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Recent Advances in Contaminated Site Remediation

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1 Introduction

The recent poisoning of thousands of people through exposure to arsenic, asbestos (Naidu et al. 1996) and benzene has highlighted the massive challenge that contaminants pose risk for both human and environmental health. Globally, there are more than 3,000,000 potentially contaminated sites (Singh and Naidu 2012) which besides posing risks to the health and well-being of humans and the environment, also represent a large lost economic opportunity. Contamination is the legacy of industrialization, inadequate environmental laws and inconsistent and lacking enforcement. At the biennial International Committee on Contaminated Land, the World Bank reported that it had integrated contamination into its 'Greening Development and Sustainable Urban Development' agenda. Although site contamination has been recognised since the 1960s, less than a tenth of potentially contaminated sites globally have been remediated due to the complex and challenging nature of both surface and subsurface contamination. These challenges are further exacerbated by the cost and technical difficulty of dealing with contaminant mixtures, as well as recalcitrant and persistent pollutants. Common contaminants include petroleum hydrocarbons, chlorinated solvents, persistent organic pollutants, pesticides, inorganics, heavy metals and radioactive constituents. These contaminants can be found in a variety of sites such as oil and gas operations, service stations, mines, industrial complexes, landfills, waterways, harbours and even in runoff from urban and residential settings.

In most countries, the scale of the problem is difficult to assess, as 'contaminated land' or 'site contamination' are often subjectively or poorly defined, even in statute. Very few efforts have been made to develop an inventory of contaminated sites in developing countries, although industrial practices and the societal drive for economic growth continue to increase contamination of both land and water bodies. Although most developing countries have stringent regulatory guidelines, adherence to and policing of these remains a major problem. The rapid expansion of the urban fringe due to mass migration of people from rural into urban areas is causing substantial

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pressure on available land for residential and other uses including infrastructure, water and power distribution. As a result, development is being driven into disused former industrial zones which are often contaminated. This has led to significant demand for remediation and protection from residual contaminants as well as cost-effective and sustainable techniques for managing contamination to ensure the land is suitable for its new, more sensitive uses.

2 Remediation Technologies

Contaminated site remediation technologies fall into two principal approaches: in-situ (soil and water are treated in the ground) or ex-situ (treatment is carried out above ground). While in-situ remediation deals with contamination without removing soil or water from the ground, ex-situ remediation requires the excavation of contaminated soil or abstraction of polluted water and/or soil vapour for treatment or disposal elsewhere. The techniques available for in-situ or ex-situ remediation can be prohibitively costly, resulting in poor rates of adoption in most countries, unless there is a very large increase in the value of the remediated site. Many different in-situ and ex-situ technologies are used to remediate contaminated soils and groundwater (Table 1). While many of these technologies are classed as ex-situ, the recent emphasis on minimisation of greenhouse gas emissions has ignited interest in in-situ technologies that do not require transport of contaminated soils to prescribed landfills. However, despite significant investment in the development of remediation technologies, especially in USA and Europe, contaminated site remediation remains a major challenge due to the complex nature of contaminants and their bioavailability, the presence of mixtures and the complexity of the local geology and hydrology. Readers are directed to an excellent publication by Davis (1997) on the pros and cons of disposal and in-situ and ex-situ remediation which provides a view of what we thought at that time.

3 Advances in In-Situ Remediation Technologies

For the last three decades, both soil and groundwater remediation technologies have continued to evolve; however, the main advance has not been many brand new technologies but rather in the application of techniques once seen as novel (for example, in-situ thermal treatment of hydrocarbon contaminated soils, etc.) and the development of novel uses of existing technologies (for example, in-situ chemical oxidation, etc.). Some of these technologies are discussed in the following sections focussing on contaminated soil and groundwater.

3.1 Contaminated Soil

Unlike the manufacturing and sensor tool industries, progress in the development of new technologies for the remediation of contaminated soils has been slow. Conventional technologies used for the remediation of contaminated soils include bioremediation using biopiles, bio-slurry reactors, thermal desorption, soil washing, bioventing, bio-slurping and air sparging (see Table 1). While most of these technologies work for hydrocarbons, their main problem with metal(loids) is their inability to degrade the metal, although the treatment may result in changing the valence state of the metal resulting in either a more or less mobile, more or less toxic constituent depending on specific geochemical conditions. Also, when introduced into the soil environment metal(loids) bind to colloidal matter forming matrices, from which the metal(loid)s can either leach down to the groundwater or be taken up by plants. Human exposure can occur via the food chain, water and soil or dust inhalation (example methyl mercury) and ingestion. The most common approach to deal with metal(loid)-contaminated soils has been excavation and transport to prescribed landfills. However, landfills are now seen to have intergenerational impacts and for this reason, some regulators in Australia have introduced additional legislation which increases landfill costs and thereby encourages in-situ management of contaminated material. Such an approach minimises greenhouse emissions from transport and at the same time forces the remediation industry to think laterally and develop new ways to manage and/or remediate metal contaminated soils. Recent advances over the last 15 years include the following technologies.

3.1.1 Electrokinetic Remediation

The technique uses low-level direct current of the order of mA/cm^2 of cross-sectional area between the electrodes or an electric potential difference of the order of a few volts per centimetre across electrodes placed in

Table 1 A summary of technologies for contaminated soil and groundwater remediation (http://www.epa.gov/superfund/remedytech/remed.htm; Naidu et al. 1996). Conventional technologies are those that are commonly used, while developing technologies are those that are still being fine-tuned, emerging technologies that are now finding success

Remediation technologies/management strategies	Mode of operation	Technology type	References
Contaminated soil			
Bioremediation	Microbial activity is optimised for degradation of contaminants especially hydrocarbons—often large volumes of soil are remediated using biopiles	Conventional	Jørgensen et al. 2000; Bento et al. 2005; Megharaj et al. 2011; Rayu et al. 2012
Phytoremediation	Plants that accumulate toxic metals or biodegrade organics in their root zone	Conventional	Cunningham et al. 1996; Pulford and Watson 2003; Gerhardt et al. 2009
Vapour extraction	Techniques range from relatively simple designs for remediation of volatile hydrocarbons in permeable soil to high-performance systems for treatment of lower-permeability soils. They include thermal desorption plants that heat soil in a rotary kiln to a temperature at which target organic compounds are transferred to the gas phase	Conventional	Frank and Barkley 1995; Zevenbergen et al. 1997; Soares et al. 2010; Chien 2012
Soil washing	A volume reduction method that uses chemicals to remove contaminants	Conventional	Semer and Reddy 1996; Mulligan et al. 2001a; Dermont et al. 2008
Solidification-stabilisation	Application of a specially formulated (usually proprietary) additive mix to generate a low-hazard, low-leachability material usually for on-site re-use	Conventional	Bolan and Duraisamy 2003; Kumpiene et al. 2006; Sarkar et al. 2012a
Electrokinetic	Application of a low-intensity current that creates a gradient for ions to move from either cathode to anode or vice versa. A new technology being trialled in Europe and USA	Developing technologies	Ottosen et al. 1997; Yeung 2006; Yeung and Gu 2011
Ultrasonic	Ultrasonic waves have been used to remediate hydrocarbon contaminated soils	Innovative and emerging	Shrestha et al. 2009; Thangavadivel et al. 2009, 2011
Thermal	Numerous in-situ and ex-situ thermal technologies are available for soil and groundwater remediation	Emerging	Mulligan et al. 2001b; Khan et al. 2004
Risk-Based Land Management	Universally accepted as a cost-effective strategy for implementing 'fit for purpose' use of contaminated land	Innovative	Ferguson et al. 1998; Naidu et al. 2008a, 2008b; Nathanail 2009; DTZ 2010
Groundwater			
Pump and treat	Operation requires pumping of contaminated water through a chemi- or bioreactor that remediates contaminants. Cleansed water is then reinjected back into the aquifer	Conventional	Mackay and Cherry 1989; Baú and Mayer 2008; Higgins and Olson 2009
In situ chemical oxidation and reduction	Involves introduction of reactive materials into the subsurface to destroy organic contaminants. A variety of chemical oxidants and reductants makes this a useful technique where intensive source-zone treatment is required	Conventional	Seol et al. 2003; Ferguson et al. 2004; Krembs et al. 2010

Table 1 (continued)

Remediation technologies/management strategies	Mode of operation	Technology type	References
Bioremediation	Range from the relatively simple (e.g. placement of oxygen or nutrient-releasing agents to stimulate biodegradation activity) to the more complex process-based systems (e.g. for chlorinated solvent source areas) including enhanced anaerobic dechlorination, anaerobic bioventing, in-situ co-metabolism and bioaugmentation	Conventional to emerging	Knapp and Faison 1997; Franzmann et al. 1999, 2000; Farhadian et al. 2008; Davis et al. 2009
Vapour extraction	Vapour-extraction techniques (soil vapour extraction, sparging and slurping) range from relatively simple designs for remediation of volatile hydrocarbons through complex multiphase extraction systems capable of dealing with soil gas, groundwater and NAPL mixtures	Conventional	USEPA 1989; Johnston et al. 1998; Johnston and Desvignes 2003; Patterson and Davis 2008
Permeable Reactive Barriers (PRBs)	PRBs offer potential for long-term, low-intensity treatment of groundwater plumes. PRBs comprise one or more zones of reactive material placed in the subsurface to degrade or sorb dissolved contaminants as the groundwater passes through	Conventional to emerging	Patterson et al. 2002, 2004; Gibert et al. 2008; Thiruvenkatachari et al. 2008
Monitored Natural Attenuation (MNA)	MNA is a risk management approach for contaminated groundwater plumes that evaluates and monitors the combined effect of natural processes (e.g. sorption, dilution, biodegradation, etc.)	Conventional	Davis et al. 1999; Franzmann et al. 1999; Prommer et al. 2002; Naidu et al. 2010, 2012
Nanotechnology-environmental remediation	A recent technology focuses on the in situ use of nanomaterials for the degradation of contaminants	Developing	Cundy et al. 2008; Karn et al. 2009; Grieger et al. 2010; Sunkara et al. 2010; Sarkar et al. 2012b
Risk-Based Management	Universally accepted as a cost-effective strategy for implementing 'fit for purpose' use of contaminated groundwater	Innovative	Swartjes 1999; Davis and Johnston 2004

the ground in an open flow arrangement. Moisture in the soil or groundwater in boreholes acts as the conductance medium. This is one of the few soil remediation technologies that has been developed during the past 20 years and is currently being extended from laboratory based studies to field remediation. This process results in significant change in pH which can be managed by using certain surfactants or buffer solutions (Yeung and Gu 2011). However, field scale remediation is still to be demonstrated from performance as well as cost perspective.

3.1.2 Thermal Immobilisation

This is not a new technology given its long use in Europe and relatively common consideration in North America. However, it has evolved considerably over the last decade and is now being used for the remediation of both organic and inorganic contaminants. While organic contaminants degrade and/or volatilise at elevated temperatures, metals are immobilised thus minimising their bioavailability and hence ability to leach or pose risk to humans (Singh et al. 2007; Gomez et al. 2009).

3.1.3 Risk-Based Land Management

This approach to manage contaminated sites was introduced in 1990s following recognition of the prohibitively expensive cost of ex-situ and in-situ remediation. Risk-based land management (RBLM) aims to manage the risks posed by historic contamination and to mitigate those risks deemed unacceptable. The decision of what level of risk is unacceptable has a socio-economic dimension but is based on robust scientific estimates of the level of risk. Together, these concepts form the basis of RBLM, which represents a mature, sustainable approach to the challenges of contamination (Ferguson et al. 1998; Nathanail and Smith 2007; Naidu et al. 2008a; Nathanail 2009). RBLM is a common and well-developed consideration for contaminated site management in the USA.

To undertake RBLM, a chemical substance must be present in a form and at level that pose risks to possible receptors, including humans. Using this as the basis for management of contaminated sites, RBLM has often been employed to demonstrate 'fit for purpose' use of the contaminated land. Using this approach, when the site is found to have contaminant levels which exceed residential thresholds but fall within commercial/industrial guidelines, the site may be used for industrial but not for residential purposes. This approach has greatly expanded the availability of inner urban land for industrial or commercial purposes which was previously unused because of contamination.

However, risk-based land management can be further refined to ensure in-situ management of contaminated sites by distinguishing between hazard and risk and, based on this distinction, minimising the risk by in-situ treatment of contaminated material. The presence of chemical substances in soils and groundwater (the hazard) is of concern, but for harm to result to the environment or human health, they must be exposed. For there is to be risk, pathways must exist which connect the sources of contamination to the receptors that can be harmed. The management of these risks posed by historically-released chemicals should drive remedial action, and secondly, the risk is a function of the dose–response relationship for each chemical substance (Naidu and Bolan 2008). This means that a chemical substance must be present in a form and at levels sufficient to pose a risk to the receptor. Contaminant bioavailability determines effective intake and hence the level of risk posed: this is a critical parameter that ought to be used in all cases of RBLM. Sites with high contaminant bioavailability may be managed with treatments that demonstrably reduce bioavailability in the long-term. An example is the immobilisation of metals to minimise their bioavailability. Immobilisation refers to the process of transferring an aqueous phase of highly-mobile metals to a solid, stable phase that is locked within the soil. This phase transfer prevents the continued migration of contaminating metal plumes and can offer a permanent solution depending on the metal and site-specific geochemistry.

The most common mechanisms for in-situ metals immobilisation are metal adsorption to soil particles or the precipitation of metal solids that are chemically fixed to soil particles. Both of these mechanisms can permanently remove metals from the aqueous phase, restoring the aquifer and the desired usability of the water. Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) has advanced this technology by developing a composite material known as MatCARE™ that immobilises both organic and metal contaminants permanently. This is a modern remediation technology for the in-situ treatment of both metals and hydrocarbon contaminated soils. The material is a composite mixture of a naturally occurring mineral that has been modified to increase its capacity to immobilise both metals and hydrocarbon contaminants. Field-scale trials conducted in 2009 demonstrated the immobilisation of these contaminants was sustainable, with no observed leaching.

Rather than using the 'fit for purpose' approach, the demonstration of limited risk to humans and the environment following immobilisation of contaminants (no matter what changes occur in the environment) ought to be sufficient to permit human occupation and use of the land. However, this approach requires significant community participation in the process to allay public fears of perceived risk from exposure to bound substances.

3.2 Contaminated Groundwater

With the exception of nanotechnology, no major new groundwater remediation technology was developed during the first decade of the twentyfirst century. However, major advances were made in existing technologies which have made the remediation process a lot more efficient. Table 1 presents a summary of existing technologies including those that may be considered innovative, emerging and developing. Rapidly advancing technologies include Permeable Reactive Barriers (PRBs), enhanced anaerobic dechlorination, especially for DNAPLs, anaerobic bioventing and in-situ co-metabolism with some new technologies including, bioaugmentation and bioengineering.

3.2.1 Permeable Reactive Barrier

This technology is an underground barrier positioned to intercept a contaminated flow and charged with special substances that remove or degrade the contaminants. While the technology initially used zero valent iron as the reactive medium for the remediation of groundwater contaminated with chlorinated hydrocarbons (with the first field trials in the early 1990s and the first commercial deployment in late 1994), recently a range of materials for the remediation of other organics have been deployed (Warner et al. 1994). For example, investigators used saturated peat in a reactive barrier for the remediation of BTEX and inorganic contaminants (see Cohen et al. 1991; Guerin et al. 2002) and polymer mat for the removal of ammonium-contaminated groundwater (see Schipper and Vojvodić-Vuković 2001). Recent studies by our group demonstrated the use of Remat^{TM} (a proprietary material) for the remediation of TCE in groundwater. Remat^{TM} was specially developed for the remediation of both chlorinated and petroleum hydrocarbons. These studies showed that zero valent iron (ZVI) was ineffective in alkaline water as it poisoned the ZVI surface with carbonate. In a further development, the team installed the PRB with wide-diameter wells through which groundwater was extracted by solar pumping through the barrier material after which the clean water was injected back into the aquifer (see Fig. 1). Recent reviews by Warner and Sorel (2003) and Thiruvenkatachari et al. (2008) present an excellent overview of PRBs and their application to

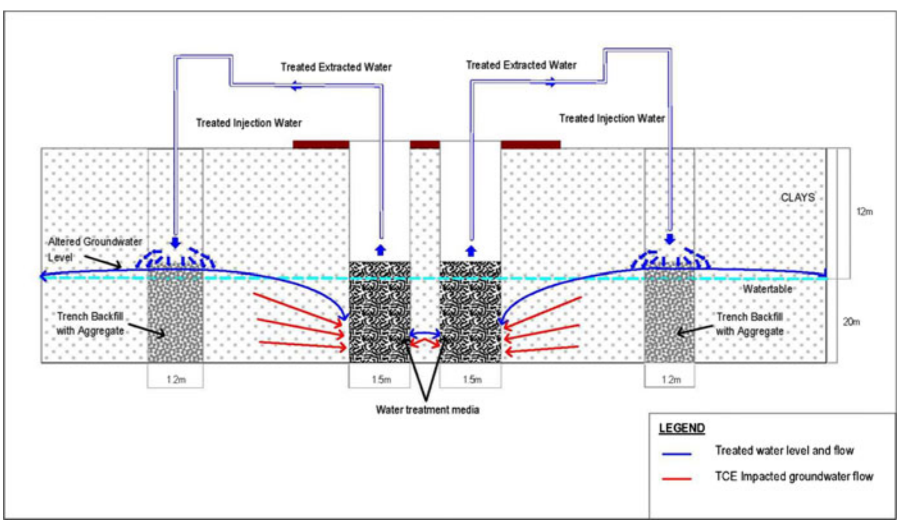

Fig. 1 Large permeable reactive barrier for the remediation of TCE-contaminated groundwater

organic and inorganic contaminant remediation in groundwater. Readers are also directed to additional reviews on PRBs by Warner (2011, 2012).

3.2.2 Bioremediation

In-situ bioremediation of contaminated groundwater is seen as a cost-effective and green technology. Often this involves the use of indigenous microbes and where in-situ bioremediation is slow, the process is enhanced via various techniques that range from biostimulation (the injection of growth substrates, co-substrates and electron acceptors which are limiting the biodegradation reaction) to bioaugmentation (the injection of bacteria to increase the subsurface population). Biostimulation requires the bacterial species or consortia responsible to degrade dissolved phase contaminants are indigenous and it assumes that reactions are limited by population densities or by the absence of key electron acceptors. Much more still needs to be done in this field to enhance success rate especially for non-aqueous phase liquids and under challenging conditions such as fractured rocks.

3.2.3 Enhanced Anaerobic Dechlorination

Chlorinated solvents are sparingly-soluble, dense, non-aqueous phase liquids (DNAPL) that can contaminate groundwater in the long term due to their persistence in the aqueous environment. Many contaminated sites occur in areas within fractured sedimentary or bedrock systems (Chapman and Parker 2005), where the released DNAPLs penetrate into the flow pathways formed by the fractures and can then rapidly dissolve and diffuse from the fractures into the matrix (Falta 2005; Chambon et al. 2010). Even after the removal of the physical source from the site, the contaminant can re-diffuse back into the fracture network for hundreds of years, causing long-term contamination of an underlying aquifer (Harrison et al. 1992; Reynolds and Kueper 2002). Such contaminated sites have proved extremely challenging and expensive to remediate. Enhanced anaerobic biodegradation has shown to be effective for the treatment of chlorinated hydrocarbon contaminated groundwater in some of these settings. The process includes adding an electron donor (hydrogen) to groundwater and/or soil to increase the number and vitality of indigenous microorganisms performing anaerobic bioremediation. A great hydrogen release material is ZVI—the hydrogen is released during the corrosion process and will continue to be released for decades and at fairly high levels depending on the amount of iron emplaced. This is another positive attribute to granular iron as a treatment material. While this approach to remediate DNAPL contamination has been successful at some sites, those with fractured rocks continue to pose significant problems in both delineating and remediating the contaminant.

3.2.4 Surfactant Enhanced In-Situ Chemical Oxidation

It is based on the ability of the surfactants to increase the aqueous solubility of and/or displace non-aqueous phase liquids (NAPLs) from porous media including fractured rocks (Taylor et al. 2001; Abriola et al. 2005). Above the critical micelle concentration (CMC) surfactant molecules aggregate to form micelles that is able to solubilise organic contaminants. The displacement of NAPLs as free products may also occur if the interfacial tension between the organic liquid and the aqueous phase is reduced to such an extent that viscous and buoyancy forces exceed the capillary forces acting on the NAPL. The contaminant that is mobilised can then be chemically oxidised. This approach has proved quite successful in soils contaminated with chlorinated hydrocarbons; however, additional design issues include assuring that newly mobilised organic chemicals are fully captured and do not migrate outside the remediation area into zones not previously contaminated.

3.2.5 Anaerobic Bioventing

It is often used for the treatment of chlorinated hydrocarbons in the vadose zone (Shah et al. 2001; Mihopoulos et al. 2002). In-situ remediation of vadose zone soils requires, among other factors, the establishment of highly reductive anaerobic conditions in the unsaturated subsurface. The process includes delivering an appropriate gas mixture into the subsurface (anaerobic bioventing) to create the conditions that enhance anaerobic biodegradation of contaminants. The gas mixture contains an electron donor for the reduction of these compounds.

3.2.6 Monitored Natural Attenuation

Although Monitored Natural Attenuation (MNA) is a management strategy, it has been extensively adopted for the remediation of groundwater in many countries. Natural attenuation includes both microbial degradation of contaminants and other processes (e.g. sorption, etc.) that either degrades or binds contaminants to sorbent (soil) (Sarkar et al. 2005; Naidu et al. 2010, 2012). For instance, in Australia, EPA Victoria has introduced Clean up to the Extent Practicable (CUTEP) that recognises natural attenuation of the contaminant in groundwater. Application of CUTEP requires regular monitoring of contaminants to demonstrate both attenuation as well as a steady decline in contaminant concentration in groundwater. However, MNA and the application of CUTEP have posed significant challenge to the management and/or remediation of Light Non-Aqueous Phase Liquids (LNAPLs). LNAPLs may consist of volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), non-volatile organic compounds and trace metals. When released into the subsurface, they can release dissolved contaminants to groundwater or VOCs into the subsurface atmosphere and potentially into indoor air for an extended period of time. In addition, sites which have complex or heterogeneous subsurface environments (such as low-permeability soils) pose particular difficulties in terms of characterisation and remediation of LNAPLs. No single technology has been identified as the best solution for all sites and all soil types contaminated with LNAPLs. LNAPL management in the subsurface is a particularly challenging problem in Australia given the wide range of soil types and hydrogeological conditions.

4 Challenges and Conclusions

Although the potential impact of contaminants on the environment and human health was first recognised more than half a century ago, contaminated sites still pose major challenges in terms of site assessment and remediation. These challenges include:

(a) inadequacy in site characterisation and delineation of subsurface contamination including soil and groundwater
(b) lack of trialled and tested tools for estimating the mass flux of contaminants
(c) cost of assessment and remediation, which is often hard to quantify
(d) lack of advanced technologies for subsurface groundwater remediation
(e) inadequacy of policies supporting or defining end points for remediation and
(f) fractured rocks and recalcitrant contaminants (such as DNAPLs) and their remedial endpoints

To sum up, there needs to be a far more consistent and global effort to develop site characterisation and sustainable but green remedial technologies, if humanity is to avoid the health and environmental well-being penalties of spreading contamination driven by the combination of world population and economic growth, which are likely to double our use of resources by the mid-twentyfirst century. Additionally, the continued stress on available water resources, in both developed and developing countries and communities require that we further isolate contaminated ground- and surface water from potable water resources, while we continue to develop reliable remediation methods.

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