RESEARCH/REVIEW ARTICLE

On-site and in situ remediation technologies applicable to metal-contaminated sites in Antarctica and the Arctic: a review

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Abstract

Effective management of contaminated land requires a sound understanding of site geology, chemistry and biology. This is particularly the case for Antarctica and the Arctic, which function using different legislative frameworks to those of industrialized, temperate environments and are logistically challenging environments to operate in. This paper reviews seven remediation technologies currently used, or demonstrating potential for on-site or in situ use at metal-contaminated sites in polar environments, namely permeable reactive barriers (PRB), chemical fixation, bioremediation, phytoremediation, electrokinetic separation, land capping, and pump and treat systems. The technologies reviewed are discussed in terms of their advantages, limitations and overall potential for the management of metal-contaminated sites in Antarctica and the Arctic. This review demonstrates that several of the reviewed technologies show potential for on-site or in situ usage in Antarctica and the Arctic. Of the reviewed technologies, chemical fixation and PRB are particularly promising technologies for metal-contaminated sites in polar environments. However, further research and relevant field trials are required before these technologies can be considered proven techniques.

Environmental metal contamination from human activities is an on-going problem in temperate and polar environments (Snape, Riddle et al. 2001; Poland et al. 2003; Santos et al. 2005; Filler et al. 2006). The legacy, exposure effects and management of metal contaminants such as copper, cadmium and lead on the environment and human health have been studied extensively in temperate environments (Hiroki 1992; Järup 2003; Taylor et al. 2010, 2013). However, environmental contamination from human activities remains understudied and unresolved in many polar regions (Muir et al. 1992; Poland et al. 2003; Chapman & Riddle 2005; Fryirs et al. 2013). The environmental character, legislation, infrastructure and logistical considerations which apply to the management of contaminants in temperate environments are substantially different to those of remote, polar environments (Snape, Riddle et al. 2001; Poland et al. 2003; Filler et al. 2006). As such, it is difficult to implement most of the techniques used for remediation in temperate environments at contaminated polar sites and there is a need to adapt and develop suitable techniques for managing metal contamination in polar environments.

Understanding the sources, species, mobility and potential impacts of metal contaminants is essential for the effective management and remediation of contaminated land (Martin & Ruby 2004). Equally critical is an understanding of the capabilities, limitations and logistical requirements of remediation technologies and operations in the context of a site. This is especially pertinent in remote and logistically constrained polar environments (Snape, Riddle et al. 2001; Poland et al. 2003; Filler et al. 2006). Remediation operations typically take place ex situ, on-site or in situ. Ex situ remediation involves the removal of contaminated soil or sediment with subsequent treatment off-site or landfilling. This

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technique is highly expensive and there are several technical issues associated with this approach. For instance, excavation may re-suspend or re-mobilize contaminants, instigating short- or long-term increases in contaminant bioavailability and consequently may facilitate contaminant fluxes into the food chain (Perelo 2010). Alternatively, on-site remediation is significantly less expensive and typically involves on-site waste reuse or excavation with treatment and reburial (Perelo 2010). The final option, in situ remediation, involves direct treatment into the ground at a contaminated site. In situ treatments are generally preferable in polar environments as they are often less disruptive to the environment, prevent the need to transport contaminated material or generate waste disposal sites and they prevent contaminant migration (Martin & Ruby 2004; Filler et al. 2006; Perelo 2010).

In response to the need for more effective and efficient approaches to managing metal contamination in polar regions, various innovative and cost-effective technologies applicable to sites in cold, remote environments are being developed and trialled. These technologies are typically applied on-site or in situ and are effective despite the logistical constraints associated with operating in polar environments. However, these technologies vary in their capacity to manage multi-metal-contaminated sites, and many sites require a combination of complementary technologies for effective remediation and long-term management. Therefore, it is imperative to understand the independent capabilities of the remediation technologies available, as well as the collective potential of the technologies.

An absence of reviews and shortage of research relevant to metal-contaminated sites in Antarctica and the Arctic presently limits our capacity to manage contaminated land in these regions. This applies particularly to on-site and in situ site remediation technologies. Therefore, this article reviews remediation technologies being developed for on-site and in situ application in Antarctica and the Arctic to provide a resource for future relevant research in polar environments. The article synthesises recent research and field trials relevant to metal-contaminated sites in Antarctica and the Arctic, and describes the importance of technology coupling for effective, long-term management. To achieve this, we examine the function of the reviewed technologies and discuss their respective advantages, limitations and potential for long-term management. Recent scientific and engineering advances from temperate environments are also identified and their applicability to metal-contaminated sites in polar environments is considered.

Metal contaminants in Antarctica and the Arctic

Metals are naturally occurring elements which are essential to many biogeochemical processes and have been widely used by humans for at least 5000 yr (Järup 2003). The adverse effects of metal exposure through their use in agricultural, manufacturing and industrial applications are widely reported (Järup 2003). As a consequence of these activities, as well as mining, smelting and landfilling, metals have become widely distributed across the globe, even in remote polar environments (Snape, Riddle et al. 2001; Duquesne & Riddle 2002; Poland et al. 2003; Santos et al. 2005). The primary forms of metal contamination in Antarctica and the Arctic are long-range airborne contamination, seaborne contamination and terrestrial contamination from human activities (Steinnes et al. 1997; Poland et al. 2003; Santos et al. 2005). In this paper, we focus on techniques for the management of terrestrial contamination from human activities.

In Antarctica, research stations represent the largest form of terrestrial human activity and consequently are the main source of locally derived contamination (Snape, Riddle et al. 2001; Poland et al. 2003; Santos et al. 2005). Active and abandoned landfills and other waste-disposal sites are the chief sources of past, present and on-going contaminant migration (Poland et al. 2003).

In the Arctic, terrestrial contamination typically results from on-going human activity in settlements and large-scale industrial operations and is generally associated with fossil fuel combustion, mining, smelting, waste generation, waste disposal and manufacturing (Steinnes et al. 1997; Poland et al. 2003). In some Arctic regions, contamination from industrial activity has almost completely destroyed entire plant communities (Walker et al. 1978; Poland et al. 2003).

Environmental setting

Antarctica and the Arctic are both cold, remote environments. However, they are distinct from one another and vary considerably from temperate environments (Poland et al. 2003). The environmental, legislative and operational differences between Antarctica, the Arctic and temperate environments have important implications for the sources, distribution and extent of contamination and can significantly influence the execution of remediation operations (Poland et al. 2003; Filler et al. 2006). Here we summarize the environmental setting of the Antarctic and the Arctic and investigate sources and the extent of metal contamination. The governing legislation and logistical challenges influencing contaminated land management and remediation operations in these environments are also reviewed.

Natural environment and human presence

Antarctica is the most remote, coldest, driest and windiest continent on Earth (Kennedy 1993; Poland et al. 2003; Huiskes et al. 2006). Temperatures range from $-90°C$ in winter to $15°C$ in summer (Poland et al. 2003; Convey 2010). Due to the extreme climate there are only a few vascular plants, which exist only in restricted areas on the Antarctic Peninsula, and flora on the continent is largely limited to cryptogamic species such as mosses, liverworts and lichens (Smith 2001; Seppelt 2002; Poland et al. 2003; Convey 2010). Robinson et al. (2003) reported that 75 species of mosses exist in maritime Antarctica, 30 in continental Antarctica and over 125 lichen species on the ice-free zones of the continent.

A large diversity of invertebrates, bird life and marine animals exist in Antarctica and depend primarily on the Southern Ocean ecosystem for food (Poland et al. 2003; Convey 2010). A recent study by Huiskes et al. (2006) reports that at least 294 insect, 229 spider and 76 crustacean species as well as 257 species belonging to other groups (including molluscs, annelids, rotifer, nematode and tardigrada) exist in Antarctica, many of which reside on the rocky, ice-free coastal land that constitutes less than 0.01% of the continent (Pickard 1986; Snape, Riddle et al. 2001). The majority of research activities and contaminated material in Antarctica is also situated on these coastal ice-free areas (Snape, Riddle et al. 2001). These coastal ice-free areas host many of the essential breeding grounds for Antarctic fauna and are a vital component of the Southern Ocean ecosystem (Pickard 1986). The vulnerability of polar species such as Antarctic amphipods to the adverse effects of exposure to contaminants in soil and groundwater justifies prompt and effective management of contaminants (Ling et al. 1998; Snape, Riddle et al. 2001; Strand et al. 2002; Poland et al. 2003; Snape et al. 2003; Bargagli 2008).

The natural environment in the Arctic has similarities to Antarctica. Like Antarctica, the Arctic is a cold, remote and challenging environment in which to operate. However, the Arctic is comprised of a cluster of landmasses which surround the Arctic Ocean rather than an isolated landmass like Antarctica. Due to its proximity to warmer continents and surrounding oceans, the Arctic is warmer, less windy and a more favourable environment for flora and fauna. The land area covered by Arctic vegetation is equivalent to 4% of the terrestrial surface of the Earth (Chapin & Körner 1995). This vegetation is largely limited to tundra regions and is strongly influenced by seasonality with plant life (grasses, flowering plants, mosses and lichen) flourishing during the spring and summer (Poland et al. 2003; Poissant et al. 2008).

The Arctic also has a large diversity of marine, bird and invertebrate inhabitants with more than 3300 insect, 300 spider, 240 bird, 75 mammal and 600 other species (consisting of amphibians, reptiles, centipedes, molluscs, oligochaetes and nematodes) residing in the Arctic (Poland et al. 2003; Wookey 2007).

Antarctica has no permanent human population and consequently there is only limited infrastructure. The majority of existing infrastructure was constructed to accommodate research activities or geopolitical events such as the International Geophysical Year in 1957–58 (Poland et al. 2003; Evans 2011; Fryirs et al. 2013). Abandoned infrastructure, buildings, fuels and waste present a major challenge for waste management in Antarctica. The attitude towards waste and abandoned buildings in Antarctica is generally dependent on the era of its establishment (Poland et al. 2003; Blanchette et al. 2004). For instance, the first forms of infrastructure in Antarctica were established by early pioneers motivated by the potential for territorial claims and national prestige (Poland et al. 2003; Blanchette et al. 2004). Therefore, the majority of buildings, relicts and artefacts from this era are perceived as historically valuable and some remain well preserved. Alternatively, buildings constructed in the mid- to late-1950s in connection with the International Geophysical Year (for example, Wilkes Station, Wilkes Land) attract varied attitudes and can be perceived as either culturally valuable or environmentally hazardous (Evans 2007, 2011; Fryirs et al. 2013) or both.

The human presence in the Arctic is also significantly different to Antarctica. The Arctic has a permanent indigenous and non-indigenous population and settlement ranges from isolated communities to cities (Poland et al. 2003; Poissant et al. 2008). Despite an on-going human presence, the human impact in the Arctic remained comparatively small until the 20th century. In contemporary times, the Arctic population and associated human and industrial activities have expanded (Poland et al. 2003). As a consequence, environmental contamination has increased and the management of contaminated land has become a serious problem (Poland et al. 2003; Poissant et al. 2008). The Arctic also has a longer historical legacy of exploration and some of this remains well preserved (Poland et al. 2003).

Environmental regulations and governance

Environmental regulations, guidelines and legislation vary significantly across the globe. In temperate regions, there are generally clear environmental guidelines for the management of contaminants.

In Antarctica, there is currently no uniform legislation, set of guidelines or legally binding process for assigning liability to environmental damage (Poland et al. 2003; Evans 2007). However, all human activities in Antarctica are governed by the Antarctic Treaty, which is facilitated through the domestic legislation of each treaty member (Snape, Riddle et al. 2001; Poland et al. 2003; Bargagli 2008). The Protocol on Environmental Protection to the Antarctic Treaty commits the Parties of the Antarctic Treaty to the protection of the Antarctic environment and its ecosystems, and designates Antarctica as a natural reserve devoted to peace and science (Snape, Riddle et al. 2001; Poland et al. 2003). Annex III to the Protocol (Waste Disposal and Management) establishes that the environment of all past and present work sites must be restored unless the site is considered to be a monument of historical value or unless disturbance would result in greater adverse impacts (Snape, Riddle et al. 2001; Poland et al. 2003; Evans 2007; Bargagli 2008; Fryirs et al. 2013; Ruoppolo et al. 2013). The Protocol also provides a framework and guidelines for waste disposal and treatment and specifies any prohibited activities such as mining and resource utilization (Poland et al. 2003; Fryirs et al. 2013).

The regulation and governance framework for contaminated site management in the Arctic is similar to countries in temperate environments, reflecting the more established and on-going human presence in the Arctic. In the Arctic, the majority of occupying nations have devised their own environmental regulations and guidelines for contaminated land management (Poland et al. 2003). Generally, this involves applying guidelines to determine whether a site can be considered contaminated; often these guidelines have different categories which apply to a specific land use status (Poland et al. 2003). It is also common in the Arctic for environmental impact assessments to be undertaken prior to remediation to allow for investigations of any post-remediation disturbances (Poland et al. 2003).

In the Arctic, many nations have passed legislation which prohibits dumping of hazardous materials and have remediation criterion for metal contamination (Poland et al. 2003; Khachaturova 2012). Also, several bilateral and multilateral agreements between nations of the Arctic exist and cover offshore activities, the management of resources and environmental issues in the Arctic (Khachaturova 2012). The establishment of the Arctic Council in 1996 has provided an intergovernmental forum for coordination amongst the Arctic nations on common issues such as sustainable development and environmental protection. The council consists of eight member nations (Norway, Denmark, Canada, Iceland, the United States, Sweden, Finland and the Russian Federation) and six working groups, one of which is the Arctic Contaminants Action Program (Khachaturova 2012). Such working groups provide increased opportunities for collaboration and coordination in the development of effective management responses to contaminated land.

Constraints associated with working in Antarctica or the Arctic

Weather, transport, human labour and financial costs all present challenges for working in polar environments and have the capacity to significantly hinder the success of remediation operations (Poland et al. 2003; Ruoppolo et al. 2013). Logistical constraints are also an important consideration when undertaking remediation operations in Antarctica and the Arctic.

Weather is a pivotal factor in any outdoor work undertaken in Antarctica and the Arctic as all modes of transport are weather dependant (Poland et al. 2003; Ruoppolo et al. 2013). Storms, blizzards, wind, fog, ice and snow can all severely disturb or cease transport operations, which can delay shipping of essential equipment (Poland et al. 2003; Hollister et al. 2007). Considering the brief nature of the Antarctic field season (approximately two to three months per year), weather can be inherently connected to the success of remediation projects.

In Antarctica, contaminated land is commonly located within close proximity to research stations (Snape, Riddle et al. 2001; Poland et al. 2003; Stark et al. 2003). This has logistical advantages and disadvantages. The chief advantage is greater access to essential infrastructure; however, essential resources and labour are in high demand throughout an Antarctic field season. This generates intense competition for time, equipment and space and can significantly hinder the ability of a team to achieve project outcomes (Poland et al. 2003; Hollister et al. 2007; Ruoppolo et al. 2013). The Arctic benefits from a closer proximity to the industrialized parts of the Northern Hemisphere, which makes obtaining equipment, labour and resources less challenging (Poland et al. 2003). However, a large portion of meta-contaminated land in the Arctic is situated in remote regions with limited access. Consequently, many of the logistical challenges faced in Antarctica persist in the Arctic (Poland et al. 2003; Filler et al. 2009).

Technologies used for contaminated land remediation also have varying logistical requirements. For example, traditional techniques used in temperate environments such as "dig and haul" require a large amount of logistical and financial support if applied in polar regions (McGowen et al. 1996; Poland et al. 2003; Filler et al. 2009). Heavy machinery, equipment, human labour and several large storage containers represent only a portion of the total support needed for such an operation (McGowen et al. 1996). Intensive operations of this nature are generally undesirable in logistically challenging polar environments. Consequently, traditional methods of remediation used in temperate environments are generally logistically impractical or inefficient and technologies which can be used on-site or in situ are preferred.

Discussion

In this section, we review technologies which can be used on-site or in situ and are suitable for the management of metal-contaminated sites in Antarctica and the Arctic. Permeable reactive barriers (PRB), chemical fixation, bioremediation, phytoremediation electrokinetic separation, land capping and lining and pump and treat systems are discussed due to, and in order of their reported application in, or potential for use in Antarctica and the Arctic (see Snape, Morris et al. 2001; Snape, Riddle et al. 2001; Poland et al. 2003; Snape et al. 2003; Bathurst et al. 2006; Filler et al. 2006; Kikuchi et al. 2006; Stevens et al. 2007; Gore 2009; Hafsteinsdóttir et al. 2011; White et al. 2012).

Permeable reactive barriers

PRB are passive barrier systems comprised of reactive materials which are installed in situ to intercept contaminated groundwater plumes. PRBs are installed down-gradient from or in the flow path of a contaminant plume. PRBs have low energy requirements making them feasible and cost-effective for long-term usage (Snape, Morris et al. 2001; Gore 2009; Higgins & Olsen 2009). When metal contaminants in the plume interact with a PRB, they react with barrier materials and are either sorbed onto PRB media or immobilized by precipitation. Barriers can be customized according to site-specific requirements and a wide range of effective barrier designs have been described (e.g., Snape, Morris et al. 2001; Babel & Kurniawan 2003; Henderson & Demond 2007; Fu & Wang 2011; Gibson et al. 2011). Selecting the most appropriate materials and design for a PRB is essential for effective long-term remediation. This is particularly relevant to polar environments where environmental factors such as inaccessibility, natural freeze–thaw cycles, slowed reaction kinetics and ice formation in barrier materials (which can temporarily or permanently alter barrier hydraulics) may significantly impede the effectiveness of remedial activities (Gore 2009).

PRBs remain an emerging technology, with only a few studies reporting on their successful use for the management of metal and petroleum hydrocarbon contaminated groundwater in cold regions, Antarctica and the Arctic (Blowes et al. 2000; Snape, Morris et al. 2001; Ludwig et al. 2002; Filler et al. 2006; Stevens et al. 2007; Kalinovich et al. 2008; Gore 2009). The main advantages of a PRB for treatment of metal-contaminated groundwater in polar regions are that they: (i) are passive low-maintenance systems which do not require power to operate; (ii) are resilient, even under extreme weather conditions; (iii) create minimal environmental disturbance; and (iv) can be decommissioned and removed when required (Snape, Morris et al. 2001; Gore 2009). However, if long-term usage of a PRB is intended, an appropriate monitoring regime is essential. Monitoring of PRBs should screen for barrier failures caused by changes in the plume flow path, damage to barrier media, media saturation and barrier congestion (Gore 2009).

The main limitations of PRBs are associated with the initial expense and challenges of installation. Also, the purpose of a PRB is to intercept contamination, rather than treat a source point. Therefore, a PRB may form a vital component in a long-term remediation strategy for a polar site but will likely form part of a treatment train with other remediation technologies (Kalinovich et al. 2008). PRBs are being continually developed to more efficiently and effectively facilitate in situ remediation of metals and can complement technologies such as chemical fixation, liners or bioremediation (Kalinovich et al. 2008). Notwithstanding some limitations, PRBs demonstrate substantial potential for the management of metal-contaminated water in Antarctica and the Arctic (Gore 2009).

Chemical fixation

Chemical fixation treatments immobilize metals in soils or sediments (Hettiarachchi et al. 2000). Fixation involves the addition of a binding agent or anion to the soil matrix to prompt chemical reactions which stimulate mineral formation (Hettiarachchi et al. 2000). Mineral formation occurs when anions react with cations to convert target metals into sparingly soluble and therefore largely inert and non-bioavailable minerals (Porter et al. 2004). Anions with the potential to form inert minerals include oxides, hydroxides, chlorides, sulphates, sulphides, phosphates, molybdites and carbonates (Porter et al. 2004). Once contaminants are converted into inert, non-bioavailable mineral forms they can be considered immobilized and their potential for environmental harm is significantly reduced (Zhu et al. 2004; Sonmez & Pierzynski 2005). Fixation is relatively cost-effective, fast and can be used at multi-metal-contaminated sites. Knox et al. (2003) reported successful immobilization of metals using fixation within seven days of reagent addition. Chemical fixation can be ideal for large-scale remediation when combined with other technologies such as PRB, phytoremediation or pump and treat systems.

Various inorganic and organic amendments have proved useful for the treatment of metals in temperate environments (US EPA 2002, 2006; Guo et al. 2006; Table 1). However, only orthophosphate-based chemical fixation treatments have been successfully trialled as an effective and economical technique for metal fixation in polar environments (Hafsteinsdóttir et al. 2011; White et al. 2012).

While an extensive literature database demonstrates the effectiveness of chemical fixation, published in situ field trials are almost absent (Hettiarachchi et al. 2000; Scheckel & Ryan 2004; Zhu et al. 2004; Sonmez & Pierzynski 2005). This presents a major shortcoming in current understanding of the technology. One of the main challenges of using chemical fixation technologies successfully is achieving homogeneity of the treatment throughout the contaminated material (Martin & Ruby 2004). Treatments can be applied to soils on-site or in situ using conventional earth-moving equipment, augers and injection grouting (Martin & Ruby 2004). However, even with these techniques it is still difficult to distribute a fixation treatment homogeneously, especially when the treated material is highly heterogeneous. Future research may provide more effective means of delivering fixation technologies in situ; in the interim this reduces its applicability in Antarctica or the Arctic.

A further difficulty associated with applying orthophosphate fixation in Antarctica and the Arctic is that reaction kinetics and formation of metal-phosphate minerals is generally slower in cold climates (Hafsteinsdóttir 2013; White et al. 2012). White et al. (2012) demonstrated the potential for fixation of metals in cold temperatures using orthophosphate but the efficacy and rate of conversion to metal-orthophosphate phases is heavily temperature dependant. The study demonstrates that Cu reacts faster with orthophosphate at 2°C than 22°C while reactions involving Pb and Zn were typically faster and more complete at 22°C than 2°C. Soil characteristics such as grain size, porosity, hydraulic connectivity, organic content and competing ion effects may also influence fixation efficiency (White et al. 2012).

Natural freeze–thaw cycling can also affect reaction rates and mineral formation and should be considered when applying orthophosphate fixation in cold environments. Temperature changes affect mineral solubility and hydration (Doner & Lynn 1989; Dietzel 2005; Hafsteinsdóttir et al. 2013) and freezing desiccates particles, thereby increasing the soluble concentrations of metals (Blackwell et al. 2010; Hafsteinsdóttir et al. 2013). This can influence reaction rates and subsequently the formation and stability of metal-phosphate minerals formed during fixation. Hafsteinsdóttir et al. (2013) examined the effects of freeze–thaw cycling during 240 freeze–thaw cycles from − 20 to + 10°C in a single metal and multi-metal system in a laboratory-based experiment. The study results indicated that in single metal systems Cu, Pb and Zn phosphates formed and were typically stable throughout the experiment, but Cu and Zn mineral formation was reduced in multi-metal systems. Competing ion effects, concentration of the phosphate treatment and amount of available water in the system were identified as possible factors for reduced fixation efficiency (Hafsteinsdóttir et al. 2013). Therefore remediation operations using orthophosphate in polar environments should be undertaken with consideration of soil character, climatic conditions and the variable reactions (reaction rates and stability of products formed) of metals to treatment with orthophosphate (White et al. 2012).

Bioremediation

Bioremediation refers to the use of biological treatments for the management and remediation of contaminated land (Tabak et al. 2005; Aislabie et al. 2006). There are various forms of biological treatments available for remediation, and selecting the appropriate form is largely dependent on the presence of appropriate microorganisms and their compatibility with the environmental

Table 1 Organic and inorganic resources available for metal immobilization.

Material	Metal	References
Lime and quicklime	Ni, Cu, Zn, Cd, Hg, Pb	Dermatas & Meng 1996; Bolan et al. 2003; Kostarelos et al. 2006
Phosphate	Cu, Zn, Cd, Pb	Ma et al. 1993; Cao et al. 2003; Basta & McGowen 2004; White et al. 2012; Hafsteinsdóttir et al. 2011
Portland cement	Cr^{3+}	Li et al. 2001; Hale et al. 2012
Bentonite	Cr, Cu, Cd	Geebelen et al. 2002; Shi et al. 2011

character of a site (Tabak et al. 2005). The three most common forms of biological treatments include biostimulation, bioaugmentation and intrinsic bioremediation (Tabak et al. 2005). Biostimulation is a method whereby bacteria are motivated to start the process of bioremediation, whereas bioaugmentation refers to the use of microorganisms to remove specific contaminants at particular sites (for instance municipal wastewater) and intrinsic bioremediation is the application of microorganisms at a site to remove harmful substances from soil and water (Tabak et al. 2005).

Bioremediation treatments rely on the use of microorganisms which reduce, eliminate, contain and transform contaminants into non-hazardous products. This is achieved by biotransformation, the process whereby microorganisms transform contaminants into non-hazardous products (Tabak et al. 2005). This requires an alteration of the structure of a compound coupled with new compound formation (Tabak et al. 2005). Biological treatments cannot degrade metals; however, they can interact with metal contaminants and alter their chemical form by changing their oxidation state via redox reactions (Tabak et al. 2005). Bioremediation can be used to immobilize metal contaminants or increase the solubility of metals to facilitate fast extraction when coupled with technologies such as pump and treat systems (Tabak et al. 2005). Increasing the solubility of metals for subsequent extraction can be achieved by microorganisms and bioleaching processes including autotrophic and heterotrophic leaching, chelation by microbial metabolites and siderophores, and methylation (Gadd 2004). These processes can prompt the dissolution of insoluble metal compounds and minerals such as oxides, phosphates, sulphides and complex mineral ores, as well as desorb metal species from exchange sites in contaminated soil (Gadd 2004). The use of bioleaching on contaminated soils is well described in the existing literature and has been applied successfully (Gadd 2004; Naresh Kumar & Nagendran 2008). However, caution should be used when undertaking bioleaching as it can prompt the solubilization of stable minerals such as pyromorphite and subsequent biogenic production of lead oxalate dehydrates (Sayer et al. 1999; Gadd 2004).

Bioremediation has been used effectively in situ at both metal and petroleum hydrocarbon contaminated sites in temperate environments (White et al. 1998; Malik 2004; Tabak et al. 2005). However, implementation of bioremediation at metal-contaminated sites in polar environments remains understudied. The main advantage of in situ bioremediation in polar environments is its potential for relatively small cost and logistical requirements compared with other remediation strategies (Tabak et al. 2005). Bioremediation can also provide benefits such as preserved structure and potential productivity of treated soil (Tabak et al. 2005; Aislabie et al. 2006). A further advantage of bioremediation is that it can be used simultaneously with other technologies such as pump and treat systems, PRB and lining systems. This can significantly increase the efficiency and effectiveness of remediation operations. The major obstacles hindering bioremediation in polar environments are extremely low and fluctuating temperatures, and nutrient deficiencies and poor water retention capacity of polar soils (Aislabie et al. 2006), which can be overcome by temperature control, fertilization and irrigation, respectively (Powell et al. 2006). Although nitrogen and phosphorus fertilizers stimulate microbial activity and cell growth in polar soils, excess application of nitrate and ammonium salts can lower soil osmotic potential and inhibit microbial activity (Walworth et al. 2005). Furthermore, many microorganisms are unable to assimilate nitrates with low uptake resulting in the pollution of ecosystems (Bell et al. 2013).

The effect of pH on bioremediation is also unclear. Ganzert et al. (2011) reported that the effect of pH on bacterial communities is insignificant in polar soils; however, Bell et al. (2013) argued that optimal microbial functioning occurs where soil pH is 6 or higher. To reduce such uncertainties and optimize treatment efficiency, it may be useful to undertake laboratory-based trials prior to field implementation.

Importing foreign taxa into Antarctica to enhance the microbial transformation of metals is prohibited by the Protocol on Environmental Protection to the Antarctic Treaty without an approved permit. Permits will only be issued for the introduction of a non-native organism for experimental scientific use and where adequate controls are in place to prevent escape or release into the Antarctic environment (Subsection 10 [3A], Antarctic Treaty [Environment Protection] Amendment Act 2010). Therefore knowledge of site characteristics, the parameters that affect microbial interaction with metals and an appropriate level of authorization is required prior to undertaking bioremediation activities in Antarctica. Since warming climates in Antarctica and the Arctic may also produce more active microbial populations, further research into microbial activity may discover additional biotechnological opportunities in relation to metal contamination (Bell et al. 2013).

Phytoremediation

Phytoremediation refers to the use of crops or plants that accumulate and immobilize metals, or grow in and stabilize metal-contaminated soil, for the remediation of contaminated land (Brown et al. 1994; Martin & Ruby

2004). There are several types of phytoremediation techniques applicable to metal-contaminated sites; the two most common types are phytoextraction and phytostabilization (Kikuchi et al. 2006; Alkorta et al. 2010). Phytoextraction uses plants to uptake and accumulate contaminants. Once metals are accumulated in a plant they are harvested, and successive crops are grown until the concentration of the contaminant is lowered and the soil is considered remediated (Brown et al. 1994). Effective phytoextraction generally requires consecutive crops and multiple years of planting, harvesting and monitoring (Brown et al. 1994; Alkorta et al. 2010).

Alternatively, phytostabilization refers to the use of metal-tolerant plants to prevent erosion and transport and leaching of contaminants (Alkorta et al. 2010). Establishing sufficient crop cover as part of phytostabilization remediation prevents dispersion of contaminated soil and simultaneously improves soil quality by increasing organic content, nutrient levels, cation exchange capacity and microbial activity (Vangronsveld et al. 1995; Arienzo et al. 2004; Alkorta et al. 2010). Plant selection is a crucial aspect of metal phytostabilization techniques and can significantly influence remediation outcomes. Ideally, plants used for stabilization should be capable of developing an extensive root system and a large amount of biomass in the presence of high concentrations of metals. Plants which can maintain minimal root-to-leaf translocation are beneficial in order to prevent transfer of metals into the animal food chain.

Phytoremediation is desirable since: (i) it can be used to facilitate in situ remediation with minimal disturbance to the natural environment; (ii) it is cost effective for larger sites characterized by low to moderate levels of contamination; (iii) it can be used on a large range of contaminants; (iv) following treatment the topsoil soil can remain in situ and is generally in a usable condition; (v) it can reduce erosion by increasing the stability of soil; and (vi) accumulation of metals from groundwater in plants can reduce contaminant migration (Mulligan et al. 2001; Khan et al. 2004).

Effective use of in situ phytoremediation in temperate environments is well reported (Brown et al. 1994; Martin & Ruby 2004; Kikuchi et al. 2006). Several studies have also demonstrated the potential for phytoremediation for hydrocarbon remediation in the Arctic, but there are few studies which report its effectiveness for metal-contaminated sites in polar environments. A pilot trial of phytoremediation in the Arctic by Kikuchi et al. (2006) reported successful phytostabilization of metal contaminants with nickel and copper concentrations in the leaves of willow trees increasing by 208 and 257 times, respectively, within 12 months. This study indicates that phytoremediation displays potential for the remediation of metal-contaminated sites in polar environments. However, further studies investigating its effectiveness for a wider range of metals under different conditions will increase current understanding of the wider potential of this technology.

The effectiveness of phytoremediation will vary depending on the concentration and mineralogical form of metals present, depth of the contaminant plumes and climatic conditions and soil moisture characteristics at a site; all of which impact on the growing potential of plants (Martin & Ruby 2004). Finding plants with a sufficient amount of aboveground biomass for harvesting is also an issue in the Arctic, where many of the plants are too small to facilitate efficient phytoremediation. Lunney et al. (2004) demonstrated the potential of *Cucurbita pepo* species for phytoremediation and attributed their performance to high transpiration volume, large aboveground biomass and composition of root exudates. The Arctic environment is also very diverse, thus selecting the most appropriate plants for phytoremediation is heavily influenced by site-specific factors such as available species, environmental conditions and the contaminants present (Lunney et al. 2004). Implementing phytoremediation in Antarctica is less feasible than in the Arctic due to the harsher climate, absence of native plants appropriate for phytostabilization or extraction and strict quarantine requirements (Poland et al. 2003). Disposal of harvested plant material can also be problematic. The Antarctic Treaty prohibits the introduction of non-indigenous plant species without a permit. A final disadvantage of phytoremediation is that it generally requires multiple growing seasons before significant reductions in contaminant concentrations can be detected (Khan et al. 2004).

Electrokinetic separation

Electrokinetic remediation of metals requires the application of a direct, low-intensity electric current through electrodes installed in a contaminated soil. These electrodes typically consist of cathode and anode arrays (Virkutyte et al. 2002; Martin & Ruby 2004; US EPA 2006). Electrochemical and electrokinetic processes are stimulated when direct current is applied and migration of charged metal ions occurs. Positive ions become attracted to the negatively charged cathode, and negative ions move toward the positively charged anode. The direction and magnitude of contaminant migration generated by electrokinetic remediation is influenced by contaminant concentrations, mobility of contaminant ions, soil type, heterogeneity and structure, pH, grain size and the mobility and the conductivity of the soil pore water, all of which influence the capacity for ionic migration (Virkutyte et al. 2002).

Effective electrokinetic remediation will separate metals and enable metal extraction for on-site or ex situ treatment or storage (Martin & Ruby 2004; US EPA 2006). Electroplating, precipitation or co-precipitation at the electrode or complexing with ion exchange resins may also follow metal-contaminated groundwater extraction (Virkutyte et al. 2002). Adsorption onto the electrode may also be possible, however, this requires an increase in the valencies of ionic species near the electrode to occur (which largely depends on soil pH) to enhance the capacity for adsorption (van Cauwenberghe 1997).

Electrokinetic remediation is effective for Ni, Cu, Zn, As, Hg, Pb, cyanides and is suitable at sites with contaminant concentrations in the range of 100–10,000 mg/L (Virkutyte et al. 2002). Electrokinetic remediation may also be successfully coupled with other in situ technologies such as PRB and phytoremediation (see Cang et al. 2011).

Electrokinetic remediation can be used in both saturated and unsaturated soils but is most efficient in soils where metal contaminants are highly soluble or overshadowed by other cations (Virkutyte et al. 2002; US EPA 2006). Where metal contaminants are insoluble, the efficiency of electrokinetic remediation can be enhanced by the addition of conditioning fluids or surfactants such as ammonia or sodium acetate which improve metal recoveries by increasing the fraction of metals in solution (Clifford et al. 1993; Mohamed 1996). Conditioning fluids and surfactants should be used only with extreme caution due to their potential to mobilize metals, which in the absence of a pump and treat system or permeable reactive barrier could be potentially damaging to the environment (Martin & Ruby 2004).

Electrokinetic remediation is generally less effective for near-surface contamination, larger sites or at sites where soil moisture content is $<10\%$, subsurface metal structures or utilities are present or at sites characterized by extensive soil heterogeneity or significantly varying concentrations of several metal contaminants (Virkutyte et al. 2002; Martin & Ruby 2004; US EPA 2006). The performance of electrokinetic remediation is also reduced at sites where non-aqueous phase liquids co-exist with metals as insoluble organics are not ionized by electrokinetic remediation and the soils in contact with them are not charged, thereby preventing their movement and removal by this technique (Virkutyte et al. 2002). In cold regions further complications may arise as a result of increased water viscosity or freezing which may hinder the kinetics of this technique by slowing reactions or reducing migration potential.

Several factors should be considered before undertaking in situ electrokinetic remediation. These factors include site-specific conditions such as soil character, contaminant types, speciation and concentrations of metals present and temperature. Factors such as the decontamination time are also important for forecasting power consumption and preventing reverse electroosmotic flow (flow from the cathode to the anode) which may instigate recontamination (Baraud et al. 1997; Baraud et al. 1998; Virkutye et al. 2002). To ensure the appropriateness of electrokinetic remediation in the context of a particular site, it is important that a thorough site assessment and consideration of the above factors is conducted prior to field implementation.

There are currently no published in situ field trials of electrokinetic remediation systems at metal-contaminated sites in polar environments. However, studies from temperate environments provide insight into the applicability of this technique in polar environments (see Acar & Gale 1995; Baraud et al. 1997; Baraud et al. 1998; Virkutyte et al. 2002; Kim et al. 2002, 2005; Hansen et al. 2013). In polar environments such as Antarctica and the Arctic, low soil moisture content, freezing groundwater, presence of hydrocarbons and buried metals at landfill sites may reduce the feasibility of this technology (Acar & Gale 1995; Virkutyte et al. 2002). Some of these limitations may be overcome with site-specific adaptations to factors such as electrode spacing. However, a pilot scale field trial to ensure the appropriateness of this technology prior to field implementation would be advantageous (Virkutyte et al. 2002).

Land capping and lining

Land capping and lining technologies (LCLs) are one of the most common technologies used for on-site contaminated land management in temperate environments (Lee & Jones-Lee 1996; McGowen et al. 1996). LCLs are widely used due to their ability to contain a contaminant source and minimize the exposure impacts of contaminants in a timely and cost effective manner (Lee & Jones-Lee 1996; McGowen et al. 1996; Meegoda et al. 2003). LCLs can also be used to increase soil shear strength and slope stability (Lee & Jones-Lee 1996). LCLs are often uniquely designed to cater for site-specific requirements and range from one-layer systems of vegetated soil to complex multi-layer systems comprised of soils and geosynthetic materials (Lee & Jones-Lee 1996; Bathurst et al. 2006; Kalinovich et al. 2008).

Field implementations of lining systems are reported for temperate environments and the Arctic for containment of metals, hydrocarbons and polychlorinated biphenyls (McGowen et al. 1996; Bathurst et al. 2006; Kalinovich et al. 2008; Baldwin et al. 2010). Lining systems have also been used for land farming and have been successfully coupled with PRB, bioremediation and phytoremediation for hydrocarbon contamination (McCarthy et al. 2004; Filler et al. 2006; Kalinovich et al. 2008). Currently there are no published studies which report on successful management of metal-contaminated land using lining systems in Antarctica.

Various factors must be considered when implementing an LCL. Material permeability, soil hydraulics, drainage pathways, mobility of contaminants and longevity of materials are critical (McCarthy et al. 2004). Lining systems installed in polar regions are more susceptible to material failure due to excessive wind, natural freeze–thaw cycling and prolonged periods of intense UV exposure (Kalinovich et al. 2008). If not maintained properly, material failure may result in the release of toxic leachate. Also, LCLs do not treat the source point of contamination, so effective containment or remediation using liners relies on coupling this technology with other complementary techniques. These problems are manageable with a rigorous monitoring and maintenance regime. However, this may reduce LCL feasibility in polar regions.

Pump and treat

Pump and treat systems are one of the most common technologies used for metal-contaminated groundwater extraction (Higgins & Olsen 2009). Pump and treat systems are designed to contain and control the movement of contaminated groundwater, reduce contaminant migration and reduce dissolved contaminant concentrations to restore the environmental health of a contaminated aquifer (US EPA 2003; Higgins & Olsen 2009). These systems operate by extracting contaminated groundwater via extraction wells, typically with submersible pumps (Higgins & Olsen 2009). Contaminated groundwater is extracted and then purified by filtration, precipitation and ion exchange/adsorption media which remove the contaminants from the groundwater (Higgins & Olsen 2009). These technologies are most effective when combined with others that isolate or remove the contamination from its source point thus preventing recontamination of groundwater (US EPA 2003). Due to a paucity of groundwater in freezing ground, pump and treat systems are limited in their potential for usage in Antarctica and the Arctic. However, pump and treat systems can be complementary to technologies such as electrokinetic separation and bioremediation which can mobilize target contaminants towards an extraction point.

Pump and treat systems are expensive to install and operate with a continual energy supply required during remedial activities (US EPA 2003, 2009). Operational costs will increase substantially when installed in logistically challenging and remote polar environments. Disposal of contaminated wastewater extracted by pump and treat systems is also a problem and reduces the feasibility of this remedial technique (US EPA 2009). Successful remediation using only pump and treat systems is unlikely, especially at sites where non-aqueous phase liquids are present (US EPA 2003EPA 2009; Higgins & Olsen 2009). In Antarctica and the Arctic it is common for hydrocarbon and metal contamination to coexist at contaminated sites and consequently this presents a serious limitation for efficient remediation (Riis et al. 2002). Despite these limitations, pump and treat systems have been demonstrated to effectively remove contaminated groundwater and can be useful when combined with other technologies which address source point contamination (US EPA 2003).

Conclusions

A range of new and innovative remediation technologies useable on-site or in situ, which are effective despite the challenges associated with operating in polar environments, are being developed or adapted for use at metal-contaminated sites. While each of the reviewed technologies demonstrates advantages, none are without limitations. Furthermore none of the reviewed technologies appear to be capable of independently remediating a metal or mixed metal–hydrocarbon contaminated site in a timely and affordable manner (Virkutyte et al. 2002). This is particularly the case for sites contaminated with multiple metals, organic contaminants and non-aqueous phase liquids. Therefore, effective management of contaminated land in polar environments may require several technologies used simultaneously (Virkutyte et al. 2002) or in sequence in a treatment train. This is due to both the current capacity of the technologies available as well as the operational complexities associated with operating in Antarctica or the Arctic.

The poor understanding of metal-contaminated land management in polar regions has resulted from a shortage of published studies detailing the interactions between in situ technologies and their potential for collective implementation and treatment. Using a combination of technologies can facilitate faster and more effective remediation of contaminants in both soil and groundwater, particularly at multi-metal-contaminated sites and at sites where metal contaminants and non-aqueous phase liquids coexist. This has critical importance in remote environments where access to sites is often short and infrequent. Another factor limiting current knowledge of remediation technologies in Antarctica and the Arctic is the lack of, or in some instances complete absence of published in situ field trials of remedial technologies. This is particularly relevant to Antarctica.

There are clear logistical and environmental advantages associated with adopting in situ technologies, and as a result they are preferable in remote, polar environments. Of the technologies discussed in this review; bioremediation, chemical fixation and PRBs appear to be particularly promising (Tabak et al. 2005; Kalinovich et al. 2008; Gore 2009; Hafsteinsdóttir et al. 2011). However, further research and field trials are required to further understand the factors influencing their wider applicability and overall performance under freezing conditions. Due to the remaining uncertainty associated with many emerging technologies they should only be applied in situ after thorough consideration of factors such as metal concentrations, mobility and speciation, soil characteristics, climate, logistical constraints and relevant regulations (Poland et al. 2003). A thorough site assessment, understanding of the contaminants at a given site and understanding of technology limitations is essential prior to commissioning in situ remediation. Such information should provide the justification for and guide the development of an appropriate strategy for in situ remediation. Remediation in polar environments remains an arduous task. However advances in science and engineering continually contribute to the development of more efficient techniques for in situ remediation at metal-contaminated sites.

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