractionation (Garcia-Rubio et al. 2011; Subires-Munoz et al. 2011). It differentiates four fractions: weak acid-soluble, reducible, oxidizable, and residual Hg. Acetic acid, hydroxylamine, and acid-stabilized hydrogen peroxide are the sequential extraction solutions for the first three fractions. The residual fraction is obtained by microwave-assisted acid digestion. The BCR is typically applied to soil with Hg concentration in tens of milligram per kilogram.

As a soft Lewis acid, mercuric Hg prefers to complex with soft ligands, such as sulfide, to form insoluble compounds (Devasena and Nambi 2013; Xiong et al. 2009b):

$$Hg^0 + S \rightarrow HgS \tag{1}$$

$$Hg^{2+} + H_2S \rightarrow HgS + 2H^+ \tag{2}$$

$$Hg^0 + Na_2S_5 \rightarrow HgS + Na_2S_4 \tag{3}$$

Table 1 Physical and chemical properties of some common mercury species (Aurivillius and von Heidenstam 1961; Myers 1986; USEPA 2007a)

Hg species	Hg valence	Molecular weight (g mol^{-1})	Density (g cm^{-3})	Solubility (g L^{-1})	Melting point (°C)	Boiling point (°C)
Hg^0	0	200.59	13.53 at 25 °C	5.6×10^{-5} at 25 °C	-39	357
Hg_2Cl_2	+1	472.09	7.15 at 19 °C	2.0×10^{-3} t 25 °C	302	384
$HgCl_2$	+2	271.52	5.40 at 25 °C	69 at 20 °C	277	302
HgO	+2	216.59	11.14 at 25 °C	0.051 at 25 °C	500	N/A
HgS	+2	232.66	8.17 at 25 °C	Red, 4.65×10^{-25} at 25 °C Black, 1.04×10^{-24} at 25 °C	583.5	N/A
CH_3HgCl	+2	251.08	4.06 at 20 °C	0.10 at 21 °C	170	N/A

N/A not available

$$\mathrm{FeS(s) + Hg^{2+} \rightarrow HgS(s) + Fe^{2+}} \quad (4)$$

$$\mathrm{FeS(s) + nHg^{2+} \rightarrow FeS{-}nHg^{2+}} \quad (5)$$

$$\mathrm{2\,FeS(s) + Hg^{0} + 4H^{+} \rightarrow HgS(s) + 2\,Fe^{2+} + H_2S + H_2} \quad (6)$$

These reactions are fundamental chemical principles that underpin the technologies to immobilize mercury in situ. As Hg also forms soluble species according to the following reactions (Cox et al. 1996; Reddy et al. 2003b):

$$\mathrm{HgS + I_2 + 2I^{-} \rightarrow HgI_4{}^{2-} + S} \quad (7)$$

$$\mathrm{Hg^{0} + I_2 + 2I^{-} \rightarrow HgI_4{}^{2-}} \quad (8)$$

$$\mathrm{HgO + 4I^{-} \rightarrow HgI_4{}^{2-} + O^{2-}} \quad (9)$$

Technologies involving mobilization of mercury species are based on forming soluble mercury complexes (e.g., $HgI_4{}^{2-}$). Depending on the remediation design, the chemical principles will be applied to transform insoluble mercury into more desired forms.

In situ mercury removal technologies

In situ thermal desorption

Thermal treatment of volatile contaminants involves heating to convert contaminants into the gaseous or vapor phase, which is then collected and further treated (USEPA 2007a). Elemental mercury is volatile and has a boiling point of 350 °C (662 °F) at 1 atm pressure, allowing it to be removed using thermal treatment (USEPA 2007a). Currently, most thermal treatment of mercury-contaminated soil occurs ex situ using thermal desorption in full-scale or pilot-scale applications. Heat and a reduced pressure volatilize mercury, which is subsequently condensed into liquid mercury (USEPA 2007a). However, ex situ thermal treatment requires soil excavation and transportation which adds significantly to the treatment costs directly and indirectly due to health and safety requirements. Soil excavation can be cost inhibitive, especially for deeper occurring mercury contamination.

To lower treatment cost, thermal treatment can also be applied simultaneously with soil vapor extraction (SVE) for subsurface soils, in which a vacuum is used to draw soil gas from the unsaturated zone and subsequently remove volatile contaminants such as Hg (Hinton and Veiga 2001; Vinegar and Stegemeier 1991). This process is called in situ thermal desorption (ISTD). During ISTD, heat is supplied to the subsurface by passing an electrical current through heating elements. There are two types of ISTD heating: thermal well and blanket heating. Thermal well heating is most common: a vertical array of heaters is placed inside wells drilled in the contaminated site (Fig. 2a). Blanket heating is less common and uses heaters installed horizontally to the surface of the remediation zone; it is only applicable to shallow contamination up to 3 ft below the surface.

For remediating mercury-contaminated soil, a specific ISTD process was developed (Vinegar and Stegemeier 2005). In this patented process, Hg desorption occurs via thermal conduction through the soil. The soil temperature can be increased to values of 600 °C. The ISTD is effective even with subsurface heterogeneities because thermal conductivity is not highly variable, only changing by a factor of approximately 4 from clay to sand (Kunkel et al. 2006). In an effort to evaluate the feasibility of using ISTD to remove elemental Hg from soils, Kunkel et al. (2006) used laboratory experimental apparatus (Fig. 2b), and they obtained >99.8 % elemental Hg removal from Ottawa sand exposed to a temperature ranging from 244 to 259 °C, well below mercury's boiling point. About 70 % of the mercury was collected in the condenser and tubing, while 30 % of the mercury was trapped in the off-gas treatment device.

It should be noted that the quick recovery of the elemental mercury in Kunkel et al. (2006) was obtained using Ottawa sand in the absence of water. In the field, the efficiency and effectiveness of thermal desorption of mercury from contaminated soils are influenced by many factors, including soil characteristics, organic matter and moisture contents, mercury concentration/speciation, and other operating conditions. Mercury in sandy soils is generally easier to treat than in finer silty and clay soils (Blanchard and Stamnes 1997), as greater interstitial spaces aid vapor movement. Organic matter and moisture in the soil can act as heat sinks and reduce treatment efficiency and increase energy consumption (Blanchard and Stamnes 1997). Longer treatment time and higher temperatures, along with reduced pressure, can usually improve mercury desorption (USEPA 2007a), but this increases the operational costs accordingly. It can also be expected that aged elemental mercury beads (coated with an oxide layer coating) may behave differently to freshly spiked mercury (as was used in this study).

One of the concerns with respect to the application of ISTD for vadose zone mercury removal is the high remediation cost associated with the high energy input. The soil temperature for mercury removal relies on the mercury redox states and physical forms present in the soil. Taube et al. (2008) performed soil heating equilibrium calculations using FactSage

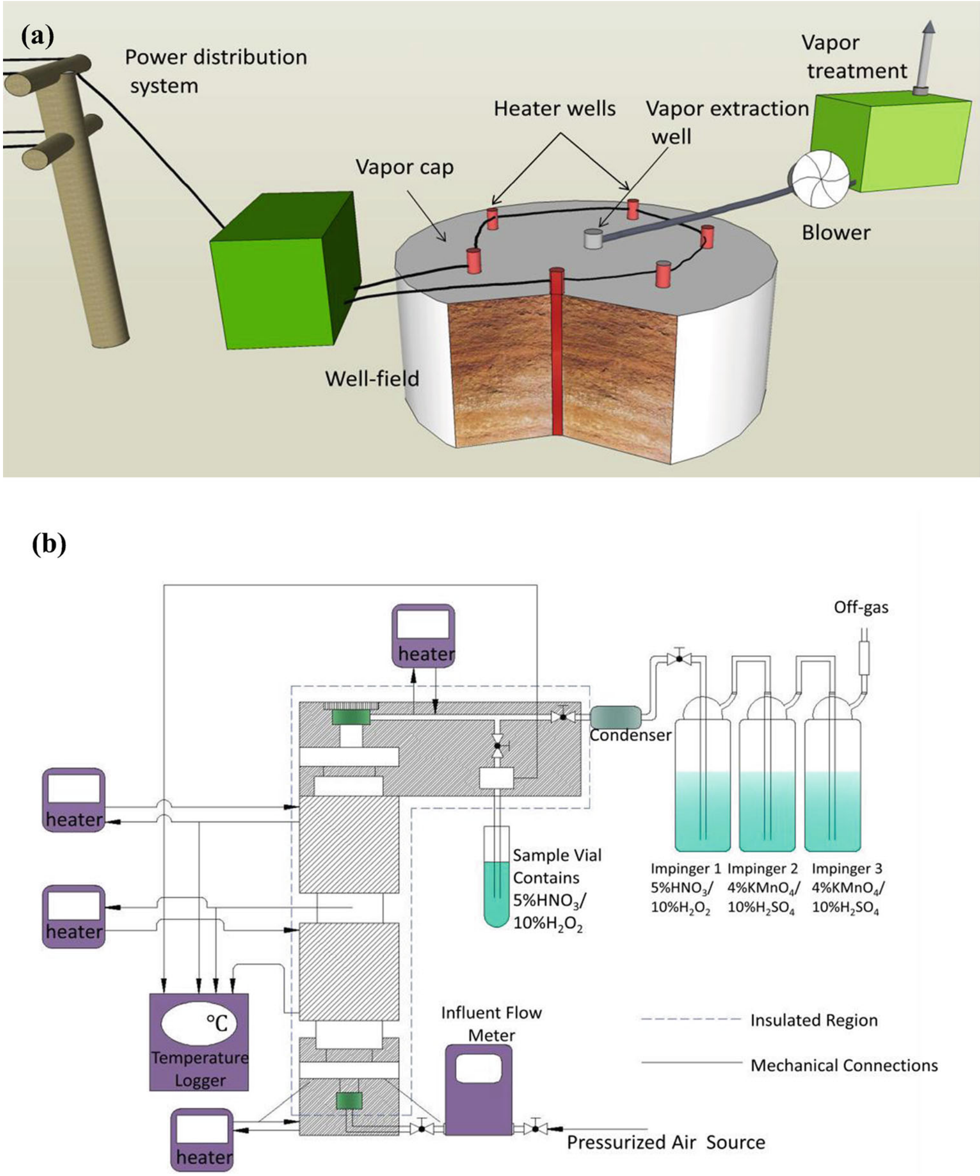

Fig. 2 **a** A typical ISTD system using thermal well heating. **b** A laboratory apparatus for studying thermal desorption of elemental mercury entrapped in sand column by Kunkel et al. (2006)

5.2, a software based on minimizing the Gibb's free energy of the system studied. The calculation results with conditions (in terms of oxygen, sulfur, and chlorine contents in the soil) are shown in Fig. 3. For example, in the presence of low levels of oxygen, the mercury species in the soil is predicted to be in the liquid, metallic form, $Hg^0(l)$, or in the solid form as HgS(s) at 20 °C. $Hg^0(g)$ would be released at 90 °C and 140 °C for $Hg^0(l)$ and HgS(s), respectively (Taube et al. 2008). The temperature at which the vaporized mercury is released from the original mercury compound follows the trend of $Hg^0(l) \approx HgCl_2 < HgS < HgO < HgSO_4$. We note that the calculated volatilization temperatures of different mercury compounds from Taube et al. (2008) are generally lower than those obtained from experiments, as shown in Table 2 (Biester and Scholz 1997; Navarro et al. 2009). Additionally, the vaporization of mercury compounds other than the gaseous Hg^0 requires much higher temperatures, which would require considerably more energy to remediate using this technology.

The thermal treatment of mercury-contaminated soil (as elemental Hg) from a former chlor-alkali plant obtained >90 % total mercury removal when soil temperature raised to 280 °C for 20 min and >99.5 % mercury removal when the treatment temperature was increased to 470 °C (Taube et al. 2008). The most significant removal below an operating temperature of 230 °C was attributed to the vaporization of relatively volatile Hg species such as Hg^0. Mercury in the pretreated samples was found to be concentrated in particles with sizes of 5–20 μm surrounded by a thin layer of much less volatile HgO/$HgSO_4$. This claim was corroborated using cross section analyses of the mercury particles mounted in epoxy, which observed greater concentrations of Hg inside the particles than on the surface. Upon heating, the Hg^0 vaporized,

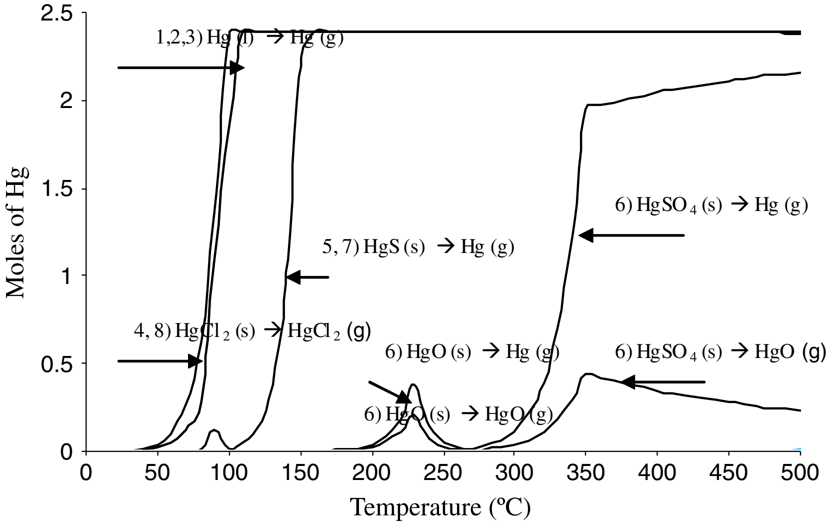

Fig. 3 Calculated temperatures for volatilization of different mercury species. The calculation numbers (*1–8*) in the *left figure* represent high (+) or low (−) availability of oxygen, chlorine, and sulfur used in the equilibrium calculations, which is listed at the *right side* (adapted from Taube et al. 2008)

lowering the Hg/S ratio (S from sulfate). The Hg^0 vaporization (up to 270 °C) was diffusion controlled rather than by the mercury speciation, indicating that the thin oxide layer covering Hg inhibited Hg^0 vaporization from the particle core. The analysis of the cooled mercury vapor deposit indicated that it was mainly composed of Hg^0 (90 %) and $HgCl_2$ (10 %), consistent with the results of heating equilibrium calculation where Hg^0 and $HgCl_2$ were the major vapor species (Fig. 3).

Kucharski et al. (2005) tested thermal desorption at laboratory and pilot scale using mercury-contaminated soils from a chlor-alkali production site in southern Poland, with an ultimate goal to apply this process in situ. In the laboratory experiment, soil temperature was raised from 40 to 60 °C, while in the pilot-scale experiment, soil was heated to a maximum average temperature of 167 °C. Concentrations of different mercury fractions in soil before and after 10 days of heating were summarized in Table 3. In both laboratory- and pilot-scale experiments, water-soluble, exchangeable, and elemental mercury fractions were reduced to undetectable levels, indicating that 100 °C is sufficient to effectively remove these three fractions. However, 100 °C was insufficient to vaporize mercury bound to fulvic/humic acid fractions or organic and sulfide fractions. A higher temperature of 167 °C removed fulvic/humic acids and organic and sulfide fractions by approximately 83 and 73 %, respectively. Even at this temperature, a recalcitrant mercury fraction remained. Overall, total mercury concentration decreased by 32 % in a laboratory experiment and by 67 % in a pilot-scale experiment. Worth noting was that satisfactory growth of Indian mustard (*Brassica juncea*) plant and tufted grass (*Deschampsia caespitosa*) was observed in the treated soil.

Inhaling of mercury vapor is an important health and safety issue when implementing in situ thermal desorption of mercury. A ground cover can be used to prevent the release of vapor into the air and enhance mercury recovery. The ground cover can also prevent moisture from infiltrating the treatment area. In addition to the health and safety concerns, pyrolysis of organic matter during heat treatment may cause explosions and damage the equipment (USEPA 2007a), and application of a high temperature may impact ecological health at the

Table 2 Desorption temperatures of different mercury phases (Navarro et al. 2009)

Phase	Desorption temperature of phase Hg (°C)
Hg^0	<100
Hg_2Cl_2	170
$HgCl_2$	<250, 220
HgO	420–550
$HgSO_4$	450–500
HgS (cinnabar)	310–330
Hg in pyrite	>450
Hg in sphalerite	600
Hg matrix bound	200–300

Table 3 Concentrations of mercury fractions in soil (mg kg^{-1} dw) from laboratory- and pilot-scale experiments (Kucharski et al. 2005)

Mercury fraction	Avg Hg conc before heating	Avg Hg conc after heating in lab exp	Avg Hg conc after heating in pilot exp
Water soluble	18.7	n.d.	n.d.
Exchangeable	221.9	n.d.	n.d.
Elemental	307.8	n.d.	n.d.
Fulvic/humic acids	169.6	165.9	28.8
Organic and sulfide	616.5	621.4	164.9
Residual	383.8	391.5	377.4
Total	1749.5	1187.0	586.9

n.d. not detected, <0.05 mg kg^{-1}

treated site (Kucharski et al. 2005). Nevertheless, ISTD provides a way to permanently recover mercury from the subsurface, albeit at a high cost (Table 5).

Electrokinetic techniques

Electrokinetic applications use a low intensity direct current between a cathode and an anode imbedded in the contaminated soil (Mulligan et al. 2001a, b; USAEC 2000; USEPA 1997a; Virkutyte et al. 2002) to facilitate the movements of ions, charged small particles, and water. Anions move toward the positively charged electrode (anode) and cations move toward the negatively charged electrode (cathode). For Hg^{2+}, the cathode can be made of iron or aluminum and the anode of carbon, titanium, or steel (Cabrejo and Phillips 2010; Doering and Doering 2006). Electrokinetic technology generally involves four processes: electromigration (transport of charged chemical species in the pore fluid), electroosmosis (transport of pore fluid), electrophoresis (movement of charged particles), and electrolysis (chemical reaction associated with electric current). Electrokinetics can efficiently extract metals from contaminated soil. Its efficiency depends on many factors, including the type and concentration of the contaminants, soil properties, and the chemistry at various interfaces in the system. A typical in situ electrokinetic system for treating Hg-contaminated soil is illustrated in Fig. 4.

The efficiency of electrokinetic soil treatment is determined by several interacting mechanisms, including advection caused by electroosmosis and hydraulic gradient, electromigration, and diffusion of the acid front to the cathode. In soils with a net negative surface charge, electroosmotic flow of pore water moves from the anode to the cathode. The acid front is produced by electrolysis of water at the anode and migrates toward the cathode by diffusion, electroosmosis, and electromigration. A base front is generated at cathode in the same manner. However, H^+ ions migrate at twice the speed of OH^- ions, which can acidify the soil between the electrodes. The electrokinetic process heavily relies on acidification as this favors the solubilization of metal contaminants. However, this may be difficult to achieve if the soil buffering capacity is high or if acidification is not environmentally acceptable. In general, electrokinetics is time consuming and is mainly applied to saturated clay soils, where other technologies may not work.

Electrokinetic remediation of Hg-contaminated soils can be difficult because Hg has a low solubility in most natural soils (Cox et al. 1996). The predominant insoluble Hg species in soils include elemental mercury (Hg^0), HgS, and Hg_2Cl_2 (Cox et al. 1996). If elemental mercury is present in the soil, the high electrical conductivity of mercury (1×10^6 s m^{-1}) could inhibit the electrokinetic process by lessening the steady-state voltage gradient (Virkutyte et al. 2002). Treating a sandy soil containing 685 mg kg^{-1} total Hg from a former chlor-alkali plant with the electrokinetic process, Hansen et al. (1997)

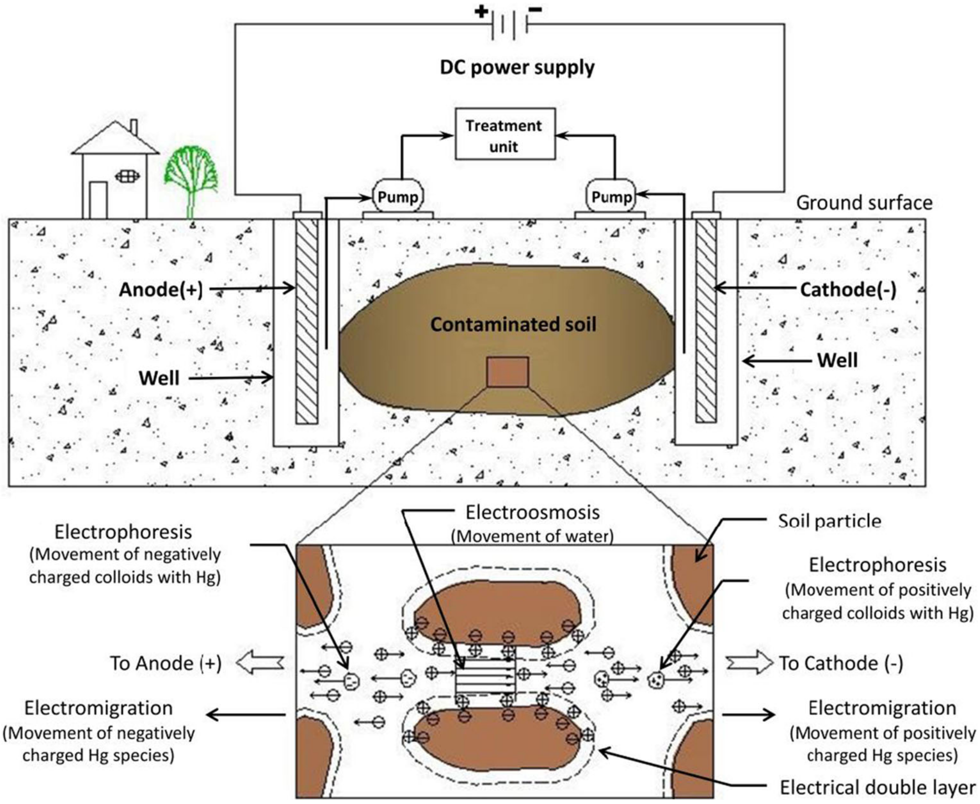

Fig. 4 Schematic of electrokinetic remediation of Hg-contaminated soils

found that although Hg had electromigrated toward the anode, the Hg removal rate was only 23 %. Introducing an I_2/I^- lixiviant solution to solubilize HgS has significantly enhanced soil remediation using electrokinetics (Cox et al. 1996). The S^{2-} in HgS is oxidized by I_2 and this releases Hg^{2+}, which is then complexed with I^- as HgI_4^{2-} (Reactions 6–8). HgI_4^{2-} ions are readily mobile through contaminated soil and removed at the anode.

Reddy et al. (2003a) have identified potassium iodide (KI) as the best mercury complexing agent among many others for $HgCl_2$ removal using electrokinetic methods. Using 0.1 M KI, they obtained ~97 % removal of spiked mercury (500 mg Hg^{2+} kg^{-1} soil) in laboratory electrokinetic experiments. This kaolin soil contained 78 % clay. The mercury removal was ~56 % for the glacial till soil that contained 36 % clay. The lower Hg removal from the glacial till soil was attributed to its higher organic matter content (2.8 %) than that in kaolin soil (~0 %). The authors further studied the effects of voltage gradients and KI concentrations on the Hg removal and found that increasing the voltage gradient from 1.0 to 1.5 VDC cm^{-1} and KI concentration from 0.1 to 0.5 M did not improve Hg removal from kaolin soil, but increased the Hg removal from the glacial till from 56 to 77 %.

Garcia-Rubio et al. (2011) observed that iodide-enhanced electrokinetic treatment of a soil from an Almaden (Spain) mining district with a high mercury concentration (1000 mg kg^{-1}) was as effective as batch extraction experiments using iodide. The Hg removal efficiency (30–35 %) was similar to the removal efficiency obtained using in situ flushing (Subires-Munoz et al. 2011). However, this electronkinetic removal was several orders of magnitude faster than flushing because of the low hydraulic conductivity ($K=2.1\times10^{-6}$ cm s^{-1}) of the soil. Although the iodide-enhanced electrokinetic treatment increased the weak acid-soluble Hg fraction from 3 to 15–30 % after treatment (which may increase the environmental risks as this fraction is most mobile), a large portion of this fraction can be effectively recovered by a subsequent acid-enhanced electrokinetic process. Worth noting is that Hg chemistry increases in complexity after the first electrokinetic treatment; the subsequent process requires careful design and operation.

In Denmark, electrokinetics was also evaluated for the removal of nonionic mercury (Hg^0) from a sandy soil (Thoming et al. 2000) contaminated by a spill accident at an industrial site. The total Hg concentration was 1200–1900 mg kg^{-1}, of which 84 % was Hg^0. The ionic mercury species content increased during the electrokinetic treatment (and Hg^0 decreased), indicating the oxidation of Hg^0. The authors attributed this to acidification increasing the oxidation rate of Hg^0. However, the net change of mercury in the soil was negligible and no mercury was transported out from the soil into the electrode compartments—most likely because Hg^0 was transformed into an insoluble species. Based on thermodynamic calculation, the authors further noted that the addition of chloride could drastically improve Hg solubility and thus improve its migration.

Soil organic matter significantly impacts the efficiency of enhanced electrokinetic Hg removal. Cox et al. (1996) observed that electrokinetic treatment of a field soil containing 11 % organic matter was much slower than treating a laboratory prepared soil containing 4 % organic matter. When iodine was added, up to 99 % of the mercury in the laboratory-prepared soil was removed, while only 6 % of the Hg was removed from the field soil. In addition to organic matter content, the Hg speciation also needs to be considered. In this case, the field soil contained HgS as the major mercury species. The authors argued that a drastic change of the soil chemistry would be required to mobilize the sequestered Hg (i.e., HgS). Therefore, insoluble Hg species such as HgS may pose little risk to humans.

To improve the removal of tightly bounded Hg from field soil, Shen et al. (2009) proposed a modified electrokinetic technique of "approaching cathodes" with I_2/I^- lixiviant. The technique was accomplished by embedding multiple cathodes in the soil bed at varying distances from the anode. The cathodes work in turn from the furthest position (with respect to anode) and the intensity of the electric field is kept same. The researchers demonstrated the technique with contaminated rice paddy soils containing 576.7 and 491.4 mg kg^{-1} Hg. The electrokinetic treatment with approaching cathodes was able to remove 89 to 92 % Hg, which was a 1.21 to 1.68 improvement of Hg removal compared to the single cathode technique. A distinct advantage was that the technique used 26.4 to 28.1 % less electricity than the single cathode technique.

In addition to iodine-enhanced electrokinetics, a series of electrochemical remediation technologies (ECRTs) that utilized redox reactions was invented by Doering and subsequently patented in the USA and Europe (Doering and Doering 2006; Doring and Doring 1997). During ECRTs, a proprietary AC/DC electrical signal is passed through the soil via paired electrodes; this generates a secondary polarization field within the soil that opposes the primary inducing field. This secondary polarization field allows the soil particles to act as capacitors that charge and discharge electricity at a very high frequency, resulting in the electrolysis of water which generates free radicals that perform redox reactions (Burks 2002). In particular, ECRTs-induced complexation (ECRTs-IC) mobilizes and transports metal complexes to the electrodes which are later removed from the soil (BNL 2002; Doering et al. 2001; Gardner 2005; USEPA 2007b). In this manner, water-insoluble HgS can be transformed into Hg^0, which in turn can be oxidized to Hg^{2+} (Doering and Doering 2006). In a high chloride environmental (brackish or sea water), chlorocomplex ions such as $HgCl_3^-$ or $HgCl_4^{2-}$ can be formed and deposited onto the anode (Doering and Doering 2006). However, organic materials or other ions may hamper this process (e.g., iron) (Burks 2002). In addition, redox reactions may also influence other equilibria, thereby changing the biogeochemistry of the treated site.

ECRTs are suitable for all soil types, and because the reaction rates are inversely proportional to grain size, ECRTs work faster in clay or silt than in sand or gravel (Doering et al. 2001). ECRTs have been successfully applied in Europe. An example is the treatment of elemental and methylmercury-contaminated sediments in the Union Canal in Scotland, where ECRTs-IC lowered mercury levels from 243 to 6 mg kg^{-1} (the cleanup objective was 20 mg kg^{-1}) within 26 days of operation (Doering et al. 2001). In the USA, ECRTs have been tested in bench scale for removing Hg from DOE's Y-12 National Security Complex (Y-12) soil. Although less effective in the field, ECRTs-IC removed 55 % of Hg after 741 h of operation, an improvement compared to the 35 % Hg removal obtained using conventional electrokinetic technology (Burks 2002). Field trials are not always successful though. An ECRT field trial conducted at the Georgia Pacific, Inc. (G-P) Log Pond located in Washington demonstrated no significant reduction in total mercury concentration. This failure could be attributable to operational problems associated with maintaining electrical connectivity (USEPA 2007b).

In summary, electrokinetic remediation technologies are suitable for clay and silty soils, applicable to various mercury complexes, and can simultaneously remove other heavy metals. Other advantages include no excavating, minimal disturbance to the contaminated site, and lower cost than other technologies like ISTD (Burks 2002; Cabrejo and Phillips 2010). However, release of gaseous mercury vapor, mercury waste disposal, and mobilization of insoluble and sequestered mercury compounds are some of the disadvantages associated with this technology (BNL 2002; Cabrejo and Phillips 2010).

In situ soil flushing/washing

In situ soil flushing involves extraction of contaminants from soil using an appropriate washing solution, such as water, containing chemicals, or an organic extractant (USEPA 1997b). The washing solution is injected into, or sprayed onto, the contaminated soil so that the contaminants are mobilized by solubilization, emulsification, or chemical reactions. The latter occurs as a result of soil pH adjustment, chelation of metal contaminants, or displacement of toxic cations with nontoxic ones (USEPA 1997a, b). The mobilized contaminants are then recovered at the surface from the underlying groundwater by "pump-and-treat" methods for contaminant removal and/or recirculation (USEPA 1997a). The process is depicted in Fig. 5 (USEPA 1997a).

Although water alone can be used as the washing solution, chemicals are often added to improve metal removal efficiency, particularly for Hg as it strongly adsorbs to soils and/or is present in insoluble complexes (e.g., HgS). Examples of chemical additives used in soil flushing include organic or inorganic acids (e.g., citric acid, tartaric acid, hydrochloric acid) and bases (e.g., sodium hydroxide), water-soluble organic solvents (e.g., methanol), complexing agents (e.g., EDTA, iodide), or combinations thereof (Mulligan et al. 2001a; Wasay et al. 1995, 2001). In addition to aqueous solutions, the use of supercritical fluids (e.g., CO_2) has been proposed and investigated for mercury extraction from soils. This requires Hg to be strongly chelated to a ligand that is soluble in the supercritical fluid, and the neutral complex formed must be soluble in the medium (Ashraf-Khorassani and Taylor 1999). In theory, methyl, phenyl, and inorganic mercury could be extracted sequentially (Foy and Pacey 2003) by varying the pressure, water, methanol, and chelator, but the cost of this technology prohibits its use at scale.

Various factors affect the mobility and migration of metal contaminants with subsurface flushing; these include the solution's leaching characteristics, soil permeability, and contaminant concentration (Truex et al. 2010; USEPA 1997a). The use of acidic washing solutions decreases soil pH and, thus, increases solubility and mobility of metal ions. Chemical additives used in the flushing solution also impact mercury removal. For example, Wasay et al. (1995) compared mercury extraction effectiveness by several solutions (including water, Na-EDTA, and KI solutions with varying pH) for a contaminated soil collected from an industrial site. An acidic KI solution with $pH<2$ was most effective; 15 pore volumes of solution removed 76 % of total Hg by forming stable HgI_4^{2-} compounds. In a more comprehensive study, Chen et al. (1995) evaluated 190 ligands for their abilities to extract and recover various heavy metals such as Cu, Pb, Cd, Zn, Ni, and Hg. They identified S-carboxymethyl-cysteine (SCMC), N-2-acetamidoiminodiacetic acid (ADA), and pyridine-2,6-dicarboxylic acid (PDA) as the three most suitable chelators for Hg. Soils and sediments with finer particles and higher organic matter content generally retained more heavy metals as hydraulic flow was less efficient. Generally, soil flushing is more suited to soils with greater permeability (hydraulic conductivity$>1.0\times10^{-3}$ cm s^{-1}), such as sandy or silty soils (Khan et al. 2004). Subires-Munoz et al. (2011) found that flushing of a soil from an Almaden (Spain) mining district with high mercury concentration (1000 mg kg^{-1}) could achieve 35 % Hg removal, which was as good as electrokinetic remediation (Garcia-Rubio et al. 2011). However, the time required to achieve this efficiency would be several orders of magnitude longer because the soil had a very low permeability ($K=2.1\times10^{-6}$ cm s^{-1}).

Recovered groundwater and washing solutions require treatment prior to be recycled or discharged to wastewater treatment plants. Removal of the metal contaminants in the treatment system may include precipitation, electrochemical exchange, ion exchange, adsorption (activated carbon), ultrafiltration, or reverse osmosis (He et al. 2010; Mulligan et al. 2001a; USEPA 1997a).

In situ soil flushing/washing technology can remove contaminants from the soil with the removal efficiencies as high as 90 % (Hinton and Veiga 2001; USEPA 1997a). This technology does not require excavation, treatment, and disposal of soil wastes—which decreases associated expenses and hazards (Khan et al. 2004). Moreover, this technology uses

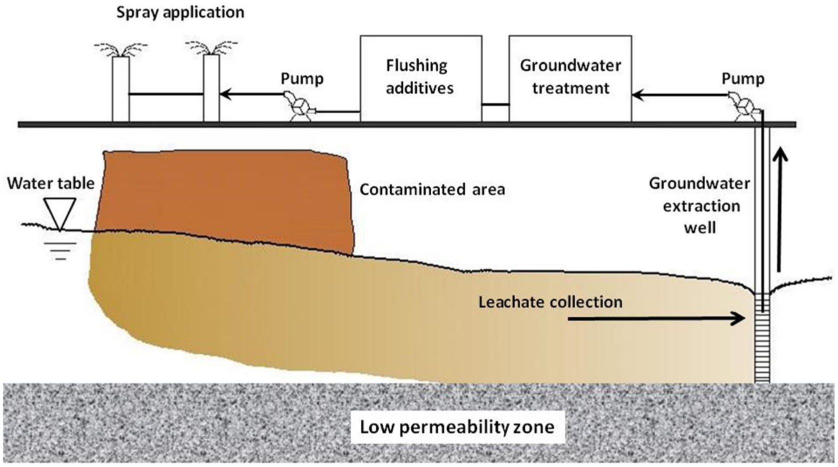

Fig. 5 A typical soil flushing system

equipment that is easy to construct and operate and allows for metal recovery (at a cost) from the flush solution (USEPA 1997b). It can be coupled with other in situ technologies such as electrokinetics (Reddy et al. 2010) to further enhance removal efficiencies. However, flushing an underlying aquifer with chemical solutions that contains solubilized contaminants has inherent risks and is often unacceptable to regulators and the public (Hinton and Veiga 2001; USEPA 1997a). To minimize such risks, the hydrogeology of the treated site must be well understood (USEPA 1997a). Lateral water flow resulting from low permeability silt zones could increase the size of the capture zone in the groundwater, cause water to bypass contaminants, and require more time and total water volume for soil flushing (Truex et al. 2010). Furthermore, the technology is relatively intrusive to the remediation areas (compared to technologies such as phytoremediation) and is yet to be demonstrated with convincing success in the field (Hinton and Veiga 2001; Kaplan et al. 2002).

Immobilization technologies

Although removal of contaminants from the site is highly desirable, it is often not feasible due to technical, environmental, geographical, social, or financial constraints (Hempel and Thöeming 1999). An example of this is deep zone mercury contamination, which is very difficult and uneconomical to remove. In such cases, immobilization technologies that isolate, solidify, and stabilize Hg in the contaminated soil are preferred in order to reduce ecological and human health risks from exposure (Hinton and Veiga 2001).

Containment

In this technique, the contaminated soils are isolated and contained by low permeability ($<1\times10^{-7}$ m s^{-1}) physical barriers, such as caps, slurry walls, grout curtains, or cutoff walls, installed around the impacted area to prevent or reduce the migration of mercury in the soil (Khan et al. 2004; Mulligan et al. 2001b). These physical barriers can be used for capping, vertical containment, or horizontal containment (Mulligan et al. 2001a).

Capping is achieved by sealing the contaminated site with a surface layer that prevents rainwater infiltration as well as gas and dust emissions (Hempel and Thöeming 1999). The capping system can also improve esthetics and provide a stable surface over the waste (USEPA 1997b). The sealing layer can be made of compacted clays, natural soils mixed with stabilizers or bentonite, or geosynthetic membranes with a low permeability (Hinton and Veiga 2001).

Vertical and horizontal barriers reduce the lateral and vertical migration of contaminants, respectively. Commonly used vertical barriers are slurry walls, grout or geomembrane curtains, and sheet pile walls (Mulligan et al. 2001a). Slurry walls are the most commonly used as they are the most cost-effective. To minimize the movement of contaminants through the barriers, vertical barriers are usually constructed to a depth that makes contact with an impermeable clay or bedrock as a horizontal barrier (Mulligan et al. 2001a). If the bottom barrier is not present or cannot be implemented, a hydraulic containment approach is employed by extracting the groundwater below the contaminated site using a pump-and-treat mechanism. While vertical barrier technology has been well developed and demonstrated, in situ horizontal barriers are challenging and still under development. A detailed description and discussion of containment using caps and vertical and horizontal barriers is provided in a 1997 EPA report (USEPA 1997b).

In the case of mercury containment, an impermeable base and cover consisting of two layers of asphalt concrete and a layer of sulfur have been used (Hempel and Thöeming 1999). Sediment caps composed of sandy or clay materials have also been studied over contaminated sediments for reducing the transport of mercury from the sediments to the overlying water (Reible et al. 2010; Wang et al. 2004). Advantages of the containment technology include:

- Low cost as it does not require excavation and disposal of hazardous waste.
- It can be applied with other technologies to enhance Hg remediation effectiveness.
- It protects the underlying groundwater or overlying water from being contaminated.

The disadvantages are:

- Contaminants are left as is on site.
- The containment site requires long-term sampling and monitoring (Johnson et al. 2010; Mailman et al. 2006; USEPA 1997b).

Solidification/stabilization

Solidification and stabilization technologies decrease the mobility and/or leachability of contaminants in soils. Solidification involves physical encapsulation of contaminated soils (for example using cement) to reduce the permeability and thereby the leachability of the contaminant. Stabilization involves chemical complexation to decrease solubility so as to minimize distribution and exposure of the contaminant (Mulligan et al. 2001a; Truex et al. 2007; USEPA 1997a, b). For ex situ treatment, solidification and stabilization technologies apply to Hg at <260 mg kg^{-1}, while thermal technologies apply to Hg at >260 mg kg^{-1}. While no regulation exists for in situ treatment, ex situ treatment using solidification/stabilization must achieve <0.2 mg Hg L^{-1} using TCLP.

Chemical stabilization approach makes use of sulfur-containing reagents such as elemental sulfur, thiosulfate, or pyrite (FeS_2) that is allowed to react with elemental mercury (Hg^0) in contaminated soil to form HgS (Reaction 1) (Hagemann 2009). Sulfide-containing reagents, such as H_2S and Na_2S, can also react with oxidized Hg^{2+} to form mercury sulfide (Reaction 2) (Hagemann 2009). HgS is a stable and insoluble compound with a solubility product of 2.0×10^{-49} in water (Wagh et al. 2000) and Hg can be considered immobilized when complexed with sulfide. Piao and Bishop (2006) studied the effectiveness of mercury stabilization with sodium sulfide using a laboratory-simulated mercury surrogate (sand spiked with mercuric nitrate) and a real mercury waste from contaminated sediment at a Superfund site. Both contained >260 mg kg^{-1} total mercury. They found that at a S/Hg molar ratio of 1, pH 6 was optimal for stabilization as the complexing efficiency attained 99 %. Anions such as Cl^-, CO_3^{2-}, and PO_4^{3-} could interfere with the reaction, but increasing the S to Hg molar ratio helped overcome this problem. Even at higher pH values (pH>10), mercury stabilization efficiency remained at approximately 98 %, indicating that sulfide-based solidification/stabilization is a very effective technique. In a field study at a chemical facility in southern Poland, addition of granular sulfur in situ lowered water-soluble Hg by nearly 65 % and exchangeable Hg by nearly 44 % (USDOE 2002). A recent study using micromodel experiments showed that elemental mercury entrapped in glass beads can be stabilized in situ by sodium polysulfide (Devasena and Nambi 2013). Over a 10-day period, 10 % of entrapped mercury was converted into HgS (Reaction 3) and 0.1 % was removed as dissolved mercury. The leaching of mercury after 10 days was minimal (<0.44 μg L^{-1}), which indicated that the remaining 90 % mercury retained in the porous media was encapsulated by the newly formed HgS.

During in situ solidification/stabilization processes, augers and digging tools are used to mix the reagents and soils (Hinton and Veiga 2001). Unfortunately, conventional equipment is only useful for shallow surface applications and may be restricted when there are clays or large rocks present (Mulligan et al. 2001a). For deep sediment mercury contamination, cement deep soil mixing (CDSM) technology may be applied. CDSM was originally developed in Japan and has gradually gained acceptance in the USA (Barron et al. 2006). A cement slurry is mixed with soil or sediment in situ using powerful augers. Depending on the design, soil-cement walls or grids or blocks consisting of multiple overlapping soil-cement columns are produced (Fig. 6) (Maher et al. 2005). In situ solidification/stabilization processes are usually preferred compared to ex situ applications because they require less labor and energy and avoid waste transportation and associated issues. We note that the extensive experience gained from widely applied ex situ solidification/stabilization of Hg-contaminated soil and wastes can be borrowed for in situ applications.

Binders used to encapsulate mercury in soils include bitumen, cement, fly ash, gypsum, magnesium hydroxide (Dolomatrix), organic polymers, and pozzolans (Hagemann 2009; Mulligan et al. 2001a). Among them, cement is the most commonly used binder (USEPA 2000b). Specialty cements are produced by various vendors, including HeidelbergCement (Depocrete^{TM}), Silicate Technology Corporation (SOILSORB^{TM}), and Waste Services NSW (EcoFix^{TM}) (Hagemann 2009). Reagents for immobilizing mercury by forming adsorbed species or insoluble mercury precipitates include chemical additives, such as calcium polysulfide, sodium dithiocarbamate, sodium metasilicate, sodium sulfide, and sulfur polymer cement (SPC) (USEPA 1997b, 2007a). The mobility of the final stabilized product containing mercury is influenced by many environmental parameters, especially pH. For example, when sulfide is used to immobilize mercury wastes, a low pH tends to increase the leachability of mercury in the soil in the form of Hg^{2+}. A higher pH can also result in more soluble mercury species such as mercurous

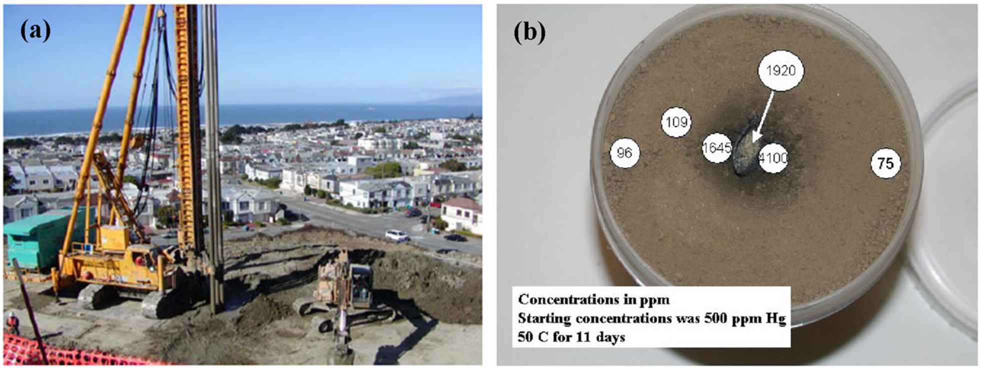

Fig. 6 **a** CDSM equipment at Sunset Reservoir, San Francisco (Barron et al. 2006). **b** Distribution of Hg in treated soil showing the effect of an ISMS treatment rod (Fuhrmann et al. 2004)

sulfate (Hg_2SO_4), mercuric sulfate ($HgSO_4$), and mercury sulfide hydrogen sulfide complex ($HgS[H_2S]_2$) (Randall and Chattopadhyay 2004). Therefore, in the solidification/stabilization process, pH adjustment needs to be considered to minimize the pH effects. Conventional cement-based solidification/stabilization technologies do not work well for immobilizing mercury as Hg does not form a low solubility hydroxide precipitate (Randall and Chattopadhyay 2004). In addition, Hg tends to hydrolyze to form mercuric oxide and remains volatile in this form (Zhang et al. 2009). As a result, chemical reagents and physical binders are usually used together to enhance mercury immobilization. Some reagents, like SPC and chemically bonded phosphate ceramics (CBPCs), can be used for both chemical stabilization and physical encapsulation (Randall and Chattopadhyay 2004).

During ex situ treatment, mercury vapor was rapidly released into the headspace when oxide or elemental mercury species were solidified in Portland cement, whereas no detectable mercury was released when stabilized with sulfide (Mattus 2003). Pretreating soil with a stabilizing agent such as sulfur or FeS can significantly reduce mercury vapor release (Svensson and Allard 2008).

Sulfur polymer stabilization/solidification technology (SPSS) is a promising technology based on SPC (Vroom 1977), which is a thermoplastic material that is commercially available under several trade names. Johnson et al. (1994) reported encapsulating solid mercury waste using a liquid polysulfide polymer and an oxidative curing agent (e.g., MnO_2). The solid waste was immersed in the liquid polysulfide and the oxidative curing agent cross-linked and hardened the polysulfide polymer to generate a solid encapsulation product. Kalb et al. (2002) and Fuhrmann et al. (2002) treated mercury-containing waste using SPC in two steps: (a) stabilizing the waste with SPC in an inert atmosphere to form a chemically stabilized mixture and (b) heating the mixture to form a molten product that was cast to obtain a monolithic final waste form. In a recent study, Lopez-Delgado et al. (2012) achieved microencapsulation of liquid mercury from the chlor-alkali industry using SPSS. Commercial gravel (<6.3 mm) and siliceous sand (<4 mm) were used as an inert aggregate and $CaCO_3$ (<0.125 mm) was used as filler. A sulfur-containing polymer (STX™ supplied by Starcrete™ Technologies Inc., Quebec, Canada) was used as thermoplastic material (i.e., SPC). The liquid mercury was first ball milled with sulfur powder at 400 rpm for 60 min to transform it to HgS. This HgS was mixed with the inert material, filler, SPC, and sulfur powder, heated to 145 °C while stirred for 30 min. The mixture was poured into stainless steel molds, which solidified into blocks after cooling. The blocks contained up to 30 % Hg and exhibited excellent mechanical properties, very low total pore volume, and extremely low permeability. TCLP results revealed that the mercury concentration in leachates was well below 0.2 mg L^{-1} stipulated in US EPA land disposal restrictions (LDRs).

Phosphate can form insoluble compounds with mercury, such as $Hg_3(PO_4)_2$. Alternatively, phosphate-based ceramics can be used to encapsulate Hg, such as the CBPC technology, patented by DOE's Argonne National Laboratory (ANL). During the remediation, sufficient water is added to the waste, followed by ground magnesium oxide and monopotassium phosphate at a 1:1 molar ratio. The final product, magnesium potassium phosphate hydrate (MKP), $MgKPO_4 \cdot 6H_2O$, is a hard, dense, and insoluble ceramic, which can encapsulate mercury in its crystalline matrix (Chattopadhyay 2003). Other reagents, such as fly ash or K_2S, may be included as binding agents. The reaction takes place spontaneously at room temperature and requires no additional energy. Furthermore, the materials needed for this technology are commercially available and relatively cheap (Chattopadhyay 2003). A more recent study (Randall and Chattopadhyay 2010) evaluated the stabilization of Hg and mercuric chloride-containing surrogate test materials using CBPC. The leachability of Hg decreased by approximately two orders of magnitude and up to a maximum of five orders of magnitude during TCLP tests. Satisfactory results within LDR requirements (<0.2 mg L^{-1}) were achieved for leachates from stabilized wastes containing <50 wt% loading of elemental Hg and $HgCl_2$. Although successful results have been demonstrated for ex situ CBPC applications, this technology has not been applied in situ.

Beside chemical reagents, adsorbents have also been used to stabilize/solidify Hg-laden wastes during some ex situ applications. In these cases, instead of forming stable sulfide or phosphate complexes, Hg strongly complexes with an adsorbent (Bessinger and Marks 2010). Bessinger and Marks (2010) evaluated the adsorbance of activated carbon (granular, fine, and powdered) in batch experiments. Powdered activated carbon (PAC) was the most effective for treating soils from a historical industrial facility with total Hg concentrations ranging from 0.46 to >270 mg kg^{-1}. The mercury was predominantly HgS (up to 60 mg kg^{-1}) with minimal elemental mercury and low levels of methylmercury. Applying PAC at 5 % decreased the mercury in the leachate to below the regulatory threshold concentration of 0.25 μg L^{-1}. Based on geochemical modeling, the authors speculated that PAC lowered dissolved mercury concentrations by forming stable mercury surface complexes and/or by adsorbing dissolved organic matter that would otherwise solubilize mercury. In another study, mercury stabilization/solidification with reactivated PAC and Portland cement was investigated (Zhang and Bishop 2002). Here, sand spiked with mercury nitrate was allowed to adsorb to reactivated PAC, which was followed by adding cement to solidify the waste and form a barrier enclosing the PAC particles—thereby reducing interference from other anions. Pretreatment of PAC with CS_2 further enhanced Hg adsorption onto PAC, possibly by forming HgS over the Hg adsorbed to the PAC surface.

Similar to PAC, functionalized zeolitic material has been tested along with Portland cement for stabilization/solidification of mercury waste prepared with mercury nitrate and sand (Zhang et al. 2009). The zeolitic material was functionalized by adding thiol groups using 3-mercaptopropyltriethoxysilane. The mercury adsorption capacity of zeolite increased by >10-fold (from 0.041 to 0.445 mmol Hg g^{-1}) in aqueous batch tests—illustrating the strong affinity of mercury for thiol groups. The final product after cement solidification showed an efficiency of 99 % efficiency. He et al. (2012a) also compared Hg removal efficiencies of thiol-functionalized Zn-doped biomagnetite particles to other commercial sorbents; they observed the greatest Hg sorption with the functionalized particles.

Zhuang et al. (2003) immobilized mercury in a contaminated soil using ferric sludge from a groundwater treatment plant. Mercury was effectively adsorbed to the ferric sludge and remained stable over 60 days, with low TCLP leachability. Similarly, mercury has been immobilized using a waste material known as aluminum drinking water treatment residuals (Al-WTRs) (Hovsepyan and Bonzongo 2009). The Al-WTRs displayed a maximum Hg adsorption capacity of 79 mg g^{-1} and the adsorption was stable over a pH range of 3 to 8. Although the experiments were conducted in aqueous solutions, the authors were confident that Al-WTRs could be used as a sorbent for soil remediation.

Fuhrmann et al. (2010) invented a novel in situ mercury stabilization (ISMS) treatment technology that differed from the traditional stabilization/solidification processes. This technology consists of treatment rods containing sulfur reagents that are inserted into contaminated soil, and Hg migrates and reacts with the reagent to form insoluble and chemically stable HgS near the rods (Fig. 6b) (Fuhrmann et al. 2004). As migration is driven by the vapor pressure of mercury in the gaseous phase, this technology is suitable for treating elemental mercury. After mercury stabilization, the treatment rods can be encapsulated and disposed of in landfills (Fuhrmann et al. 2010). The sulfur reagent can be elemental sulfur, sodium sulfide, sulfur polymer cement, and/or any other suitable sulfur species that can form a stable mercury sulfide compound. The researchers suggested that migration of mercury to the treatment rods can be expedited by heating or evacuating the soil (Fuhrmann et al. 2010). Successful bench-scale studies using this technology have been achieved, showing that ISMS can be effective in concentrating and extracting Hg in surrogate sandy soils spiked with elemental mercury (Fuhrmann et al. 2004; Kalb and Milian 2008). However, as this process is diffusion controlled, it may take an extended period of time to achieve remediation targets.

In summary, solidification and stabilization technology is (1) commercially available, (2) acceptable to US regulatory agencies because no transportation of wastes is required, and (3) effective in immobilizing contaminants and meeting regulatory cleanup levels (Mulligan et al. 2001a; USEPA 2007a). However, it is also a technology that may (1) increase the volume of contaminated area, (2) pose risks longer term, and (3) introduce chemicals that can be a problem themselves (USEPA 1997b, 2007a).

Vitrification

During in situ vitrification processes, contaminated soils are heated to melting point and cooled to form a solidified, chemically inert, vitreous mass wherein the contaminants are immobilized (Mulligan et al. 2001a; USEPA 1997b). Vitrification uses thermal energy to entrap contaminants. Broadly speaking, it is therefore a solidification/stabilization technology.

Successful vitrification requires sufficient glass-forming materials (SiO_2) (>30 wt%) and combined alkali (Na+K) (>1.4 wt%) in the soil (USEPA 1997b). Vitrification can be used for mixed contamination and used in combination with other solidification/stabilization technologies. It may be applied to soils containing organics as combustion of organic materials may reduce the energy requirement. As high concentrations of soil organic materials can generate large volumes of off-gas (and potentially gas emissions), this technology may not be applicable for soils with an organic content exceeding 7 to 10 wt% (USEPA 2007a). In addition, vitrification is affected by the soil's clay and moisture contents—similar to thermal desorption treatment. Soils exceeding a 25 % moisture content may require pretreatment (USEPA 1997b), chloride in the soil may enter off-gas and form solid chloride residues, and toxic compounds such as dioxins and furans may be produced in the off-gas during vitrification (USEPA 1997b). Due to high volatility and low glass solubility of mercury (<0.1 %), vitrification may be best suited to treating soils with low mercury concentrations (USEPA 1997b).

Many large-scale and pilot-scale sites contaminated with mercury have been treated using in situ vitrification (USEPA 1997b). At the Parson Chemical/ETM Enterprises Superfund site (Grand Ledge, MI, USA), the soil contained Hg (<34 mg kg^{-1}) and other organic and inorganic contaminants. Here, full-scale in situ vitrification commenced in May 1993 and continued until May 1994 (USEPA 1995). After vitrification, the surface soil mercury content was below 40 μg kg^{-1} (due to vaporization) and leachability was below 0.2–0.23 μg L^{-1}—which met the required standards.

Generally, in situ vitrification is applicable to treating large volumes of shallow soils (6–20 ft) (Mulligan et al. 2001a; USEPA 1997b). It does not require excavation and off-site treatment and may be applied to a mixture of contaminants. Also, vitrification decreases the volume of the contaminated site due to the removal of organic material. However, this technology is limited to soils contaminated with low concentrations of mercury, is energy intensive, and requires treatment of the off-gases (USEPA 2007a).

Other promising technologies

Phytoremediation

Phytoremediation makes use of plant growth to degrade or remove hazardous compounds from a contaminated area. Phytoremediation for metals is dependent on the microbial community interfacing the plant roots and surrounding soil. These microbes facilitate plant uptake and/or stabilization of the metals. The complex interactions among the roots, microbes, metals, and soils make phytoremediation relatively site specific. The four major types of phytoremediation are phytoextraction, phytostabilization, phytovolatilization, and phytodegradation (Fig. 7). Phytodegradation is only relevant to the breakdown of organic contaminants. *Phytoextraction* transfers and accumulates metal contaminants into harvestable plant biomass (shoots, leaves, etc.). *Phytostabilization* refers to the transformation or complexing of metal contaminants within the soil of the root zone (Mulligan et al. 2001a). *Phytovolatilization* involves transforming contaminants into volatile forms and transpiring them into the atmosphere. Further information regarding phytoremediation is available in excellent reviews (Baker et al. 2000; Henry 2000; Kramer 2005; Pulford and Watson 2003; Salt et al. 1995).

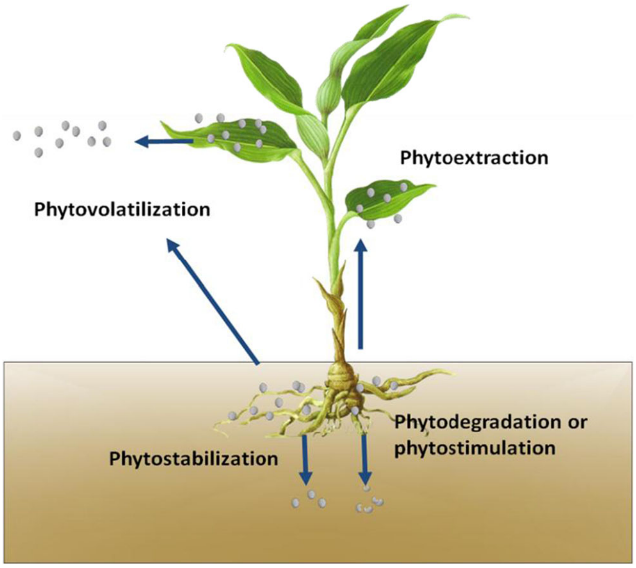

Fig. 7 Illustration of the four phytoremediation processes

The phytoextraction of Hg from contaminated soils and sediments is largely limited by its low bioavailability. This is because most Hg in soil is firmly bound to organic matter or sulfides, and usually only trace concentrations of Hg are found in the aqueous phase. A study on the changes of Hg fractionation in soil induced by willow found that only 0.2 % of total Hg in soil was accumulated in plants after 76 days of cultivation (Wang et al. 2005). The major Hg fractions (Hg bound to organic matter, sulfides, etc.) remained stable. Hg transfer to shoots only accounted for 3 % of the total Hg accumulated in the plants—the majority of the bioavailable Hg was in the root systems. Similar results were obtained using many other plants, including terrestrial plants such as garden pea, spring wheat, sugar beet, oil-seed rape, white clover, and willow (Greger et al. 2005); Indian mustard (Shiyab et al. 2009a, b); agricultural crop plants such as barley, yellow lupin, white lupin, lentil, and chickpea (Rodriguez et al. 2003, 2007); red fescue, meadow grass, horseradish, and Jerusalem sunflower (Sas-Nowosielska et al. 2008), as well as Chinese brake fern (*Pteris vittata*) and Boston fern (*Nephrolepis exaltata*) (Chen et al. 2009). In a recent study, Liu and Wang (2014) reported the highest ever-reported phytoextraction of Hg from $HgCl_2$ solution (10 μg L^{-1}) by a plant species (*Trifolium repens*). After 7 days of treatment, the Hg concentrations in the root, stems, and leaves of *T. repens* averaged 22.63, 53.98, and 22.98 mg g^{-1}, respectively. Their data indicated that the majority of the extracted Hg was transferred to the plants above the roots. However, the ability of this plant to extract less bioavailable Hg species from contaminated soil is yet to be determined.

Su et al. (2007) investigated three plants (Indian mustard, beard grass, and Chinese brake fern) for phytoremediation and identified Chinese brake fern as a potential candidate for extracting mercury from soil. The plant accumulated the highest amount of mercury (1.5 mg g^{-1} in the shoots) from soils spiked with $HgCl_2$ (achieving a final Hg concentration of 1 mg g^{-1}) without visual stress symptoms. Examples of other research reporting phytoextraction of Hg from contaminated soil are summarized in Table 4.

To increase the bioavailability of mercury in soils for phytoextraction, chelating agents such as EDTA, iodide, and sulfur-containing compounds were used. Application of EDTA significantly increased the total amount of Hg accumulated by plants, particularly in plant shoots, in soils contaminated with $HgCl_2$, $HgSO_4$, or $Hg(NO_3)_2$ (Smolinska and Cedzynska 2007). Iodide that is known to mobilize mercury (Wasay et al. 1995) has also been evaluated for enhancing phytoextraction. However, high concentrations of KI (>0.2 mM) in soil were toxic to the plants (Wang and Greger 2006). At lower concentrations (0.1 mM), iodide improved mercury accumulation in willow's leaves (5-fold), branches (3-fold), and roots (8-fold). Adding iodide did not enhance mercury translocation to the shoots, where less than 1 % of the Hg had accumulated. A point worth noting is that the use of chelating agents could increase mercury leaching from soil into groundwater, so the risks should be carefully evaluated (Smolinska and Krol 2012).

The use of nontoxic thiol-containing solutions has also been investigated for enhanced Hg accumulation in aboveground plant biomass. In a field study of a mercury-contaminated mine site (1.3 to 4.5 mg kg^{-1}) in New Zealand, adding sodium thiosulfate significantly enhanced Hg extraction to the shoots (~3–10 mg Hg kg^{-1} dw) and roots (~9–15 mg Hg kg^{-1} dw) of the Indian mustard plant (*B. juncea*) (Moreno et al. 2005). The increase in Hg extracted was proportional to the amount of $Na_2S_2O_3$ added. Similarly, applying ammonium thiosulfate increased Hg accumulation in the shoot tissues of *B. juncea* from <1 to >40 mg kg^{-1} at a site containing Hg at 2.82 mg kg^{-1} of soil.

Smolinska (2014) recently investigated the enhanced phytoextraction of mercury-contaminated soil by *Lepidium sativum* L. using green waste compost as an amendment. The green compost was composed of leaves, grasses, branches, and other green wastes and, therefore, had high content of organic matters. The use of green compost increased not only the accumulation of Hg by the whole plant but also the translocation of Hg to the shoots. The highest increase of Hg accumulation in the plants was 30 % when a soil/compost ratio of 4:1 (Hg concentration as $HgCl_2$ 10 mg kg^{-1}) was applied compared to the control (no compost amendment). The highest increase of Hg amount in the shoots was observed when a soil/compost ratio of 2:1 was applied, with 63 % of Hg translocated to the stems and leaves. In addition, the application of compost decreased the leaching of Hg from soil both in acidic and neutral solutions. The improved performance was attributed to the high organic contents in green compost. The soluble organic Hg complex benefited the bioaccumulation of Hg, yet the insoluble organic matters trapped Hg in the growing medium. Therefore, green compost has the potential to be an economical substance that can increase the efficiency of Hg phytoextraction without causing the risk of leaching.

Plants transformed with mercury transport genes, such as *merP*, *merT*, and *merC*, facilitate mercury uptake and translocation to specific plant organelles and tissues—thereby enhancing Hg phytoextraction (Henry 2000; Ruiz and Daniell 2009). Twice as much mercury was extracted by *Arabidopsis thaliana* and tobacco plants when they were modified with the *merC* gene (Sasaki et al. 2006). At the end of extraction/accumulation, the plants will have to be disposed of appropriately by drying, incinerating, gasifying, pyrolysis, acid extraction, anaerobic digestion, or extracting the oil and chlorophyll fibers (Mulligan et al. 2001a).

Phytostabilization involves the use of plant root to reduce contaminant mobility and bioavailability through sorption, precipitation, complexation, or reduction (Henry 2000). While this approach can be advantageous (effective, rapid, and requires no disposal), the disadvantages include limited use of the soil, potential metal leaching, and contaminant toxicity to soil microorganisms (Cabrejo and Phillips 2010; Henry 2000). In the past two decades, there have been numerous studies identifying appropriate plants able to stabilize mercury. Sas-Nowosielska et al. (2008) compared Hg uptake by willow and grasses. While willow accumulated the greatest amount of Hg, its root system is predominantly located in the upper soil layer, which is not desirable for phytostabilization. Grasses such as meadow grass and fescue accumulated less mercury but created a good soil penetration and stabilization system. Interestingly, there was an inverse correlation between the number of sulfur amino acid decomposing bacteria and root mercury content although the reasons were not clear.

Elemental mercury is unique in that it is the only volatile metal and, therefore, be removed via phytovolatilization. In this approach, organic mercury or mercuric ion is transformed to less toxic elemental mercury (Hg^0), which is released into the atmosphere.

Genes that are able to transform and detoxify mercuric species were first identified in mercury-resistant bacteria (Summers 1986). Most notably, bacteria containing the mercuric reductase gene (*merA*) and organomercurial lyase gene (*merB*) were able to reduce and demethylate mercury. The *merA* gene encodes mercuric reductase which converts ionic mercury to elemental mercury, whereas organomercurial lyase encoded by *merB* gene catalyzes the demethylation and formation of Hg^{2+} from methylated mercury. However, because bacteria require special conditions (Che et al. 2003), they are not effective for field applications. As plants have a much greater biomass, Meagher's research group at the University of Georgia developed a strategy using genetically engineered plants to

Table 4 Natural plants able to phytoextract and phytostabilize Hg in contaminated soil

Plant	Medium Hg conc	Hg conc in shoot (mg kg^{-1})	Hg conc in root (mg kg^{-1})	Reference
Atriplex conodocarpa	17.3 mg kg^{-1} (potting mix spiked with $HgCl_2$)	0.20±0.07	0.87±0.06	Lomonte et al. (2010)
Au. caespitosa		0.19±0.07	1.01±0.05	
Atriplex conodocarpa	3.5–8.4 mg kg^{-1} (biosolids collected from Melbourne Water's Western Treatment Plant)	(74.3±1.1)×10^{-3}	Not detectable	Lomonte et al. (2010)
Au. caespitosa		(57.3±25.9)×10^{-3}	Not detectable	
Chinese brake fern (*Pteris vittata*)	250 mg $HgCl_2$ kg^{-1} soil ($HgCl_2$ spiked as powder)	123±88	749±330	Su et al. (2007, 2008)
	500 mg $HgCl_2$ kg^{-1} soil	540±393	1525±786	
	1000 mg $HgCl_2$ kg^{-1} soil	1469±761	6802±3325	
Barley (*Hordeum vulgare*)	32.16 mg kg^{-1} (Almadén contaminated soil)	0.76	N/A	Rodriguez et al. (2003, 2007)
	33.56 mg kg^{-1} ($HgCl_2$ spiked Almadén soil)	2.70		
White lupin (*Lupinus albus*)	32.16 mg kg^{-1} (Almadén contaminated soil)	0.16	N/A	
	33.56 mg kg^{-1} ($HgCl_2$ spiked Almadén soil)	1.00		
Lentil (*Lens esculenta*)	32.16 mg kg^{-1} (Almadén contaminated soil)	1.13	N/A	
	33.56 mg kg^{-1} ($HgCl_2$ spiked Almadén soil)	4.00		
Chickpea (*Cicer aretinum*)	32.16 mg kg^{-1} (Almadén contaminated soil)	0.17	N/A	
	33.56 mg kg^{-1} ($HgCl_2$ spiked Almadén soil)	0.90		
Silene vulgaris	Control (soil C Typic Calcixerept, pH>7)	0.024±0.002	0.010±0.001	Pérez-Sanz et al. (2012)
	0.6 mg kg^{-1} (soil C spiked with $HgCl_2$)	0.07±0.01	0.38±0.20	
	5.5 mg kg^{-1} (soil C spiked with $HgCl_2$)	0.55±0.08	3.7±0.9	
	Control (soil A Typic Haploxeraft, pH≈7)	0.052±0.009	0.003±0.007	
	0.6 mg kg^{-1} (soil A spiked with $HgCl_2$)	0.11±0.03	0.58±0.05	
	5.5 mg kg^{-1} (soil A spiked with $HgCl_2$)	0.98±0.21	2.9±1.3	
Lepidium sativum L.	10 mg kg^{-1} (spiked with $HgCl_2$, soil amended with green compost 2/1)	~0.86	~0.58	Smolinska (2014)
	100 mg kg^{-1} (spiked with $HgCl_2$, soil amended with green compost 2/1)	~6.2	~5.0	

transform and detoxicate mercury (Bizily et al. 1999, 2000; Lyyra et al. 2007; Meagher and Heaton 2005; Rugh 2001; Rugh et al. 1996, 1998). In the phytovolatilization process, plants containing both *merA* and *merB* genes are able to transform methylmercury into Hg^0 and subsequently release it to the air. During the past decade, there have been an increasing number of studies of this process. Various plants have been genetically modified and tested for mercury removal effectivity, including rice (*Oryza sativa*) (Heaton et al. 2003), cottonwood trees (*Populus deltoides*) (Che et al. 2003), *A. thaliana* (Rugh et al. 1996), tobacco (*Nicotiana tabacum*) (Heaton et al. 1998, 2005), yellow poplar (*Liriodendron tulipifera*) (Rugh et al. 1998), and sweetgum (Dai et al. 2009).

However, phytovolatilization does not remove or immobilize mercury permanently and the released mercury will be cycled back into soils and waters. In addition, genetically engineered plants with both *merA* and *merB* genes are not permitted for use in the environment (Henry 2000). The health and safety issues associated with mercury phytovolatilization from large sites must be considered. To address the issue associated with Hg^0 volatilization, an alternative strategy was developed where ionic mercury was sequestered inside the cell by a chelating agent (Ruiz and Daniell 2009). There is a bacterial gene coding for polyphosphate kinase (*ppk* gene) that synthesizes polyphosphates. These polyphosphates chelate heavy metals and enhance tolerance and accumulation of Hg^{2+} in tobacco plants (Nagata et al. 2006). Nagata and coworkers further demonstrated enhancement and acceleration of Hg^{2+} uptake in tobacco by integrating *merT* gene in polyphosphate kinase gene (*ppk*)-transgenic tobacco (Nagata et al. 2009). Although expression of *MerT* had no significant effect on the mercury tolerance of *ppk*-transgenic tobacco, introduction of the gene increased Hg^{2+} uptake rate by approximately 2-fold at low Hg^{2+} concentrations (<1.25 μM). In another study, the same group developed a *ppk/merT/merB*-transgenic tobacco plant that significantly improved methylmercury tolerance and Hg accumulation compared to the wild-type and *ppk/merT*-transgenic tobacco callus (Nagata et al. 2010). By expressing mouse metallothionein gene (*mt1*) in plant cells, Ruiz et al. (2011) were able to obtain high mercury resistance and increase Hg accumulation in the plant leaf (up to 106 ng) from culture media containing $HgCl_2$. The results could be attributed to the Hg-scavenging effect of the protein metallothionein, which not only reduces toxicity but also facilitates Hg extraction. However, useful as these plants are, the use of transgenics in the field is viewed unfavorably by the public and perceived as a danger by environmental regulators.

Phytoremediation studies have increased rapidly over the last two decades. However, compared with the extensive laboratory studies on phytoremediation, results from field demonstrations are still very limited, particularly for mercury (Moreno et al. 2005). Not only is this technology relatively immature and requires lengthy duration, but the plant growth and removal effectivities are affected by environmental variables such as toxicity induced by the contaminants, presence of other contaminants, low pH, low nutrient availability, salinity, insufficient aeration, and low water availability (Robinson et al. 2006). All these factors may hinder the success of phytoremediation.

Overall, in situ application of phytoremediation for Hg-contaminated soils and sediments has notable advantages. It minimizes the disturbance of the site and surrounding environment and reduces the spread of contamination via air and water (Henry 2000). If the plants used are diversified properly, multiple contaminants can be remediated simultaneously (ITRC 1997). It is an environmentally friendly and cost-effective technology that can be applied to a large area. Moreover, this technology has high esthetic value and public acceptance. However, it has limitations as it is generally a slow process and is restricted to sites with shallow, low levels of contamination that occurs within the plant root zone. In addition, the harvested plant biomass is classified as RCRA (Resource Conservation and Recovery Act) hazardous waste and needs off-site treatment. Other concerns associated with phytoremediation include consumption of contaminated plants by animals and insects and consequences in the food chain, introduction of invasive and nonnative remediative plants, and dependence on climatic conditions.

Nanotechnology

Due to their small size and unique properties, nanoparticles offer exciting opportunities for applications as diverse as electronic manufacturing, drug delivery, and environmental remediation. Recently, Zhao and his research group invented a novel in situ mercury immobilization technology by injecting stabilized iron sulfide nanoparticles into the soil (Gong et al. 2014; Xiong et al. 2009a; Zhao et al. 2009). In this technology, a FeS nanoparticle suspension was prepared by mixing $FeSO_4$ with sodium carboxymethyl cellulose (CMC) and then adding Na_2S at a 1:1 Fe to S molar ratio. The FeS nanoparticles were stabilized by CMC. Furthermore, FeS was stable and insoluble in water (solubility product constant of 8×10^{-19}) and unavailable to biota (Zhao et al. 2009). Using laboratory-scale batch and column tests, the authors demonstrated that FeS could effectively immobilize Hg^{2+} in the sediment and the effectivity increased with FeS/Hg molar ratio. The authors proposed that mercury was immobilized by ion exchange or adsorption (see Reactions 1–3) (Xiong et al. 2009b).

Although still at an early developmental stage, this technology shows promise for in situ mercury remediation, as it requires low cost and energy input and the preparation can be conducted on site (Xiong et al. 2009a). Because of high mobility of FeS nanoparticles, it may be applied to both soil and sediment (Xiong et al. 2009b). However, there are unanswered questions with this technology regarding the effects

Table 5 Summary of various in situ soil mercury remediation technologies

Technology	Description	Status	Positives	Negatives	Applicability	Costs	In situ application
In situ thermal desorption (ISTD)	Mercury is converted to gaseous or vapor phase from the contaminated sites by heat treatment and then collected and treated	Pilot scale	No treatment depth limitation; less sensitive to subsurface heterogeneities	High cost; potential risks from release of mercury vapor; negative impacts on the ecological health at the treated site	Sandy soil; mobile mercury species (e.g., after-soluble, exchangeable, and elemental mercury)	\$50 to \$250/ton of soil (Stegemeier and Vinegar 2001)	Pilot-scale experiment using mercury-contaminated soil obtained from a chemical factory located in southern Poland (Kucharski et al. 2005)
Electrokinetics	A low intensity direct current is passed between a cathode and an anode imbedded in the contaminated soil so that mercury ions move toward the oppositely charged electrodes	Full-scale applications in Europe; pilot scale, bench scale, and laboratory scale in the USA	No excavation required; little disturbance to contaminated site; simultaneous removal of other contaminants; relatively lower cost	May need complexing agents to mobilize mercury; concerns associated with release of mercury vapor, disposal of mercury waste, and mobilization of insoluble and nontoxic mercury compounds	All soil types, especially clay soil; inorganic mercury species	\$20–\$225/cubic yard in 1997 (Cauwenberghe 1997) ECRTs cost \$135/cubic yard for remediation volumes on the order of 3000 cubic yard to less than \$35/cubic yard for volumes in excess of 100,000 cubic yard in 2002 (Burks 2002)	Union Canal, Scotland (Doering et al. 2001) Georgia Bellingham Bay, Bellingham, WA (USEPA 2007b)
In situ soil flushing	An appropriate washing solution is injected into or sprayed onto the contaminated soil so that the contaminants become mobilized and can be later extracted	Laboratory scale Ongoing field test	Efficient in removing Hg from subsurface soil; does not require excavation, treatment, and disposal of soil wastes; treatment equipment is easy to construct and operate; can be coupled with other in situ technologies for better Hg removal	Requires chemical additives; solubilizing contaminants poses risks and is unacceptable to regulators and public; intrusive to the treated area	Homogeneous, permeable soils with permeability greater than 1×10^{-3} cm/s; mobile mercury species	\$60–130/cubic yard (USEPA 1997b)	Lipari Landfill, NJ (USEPA 2002)
Containment	Contaminated soils are isolated and contained by low permeability physical barriers to prevent or reduce the migration of mercury in the soil	Commercial	Low cost; does not require excavation and disposal of hazardous waste; can be applied together with other technologies to enhance Hg remediation effectiveness; protects groundwater from being contaminated	Leaves the contaminants as is on site; requires long-term sampling and monitoring of the treated sites and underlying groundwater	Contaminated soils of low hazard and mobility; not applicable if there exists a more permanent and cost-effective remedy, implementation is difficult, or there is potentially high risk	\$5–15/square foot (vertical barriers) (USEPA 1998)	Wyckoff/Eagle Harbor– West Harbor OU, WA (USEPA 2011b)
Solidification/stabilization	Contaminated soils are mixed with treatment reagents to reduce the mobility and/or permeability of contaminants by physical encapsulation and/or chemical stabilization	Commercial	Mature and commercially available; receptible to US regulatory agencies; effective in immobilizing contaminants and meeting regulatory cleanup levels	Can increase the volume of the contaminated area; may pose risks in a longer term; introduces chemical agents that may cause problems themselves	The applicability depends on the mobility of mercury	Averaging~\$194/cubic yard (USEPA 2000b)	Savannah River (USDOE)−Old F-Area, SC (USEPA 2000b) Dwory facility, Oswiecim, southern Poland (USDOE 2002)
Vitrification	Contaminated soils are heated and molten by high temperature treatment and cooled to form a solidified, chemically inert, vitreous mass wherein the	One Superfund site field test Numerous pilot-scale tests	Can be used for mixed contamination; can be applied together with other technologies; does not require excavation and off-site treatment; reduces volume of the contaminated site	Energy intensive; requires treatment of the off-gases; high cost	Soils of shallow depths (6–20 ft) and of large volume; soils contaminated with low concentrations of mercury; not applicable for soils with organic content of more than 7 to 10 wt%	\$267/cubic yard (USEPA 2007a)	Parsons/ETM, Grand Ledge, MI (USEPA 1997c)

Table 5 (continued)

Technology	Description	Status	Positives	Negatives	Applicability	Costs	In situ application
	contaminants are immobilized						
Phytoremediation	Green plant is used to clean up mercury-contaminated site through phytoextraction, phytostabilization, or phytovolatilization	Pilot scale; ongoing field test	Minimizes the disturbance of the soil and surrounding environment; multiple contaminants can be remediated simultaneously; environmental-friendly; cost-effective; can be applied to a large area; high esthetic value and public acceptance	This technology is still immature; requires lengthy remediation duration; vulnerable to environmental conditions; harvested plant biomass needs off-site treatment; consumption of contaminated plants by wildlife; introduction of invasive and nonnative remediative plants; phytovolatilization does not remove or immobilize mercury permanently; genetically engineered plants with both *merA* and *merB* genes are not permitted for use; release of mercury vapor from phytovolatilization process	Sites with shallow contamination; sites with low contaminant concentrations	\$37–\$155/cubic yard (USEPA 2000a)	Tui base-metal mine, Mount TeAroha, North Island, New Zealand (Moreno et al. 2005); INEEL superfund site, ID (USEPA 2000a)
Nanotechnology	Stabilized iron sulfide nanoparticles are injected into the contaminated soil to immobilize mercury by ion exchange or adsorption	Laboratory-scale preliminary test	Does not use any toxic reagents; preparation can be conducted on site; low cost and energy requirements	Immature technology; health and safety concerns about the use of nanoparticles	Both surface and subsurface soil; elemental and mercuric mercury	\$1.12/cubic yard (chemical cost only) (Xiong et al. 2009a)	N/A

of effectivity of soil parameters, best deployment strategy, and the impacts on the environment (Cabrejo and Phillips 2010). Because mercury stays in the soil after treatment in nanoparticle forms, its leachability and bioavailability are still of concern. The methylation potential of dissolved Hg(II) and sulfide, nanoparticulate HgS, and microparticulate HgS was compared in a sediment containing sulfate-reducing bacteria (Zhang et al. 2011). Methylmercury production was insignificant for microparticulate HgS after 24 h of incubation, while more than 2 % of nanoparticulate HgS was transformed to methylmercury. The methylation transformation efficiency was even higher (6–10 %) when a freshly prepared HgS suspension was added. Bearing this in mind, nanotechnology options must still be rigidly evaluated before field trials.

Comparison of technologies

A summary of the various in situ mercury remediation technologies is provided in Table 5. All of the in situ technologies for Hg remediation are still under development. Theoretically, removal technologies are more desirable because the contaminants can be permanently removed from the site, but implementing the technology can be very costly. In situ thermal desorption can be expensive, but it effectively removes the most mobile and bioavailable species (e.g., water-soluble, exchangeable, and elemental mercury). Electrokinetics is particularly suitable for clay soils (where other technologies are unfeasible). In situ soil flushing/washing can efficiently remove Hg from contaminated soils if an appropriate washing solution is used, but the method is intrusive and has limited field examples. In situations where mercury removal is simply not economically or technically possible, immobilization is preferred as long as it meets the regulatory goals and a long-term monitoring program is established. Containment aims at preventing the migration of contaminants from the impacted site and is generally not considered “treatment technology.” Compared to other in situ remediation technologies, in situ solidification/stabilization is better developed for treating Hg contamination and accepted by US regulators. Vitrification is costly but can treat organic and inorganic contaminants simultaneously. Phytoremediation has the potential for treating shallow subsurface areas with low Hg contamination, but this technology is not well developed. Nanotechnology has shown some potential in the laboratory but is still in its infancy.

Conclusions

Mercury contamination in soils and sediments is a serious threat to the environment and human health. The unique properties of metallic Hg and Hg chemical species make its remediation complicated and costly. Therefore, it is vital to effectively evaluate, select, and design an appropriate remediation strategy for Hg-contaminated soils and sediments.

Many factors need to be considered when selecting a mercury remediation technology. Mercury speciation within a contaminated site must be well understood because it determines the toxicological effects as well as the environmental fate and transport of mercury. For example, Hg^0 has relatively lower boiling point than other species and this makes thermal treatment more applicable for its removal. Other important factors include the physico-chemical properties of the soil/sediment and distribution of the contaminant. To conclude, different remediation technologies have their own pros and cons as summarized in Table 5, and the selection of an appropriate technology is site specific and needs to be carefully considered and evaluated.

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