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RESEARCH/REVIEW ARTICLE

On-site and in situ remediation technologies applicable to petroleum hydrocarbon contaminated sites in the Antarctic and Arctic

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Abstract

Petroleum hydrocarbon contaminated sites, associated with the contemporary and legacy effects of human activities, remain a serious environmental problem in the Antarctic and Arctic. The management of contaminated sites in these regions is often confounded by the logistical, environmental, legislative and financial challenges associated with operating in polar environments. In response to the need for efficient and safe methods for managing contaminated sites, several technologies have been adapted for on-site or in situ application in these regions. This article reviews six technologies which are currently being adapted or developed for the remediation of petroleum hydrocarbon contaminated sites in the Antarctic and Arctic. Bioremediation, landfarming, biopiles, phytoremediation, electrokinetic remediation and permeable reactive barriers are reviewed and discussed with respect to their advantages, limitations and potential for the long-term management of soil and groundwater contaminated with petroleum hydrocarbons in the Antarctic and Arctic. Although these technologies demonstrate potential for application in the Antarctic and Arctic, their effectiveness is dependent on site-specific factors including terrain, soil moisture and temperature, freeze–thaw processes and the indigenous microbial population. The importance of detailed site assessment prior to on-site or in situ implementation is emphasized, and it is argued that coupling of technologies represents one strategy for effective, long-term management of petroleum hydrocarbon contaminated sites in the Antarctic and Arctic.

The management of petroleum hydrocarbon contaminated sites is an ongoing environmental, scientific and engineering issue (Poland et al. 2003; Filler et al. 2006). Petroleum products are the principal energy source in the Antarctic and Arctic and represent the primary source of hydrocarbon contamination in these regions (Snape et al. 2001; Poland et al. 2003; Filler et al. 2006). Petroleum hydrocarbons exist as light and dense non-aqueous phase liquids and are introduced into the environment through natural seepage and fuel spills (Leewis et al. 2013). Fuel spills in the Antarctic and Arctic typically occur alongside natural resource exploration or during the extraction, transportation and storage of petroleum hydrocarbons, often as a consequence of infrastructure failure or human error (Poland et al. 2003; Yang et al. 2009; Manzetti 2014).

The environmental effects of petroleum hydrocarbon contamination are well understood in temperate regions but remain understudied in cold regions (Filler et al. 2006; Yang et al. 2009). Managing petroleum hydrocarbon contaminated soil in remote, cold regions such as the Antarctic and Arctic can often be confounded by a lack of infrastructure, logistical constraints and extreme weather (see Poland et al. 2003; Filler et al. 2006;

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Camenzuli et al. 2013 for detailed reviews). The financial expense associated with implementing traditional remediation approaches in remote, cold regions can also be significant (Poland et al. 2003; Camenzuli et al. 2013; Leewis et al. 2013). These obstacles have the potential to lengthen timeframes for remediation or entirely prevent the commencement of remediation operations at petroleum hydrocarbon contaminated sites in the Antarctic and Arctic (Poland et al. 2003; Filler et al. 2006; Camenzuli et al. 2013).

Remediation in the Antarctic and Arctic has traditionally relied upon ex situ remediation strategies which require the removal of contaminated material by excavation with subsequent treatment or off-site storage (Deprez et al. 1999; Martin & Ruby 2004; Harms & Wick 2006; Camenzuli et al. 2013). Ex situ remediation approaches can be advantageous in the presence of severe contamination of highly hazardous compounds (Tomei & Daugulis 2013). However, such approaches are expensive, logistically inefficient and may result in further damage to the natural environment. For instance, excavation can result in the re-suspension of contaminants and can instigate permafrost melt, which may result in altered groundwater flow, soil shrinkage, land slumping or salinization (Aislabie et al. 2004; Martin & Ruby 2004; Perelo 2010; White et al. 2012; Camenzuli et al. 2013). Site degradation associated with excavation represents a serious concern, particularly in Antarctica, where the Protocol on Environmental Protection to the Antarctic Treaty (also known as the Madrid Protocol; 1998) stipulates that remediation operations must not result in greater environmental impacts than the "do nothing" approach (SCAR 1993). In response, there is a need to adapt existing technologies or develop new, safe, efficient and cost-effective approaches for managing petroleum hydrocarbon contaminated soil in cold regions.

Recent developments in science and engineering have adapted existing technologies and provided new, effective technologies for contaminated site management (Filler et al. 2006). However, many of these technologies remain in their developmental stages with further research required before they can be considered to be environmentally safe or reliable over extended timeframes (Snape et al. 2001; Filler et al. 2006; Yang et al. 2009; Camenzuli et al. 2013). A benefit of many of the technologies currently being adapted or developed for use in the Antarctic or Arctic is that they can be applied on-site or in situ which is logistically favourable, less disruptive to the environment and minimizes the need for transporting contaminated material or generating additional waste disposal sites (Martin & Ruby 2004; Filler et al. 2006; Perelo 2010).

Technology coupling is also advantageous and can increase the efficiency and spectrum of contaminated site management (Tomei & Daugulis 2013). Technology coupling is particularly favourable at sites co-contaminated with metals and petroleum hydrocarbons, where remediation of co-contaminated soil by the use of a single technology is challenged by the unique and occasionally conflicting chemistry, toxicity and remediation requirements of individual pollutants (Dong et al. 2013). Furthermore, the biodegradation of petroleum hydrocarbons can be suppressed in the presence of metal contaminants which can inhibit the activity of degrading bacteria (Al-Saleh & Obuekwe 2005; Alisi et al. 2009; Dong et al. 2013). Technology coupling may also be required at highly heterogeneous sites, that is, characterized by variable subsurface flow rates, soil types or an uneven distribution of contamination (Filler et al. 2006; Camenzuli et al. 2013). Therefore, it is essential to develop an understanding of the capability of each technology for use independently or for coupled use by either simultaneous application or as a component in a treatment train (Jackman et al. 2001; Cang et al. 2011; Camenzuli et al. 2013).

This article reviews five technologies that are being adapted for on-site or in situ remediation of soils contaminated with petroleum hydrocarbons in the Antarctic and Arctic, namely, bioremediation, landfarming, biopiles, phytoremediation and electrokinetic remediation. Permeable reactive barriers (PRBs) are also reviewed in their potential to capture and remove petroleum hydrocarbons from groundwater in the Antarctic and Arctic. These six technologies were selected because of their suitability to cold regions and because of the high level of interest in the applicability of these technologies to the Antarctic and Arctic, as demonstrated by recent research (Aislabie et al. 2004; Filler et al. 2006; Camenzuli et al. 2013; Leewis et al. 2013; Mair et al. 2013; Mumford et al. 2013). Current research surrounding the aforementioned technologies is reviewed with respect to their purpose, advantages, limitations and potential for long-term management at petroleum hydrocarbon contaminated sites in the Antarctic and Arctic. In instances where a shortage of research in the Antarctic and Arctic exists, recent research from temperate, alpine and lower latitude cold environments with relevance to the Antarctic and Arctic is considered and discussed.

Petroleum hydrocarbon contaminated soil in the Antarctic and Arctic

Petroleum hydrocarbon contamination in Antarctica is typically concentrated around active and abandoned

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research stations (Snape et al. 2001; Poland et al. 2003; Stark et al. 2003; Curtosi et al. 2007). Snape et al. (2001) identified petroleum-derived contamination as the most significant environmental pollution issue in the Antarctic. In recent years, several studies describing the distribution and environmental effects of petroleum-derived contamination at Antarctic research sites have addressed localized contamination at the US McMurdo Station, Australia's Casey Station, the British Rothera Station and New Zealand's Scott Base (Deprez et al. 1999; Snape et al. 2001; Poland et al. 2003; Saul et al. 2005; Stark et al. 2006; Klein et al. 2012).

In the Arctic, exploration, extraction and transport of petroleum reserves are the primary sources of petroleum hydrocarbon contamination (Poland et al. 2003; Aislabie et al. 2004; Fritt-Rasmussen et al. 2012; Akbari & Ghoshal 2014; Manzetti 2014). In Alaska alone, 407 spills were reported between 1996 and 1999 and more than 1000 hydrocarbon contaminated sites have been reported in areas coordinated by the US Department of Defence (Reynolds & Koenen 1997; Poland et al. 2003; Yergeau et al. 2012; Leewis et al. 2013).

Soils contaminated with petroleum hydrocarbons in cold regions vary to those in temperate regions in several ways. First, lower temperatures can result in increased hydrocarbon viscosity, reduced evaporation of volatiles and decreased water solubility, all of which challenge the potential for natural attenuation (Atlas 1991; Margesin & Schinner 2001; Filler et al. 2006). Light fuels with a high vapour pressure such as aviation fuel readily volatilize from Antarctic soil (Webster et al. 2003; Aislabie et al. 2004). However, because of their low viscosity, they are more mobile and therefore capable of migrating through unfrozen soil (Gore et al. 1999; Webster et al. 2003; Aislabie et al. 2004). Heavier fuels such as engine oil are less volatile and demonstrate slower migration rates through unfrozen soil due to a higher viscosity (Gore et al. 1999; Aislabie et al. 2004). Decreased water solubility at low temperatures can also result in the transport of free-phase petroleum hydrocarbons, challenging the toxicity thresholds of hydrocarbon degraders and surrounding ecosystems (Brakstad 2008).

Second, natural freeze–thaw processes can instigate effective soil displacement, altering the movement of petroleum hydrocarbons in areas of freezing ground (Balks et al. 2002; Filler et al. 2006; Curtosi et al. 2007; Siciliano et al. 2008). Soil displacement can enhance the commonly uneven distribution of petroleum hydrocarbons, associated with the history of contamination and preferential contaminant sorption to soil constituents, potentially reducing contact between petroleum hydrocarbons and microorganisms (Harms & Wick 2006). Upon thawing of the active soil layer, downward migration of petroleum hydrocarbons may be limited by an ice-lens that often forms at the top of the permafrost (Chuvilin et al. 2001; Aislabie et al. 2004; Filler et al. 2006). Studies in the Arctic demonstrate that petroleum hydrocarbons can move through these ice-lenses into frozen soil via cracks, fissures and unfrozen pore water, resulting in the migration of fuel into previously uncontaminated soils (Aislabie et al. 2004). Petroleum hydrocarbon contamination has also been observed to significantly influence the liquid water content in frozen soils, influencing secondary frost heave and the accumulation of segregated ice seams (Siciliano et al. 2008). Similarly, petroleum hydrocarbons in sandy Arctic soils exposed to freeze–thaw can move ahead of the freezing front, implying that when soils are cooled from the surface down through the active layer, hydrocarbons can migrate toward the permafrost (Chuvilin et al. 2001; Aislabie et al. 2004). Dissolved and particle-associated petroleum hydrocarbons in surface and subsurface soils can also be mobilized upon thawing and have the potential to migrate to offshore marine environments (Kennicutt & Sweet 1992; Deprez et al. 1999; Snape et al. 2001; Aislabie et al. 2004).

Residual petroleum hydrocarbons in soil are also an issue in cold regions and have been found to contaminate soils for more than 40 years at Antarctic research stations such as McMurdo and Wilkes, which were established during the International Geophysical Year of 1958 (Aislabie et al. 2004; Klein et al. 2012; Fryirs et al. 2013; Fryirs et al. 2014). Detailed descriptions on the impact of petroleum hydrocarbon contamination on natural thermal and moisture regimes, soil pH and nutrient activity in cold regions are reported elsewhere (Atlas 1981; Grechishchev et al. 2001; Balks et al. 2002; Filler et al. 2006).

Remediation technologies applicable to soil

Bioremediation

Bioremediation can provide an environmentally sensitive and cost-effective method for in situ remediation of petroleum hydrocarbon contaminated soil in the Antarctic and Arctic (Mair et al. 2013; Tomei & Daugulis 2013). Bioremediation aims to accelerate the rate of natural attenuation of petroleum hydrocarbons by optimizing environmental conditions for microbial activity (Greer et al. 2010). Successful bioremediation of petroleum hydrocarbon contaminated soils in the form of biostimulation and bioaugmentation has been widely reported in the Antarctic and Arctic (Brakstad 2008; Filler et al. 2008; Bej et al. 2010; Greer et al. 2010; Rayu et al. 2012).

Biostimulation. Biostimulation of indigenous soil microorganisms through nutrient addition and optimization of environmental conditions such as oxygen content, pH and temperature has been well reported in cold regions (Delille et al. 2003; Walworth et al. 2007; Das & Chandran 2011; Dias et al. 2012; Mair et al. 2013). In the Antarctic, limited nitrogen, cold temperatures and water availability contribute to significantly slower degradation rates of total petroleum hydrocarbons (TPH), relative to temperate regions (Ferguson et al. 2003; Walworth et al. 2007).

Okere et al. (2012) investigated the natural attenuation potential of indigenous microorganisms on Livingstone Island, Antarctica, for degradation of ^{14}C-labelled phenanthrene at 4, 12 and 22°C. The results provided evidence of evaporation but little biodegradation at 4°C, consistent with previous findings (Snape et al. 2005; Snape et al. 2006; Revill et al. 2007; Dias et al. 2012). However, the addition of nitrogen, peaking in the range 1000–1600 mg N kg-soil-H_2O^{-1} enhanced the mineralization of ^{14}C-octadecane in soils from Old Casey Station, Antarctica (Ferguson et al. 2003). Ratios of n-C17/pristane and n-C18/phytane indicated that low nutrient levels were the primary limiting factor for biodegradation, rather than water availability (Ferguson et al. 2003). In a similar field trial at Old Casey Station, Powell et al. (2006) observed increased hydrocarbon degradation following nutrient addition in both anaerobic and aerobic soils, reporting an increase in the abundance of denitrifying microorganisms. Their study demonstrated that when the denitrifying community is exposed to oxygen, hydrocarbon degradation in Old Casey soils is suppressed (Powell et al. 2006). Similarly microbial respiration, and corresponding petroleum hydrocarbon degradation, was maximized at 604 mg N kg-soil-H_2O^{-1} in sub-Antarctic soils (Walworth et al. 2007). Alternatively in petroleum hydrocarbon contaminated soils in the Géologie Archipelago (Terre Adélie, Antarctica), little difference in hydrocarbon-utilizing microbial assemblages was detected in nutrient amended and non-nutrient amended plots (Delille et al. 2003). The inhibitory effects of excess nutrient addition on soil osmotic potential and its implications for biodegradation of petroleum hydrocarbons have been well reported in sub-Antarctic soils (Walworth et al. 2006, 2007).

Analyses of microbial communities at several sites in the Northern Hemisphere indicate the presence of indigenous cold-adapted hydrocarbon-degrading microorganisms capable of facilitating bioremediation by biostimulation (Rike et al. 2001; Rike et al. 2003; Paudyn et al. 2008; Chang et al. 2010; Bell et al. 2013). Mair et al. (2013) reports that nutrient addition at 20°C removed >90% of soil TPH, whereas only 69% TPH removal was reported at 10°C at a former alpine military site in Italy (Mair et al. 2013). The influence of temperature on microbial metabolism is well documented (Leahy & Colwell 1990; Delille 2000), with microbial metabolism doubling for every 10°C increase in temperature between 10°C and 40°C (Delille 2000). Alternatively, Rike et al. (2003) observed biodegradation at sub-zero temperatures, inferring that zero degrees may not be the limit for bioremediation in the Arctic. Børresen et al. (2007) also observed mineralization of hexadecane and phenanthrene in both nutrient amended and non-nutrient amended Arctic soil at −5°C. The presence of hydrocarbon degrading bacterial populations in permafrost soils from a petroleum hydrocarbon contaminated site in the Norwegian archipelago of Svalbard further support claims of biodegradation below 0°C (Børresen et al. 2003).

Chang & Ghoshal (2014) applied respiratory quotients to link measured CO_2 and O_2 to biodegradation of petroleum hydrocarbons in soils from Nunavut, Canadian Arctic. Through assessment across various soil types, nutrient treatments and temperature regimes (including freeze–thaw), respiratory quotient values proved to be feasible for tracking the biodegradation of petroleum hydrocarbons in cold climates (Chang & Ghoshal 2014). Similarly respirometry, accompanied by TPH analyses, also assisted in the investigation of comparative biodegradation rates of diesel and synthetic diesel in Alaskan soils (Horel & Schiewer 2009). Results at 6°C indicate <5% mineralization of diesel fuel while synthetic diesel reported consistent degradation across a four-week study (Horel & Schiewer 2009). Furthermore, biodegradation of synthetic diesel was accelerated by 50% following nutrient addition over unamended soils spiked with synthetic diesel (Horel & Schiewer 2009).

In addition to nutrient application, injection of air into the subsurface at low flow rates, referred to as bioventing, can enhance bioremediation of petroleum hydrocarbons (Filler et al. 2006). However under low oxygen conditions, bacterial communities have demonstrated ongoing petroleum hydrocarbon degradation (Powell et al. 2006) and utilization of iron, manganese and sulphate as electron acceptors has been identified (Walworth et al. 2013; Yeung et al. 2013). Implementation of a "microbioventing" system (comprising small air injection rods) in the sub-Antarctic successfully enhanced biodegradation rates to 10–20 mg/kg per day under unamended aerobic conditions (Rayner et al. 2007). This study suggests that from a peak concentration of 7000 mg/kg TPH, concentrations of ca. 200 mg/kg TPH could be achieved within one or two years of continual operation. A laboratory incubation study on petroleum hydrocarbon contaminated soils from Macquarie Island indicates that oxygen levels of 10.4% maximized biodegradation of petroleum hydrocarbons, providing target concentrations for bioventing in sub-Antarctic soils (Walworth et al. 2013).

In soils from the Canadian High Arctic, Sanscartier et al. (2011) found that high air flow resulted in degrader counts two orders of magnitude larger and TPH biodegradation 50% greater than under low aeration at 7°C. This high aeration rate was equivalent to that used in a field-scale heated biopile system (Sanscartier et al. 2009). Similarly, King et al. (2014) found that bioventing was most effective (82.0–92.5% hydrocarbon removal) when soil at 10°C was amended with nutrients and strongly aerated (275 cm^3/min). King et al. (2014) also observed that freshly contaminated soil is not as amenable to bioventing as acclimated soil, suggesting that aeration is most effectively applied two to three years following a spill in cold climates.

While biostimulation in petroleum hydrocarbon contaminated marine sediments remains to be trialled, investigation of biodegradation in polar marine sediments has been addressed (Filler et al. 2006). As part of a five-year investigation into the impacts of Special Antarctic Blend (SAB) diesel on the seabed of O'Brien Bay, near Casey Station, Antarctica, Woolfenden et al. (2011) observed TPH removal rates of 245 mg/kg per year in marine sediment spiked with SAB. While concentrations fell markedly from 2020 ± 340 to 800 ± 190 mg/kg, after five years the SAB-spiked sediment was still contaminated relative to natural organic matter (160 ± 170 mg/kg) (Woolfenden et al. 2011). These findings are consistent with Powell et al. (2007), who observed that the longevity of hydrocarbons in Antarctic marine sediments can be variable, even within a relatively small geographical area. Associated with this five-year investigation at O'Brien Bay, Thompson et al. (2006) investigated the biodegradation of used, unused and biodegradable lubricants in marine sediments. After five weeks, a 37% decrease in the concentration of biodegradable lubricants was observed while used and unused lubricant concentrations decreased by 20%. Failure of the biodegradable lubricant to break down to recognized biodegradable thresholds and the resistance of lubricant additives, alkylated naphthalenes and diphenylamines, to degradation presented concerns because of their environmental toxicity (Thompson et al. 2006). Antarctic marine bacteria isolated from Terra Nova Bay have also shown to exhibit gradual mineralization of diesel at 4°C, with 57% degraded compared to 86% degraded at 20°C following 60 days incubation (Michaud et al. 2004).

Bioaugmentation. Bioaugmentation can encompass the addition of a pre-adapted bacterial strain, addition of a pre-adapted consortium or introduction of genetically engineered bacteria to target specific contaminants at a site (Tyagi et al. 2011). Characterization of hydrocarbon-degrading microorganisms in Antarctic soils demonstrates that isolation of psychrotolerant bacteria capable of metabolizing petroleum hydrocarbons in pure cultures can assist in the development of tailored bacterial formulae for bioaugmentation (Sutton et al. 2013; Vázquez et al. 2013). Stallwood et al. (2005) isolated *Pseudomonas borealis* from clean and petroleum hydrocarbon contaminated soils of the South Orkney Islands, Antarctica. Application of *Pseudomonas borealis* to petroleum hydrocarbon spiked microcosms resulted in a mean decrease in alkanes (C_{16}–C_{20}) by 45% after 18 weeks (Stallwood et al. 2005). However in microcosms where biostimulation (nutrient addition) and bioaugmentation with *P. borealis* were coupled, 100% removal in alkanes was recorded. Kauppi et al. (2011) observed accelerated biodegradation following nutrient addition to diesel contaminated boreal soil, while microbial inocula alone did not significantly degrade diesel fuel. Similarly, in small-scale biopiles comprising Arctic soil contaminated with weathered diesel fuel, Thomassin-Lacroix et al. (2002) reported no significant difference between TPH concentrations in control versus inoculated biopiles at 7°C across 65 days.

Ruberto et al. (2003) isolated *Acinetobacter* sp. from jet-fuel and gas–oil contaminated soils from King George Island, Antarctica. In microcosms inoculated with *Acinetobacter* sp. and contaminated soil, a decrease in contaminant concentration of 75% was recorded after 50 days (Ruberto et al. 2003). In contrast to Stallwood et al. (2005), addition of nitrogen and phosphorus to microcosms did not influence biodegradation beyond 75% after 50 days. Madueño et al. (2011) also found that *Sphingobium* sp., isolated from polyaromatic hydrocarbon contaminated soils in central Patagonia, Argentina, could be suitable for bioaugmentation in cold region soils. Species such as *Pseudomonas* sp., *Acinetobacter* sp. and *Sphingobium* sp. suggest that hydrocarbon degraders are components of indigenous Antarctic and Arctic microbial communities, potentially combating quarantine restrictions associated with the introduction of non-indigenous microorganisms to Antarctica and relieving the requirement for controversial genetic modification (Stallwood et al. 2005; Vázquez et al. 2013).

Accompanying the biodegradation of petroleum hydrocarbons in soils is the requirement for suitable end-points for decommissioning bioremediation operations in Antarctica and the Arctic. Schafer et al. (2007) identified soil biogeochemical toxicity end-points based on sensitivity of nitrification, denitrification, carbohydrate use and total soil respiration at Macquarie Island. Similarly, through dose-response modelling of the bacterial *amoA* gene, Van Dorst et al. (2014) determined an average effective concentration responsible for a 20% change in phylogenetic diversity of 155 mg/kg as an indicator of soil health at Macquarie Island. In addition, microbial gene abundance has also been recently investigated for the development of remediation guidelines in polar soils (Richardson et al. 2014). Results from petroleum hydrocarbon contaminated soils at Casey Station, Antarctica, suggest that changes in microbial genes in response to fresh contamination may act as a suitable indicator of soil health (Richardson et al. 2014). However the response of genes to weathered hydrocarbons requires further investigation (Richardson et al. 2014).

Research into bioremediation and the processes governing the microbial degradation of hydrocarbons has also contributed to the development of other technologies, such as biopiles, phytoremediation and landfarming, which utilize the principles of bioremediation for petroleum hydrocarbon remediation.

Landfarming

Landfarming is one of the most commonly used technologies used for the remediation of petroleum hydrocarbon contaminated soil (Filler et al. 2009). Landfarming involves treating a flat layer of contained, contaminated soil (up to 1.0 m in thickness) by applying nutrients and aerating the soil through periodic tilling to promote the biodegradation and volatilization of petroleum hydrocarbons (Paudyn et al. 2008; Filler et al. 2009). Treatment strategies vary for landfarms and can be tailored according to site-specific characteristics including climate, location, soil type and temperature (Paudyn et al. 2008). Nutrient amendments, pH buffers and bulking agents may be applied to stimulate aeration of co-substrates, microbial metabolism or bacterial inoculations and can significantly increase remediation efficiency (Straube et al. 2003; Paudyn et al. 2008; Filler et al. 2009). The success of landfarming in temperate environments is well reported (McCarthy et al. 2004); however, landfarming trials in cold regions are comparatively scarce and field trials from the Antarctic and Arctic have revealed conflicting results (Delille 2000; Aislabie et al. 2004; McCarthy et al. 2004; Paudyn et al. 2008; Chang et al. 2010).

Delille (2000) studied the effects of diesel fuel addition on Antarctic bacterial assemblages in four contaminated soils over one year. The results demonstrated that petroleum hydrocarbon degrading bacterial abundance increased after diesel addition; however, heterotrophic bacterial abundance may significantly decrease under the same conditions (Delille 2000). In all cases, the stimulatory effects of diesel addition disappeared within four months of contamination (Delille 2000; Aislabie et al. 2004). Antarctic soils are thermally unstable and experience large temperature fluctuations, multiple summer freeze–thaw cycles and desiccation (Aislabie et al. 2004). These extreme fluctuations can seriously affect bacterial activity, which must acclimate continuously and be capable of rapidly switching on and off activity (Aislabie et al. 2004). Environments where temperature is more stable may be more favourable for bacterial growth than Antarctica (Aislabie et al. 2004). Although Delille (2000) demonstrated the presence of indigenous petroleum hydrocarbon-degrading bacteria suitable for landfarming exists, the additional environmental complications surrounding landfarming renders this technology less favourable in Antarctica.

Paudyn et al. (2008) demonstrated successful landfarming of petroleum hydrocarbon contaminated soil at Resolution Island, Canadian Arctic. Trial landfarm plots established in 2003 were used to compare four condition sets: aeration daily by rototilling, aeration every four days by rototilling, aeration every four days by rototilling with fertilizer addition, and an unmodified control plot. Enhanced bioremediation with fertilizer saw a decrease in mean soil TPH concentrations to 200 mg/kg from an initial concentration of 2800 mg/kg (Paudyn et al. 2008). Significant petroleum hydrocarbon losses associated with rototilling were also observed in the aerated plots which revealed an 80% reduction in soil TPH concentrations (Paudyn et al. 2008). Soil TPH also declined in the control plot, but remained above 1000 mg/kg (Paudyn et al. 2008). Similar pilot-scale landfarming experiments have investigated the compositional changes in semi- and non-volatile petroleum hydrocarbon fractions from Resolution Island, Canadian Arctic (Chang et al. 2010). Analogous with the findings of Paudyn et al. (2008), nutrient amendments and periodic 10-day tilling reduced TPH concentrations by $>60\%$ over a two-month period (Chang et al. 2010). These studies demonstrate the important role of nutrient addition and bioremediation in landfarms but also illustrate that aeration alone is effective at reducing soil TPH (Paudyn et al. 2008).

Landfarming has also been applied in Alaska (Kellems & Hinchee 1994; Reynolds et al. 1994; Reynolds et al. 1998; Chatham 2003), where summer temperatures are warmer than the Canadian Arctic, but where rates of biodegradation and volatilization have been shown to be substantially slower, limiting our understanding of the microbial contribution to landfarming in Alaska (Paudyn et al. 2008). Uncertainty over the efficacy of landfarms

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also occurs at sites where landfarming has been used in conjunction with seeding. In such cases, observable reductions in TPH may be the result of volatilization from tilling rather than biodegradation (Filler et al. 2006).

Landfarming has several advantages. First, the equipment and energy consumption requirements are relatively modest (Filler et al. 2006). The logistical requirements of landfarms are also comparatively small, and consequently landfarming is more cost-effective than many alternative approaches to the remediation of petroleum hydrocarbon contaminated soil (Filler et al. 2006; Bolton 2012). However, managing air quality associated with volatilization of petroleum hydrocarbons from uncovered landfarms represents a limitation of this technique and often requires an emission control system to address reduced air quality (Bolton 2012; Environment Canada 2013). This can increase operating costs and emphasizes the advantages of soil stabilization through technologies such as phytoremediation (Bolton 2012). Furthermore, since the degradation of petroleum hydrocarbons is slower in cold regions, it is important to ensure that off-site migration of petroleum hydrocarbons from contaminated soil into groundwater does not occur during remediation. Leachate can be regulated by constructing natural or engineered berms and through the application of clay and polymer based liners at the base of the site which allows pumping and redistribution of leachate across the landfarm (Paudyn et al. 2008; Filler et al. 2009; Environment Canada 2013; Hosney & Rowe 2014). Finally, excess soil moisture ($>33.0\%$) can lead to poor aeration, reduce the degradation rate of petroleum hydrocarbons and encourage contaminant migration; thereby reducing the effectiveness of landfarming (Bolton 2012).

Biopiles

Biopiles contain contaminated soil that has been treated with nutrients and water and piled in a contained, covered and lined installation similar to a modern landfill (Sanscartier et al. 2009). Biopiles have been used effectively in temperate regions (Samson et al. 1994; Pollard et al. 2008); however, there have been very few field trials in cold regions (Delille et al. 2008; Sanscartier et al. 2009). Biopiles typically contain passive or active aeration and heating systems to optimize soil temperature, encourage microbial activity and enhance natural contaminant biodegradation rates (Aislabie et al. 2006). Air pumps distribute oxygen more evenly and efficiently throughout biopiles and so are often preferred; however, their large energy requirements reduce their feasibility in remote, cold regions (Sanscartier et al. 2009). Another issue associated with aeration is reduced air quality pertaining to the heightened volatilization of low molecular weight organic compounds, generating concerns for environmental health (van Loon & Duffy 2000; Sanscartier et al. 2009). Similar to landfarms, air filtration systems can be implemented to reduce contamination by volatilization (Sanscartier et al. 2009; Environment Canada 2013). Air humidification systems can reduce volatilization by promoting biodegradation due to high soil moisture content (which reduces the soil-pore space available for diffusion) and increased bioavailability of adsorbed organic compounds that have been displaced from soil particles by water (Batterman et al. 1995; Sanscartier et al. 2009). Heating cables and blankets may be used as an alternative to air pumps but tend to be less efficient (Filler et al. 2001). Volatilization associated with low water availability can also discourage microbial activity, so heating systems should be used with caution (Sanscartier et al. 2009; Bolton 2012). Because of the environmental health risks associated with biopiles, they are not recommended for the treatment of soil comprising $>50\%$ total volatile organic compounds (Jørgensen et al. 2000).

Mohn et al. (2001) constructed two passively aerated biopile systems to treat soil contaminated with Arctic diesel at two different sites in the Canadian Northwest Territories. Extensive TPH reductions in soil after one summer were observed with concentrations declining from 196 to 10 mg/kg at the first site and from 2109 to 195 mg/kg at the second site; in both cases biodegradation was identified as the primary removal mechanism (Mohn et al. 2001). Addition of nutrients including ammonium chloride and sodium phosphate further enhanced TPH removal (Mohn et al. 2001). Inoculation with cold-adapted mixed microbial cultures also encouraged TPH removal in biopiles (Mohn et al. 2001).

Reimer et al. (2003) successfully trialled an alternative approach to air pump–heated biopile systems in the Canadian Arctic, whereby air was heated and then injected into contaminated soil. A soil temperature of approximately 15°C was maintained, despite daily ambient temperatures dropping below -40°C (Reimer et al. 2003). Soil TPH was reduced by approximately 60% from initial concentrations as high as 5000 mg/kg. Wind-powered biopile systems have also been used to successfully treat up to 15 000 m^3 of petroleum hydrocarbon contaminated soil in the Canadian Northwest Territories (Pouliot et al. 2001). In this study, soil TPH was reduced from approximately 7000 to 800 mg/kg over a two-year period. Similarly, McCarthy et al. (2004) used this technique to reduce soil TPH levels from 1400 to 430 mg/kg in 3600 m^3 of petroleum hydrocarbon contaminated soil in an Alaskan based study by the 55th day of the field trial. Delille et al. (2008) effectively reduced TPH concentrations in sub-Antarctic soils contaminated with diesel to $<7\%$ in unfertilized biopiles and to $<1\%$ in biopiles treated with fish compost in one year. Although the biopiles efficiently reduced TPH concentrations to below the 100 mg/kg study target, a residual toxicity determined with Microtox assay was reported in the fish compost treated biopiles (Delille et al. 2008).

Sanscartier et al. (2009) examined the effect of humidifying air for petroleum hydrocarbon remediation within an aerated biopile. Three 4 m^3 biopiles containing diesel contaminated fuel were constructed and operated for 10 months at a Canadian Forces Base in Kingston, Ontario, Canada. The first biopile ($11\,000 \pm 5000$ mg/kg soil TPH) was actively heated with an aeration system, the second biopile (9600 ± 4400 mg/kg soil TPH) was aerated, heated and received water by humidification, and the third biopile ($13\,000 \pm 9000$ mg/kg soil TPH) was passively aerated by pipes protruding from the soil profile (Sanscartier et al. 2009). Increases in microbial activity and substantial decreases in TPH were observed in all systems (Sanscartier et al. 2009). The humidified biopile system effectively maintained optimal soil moisture conditions and demonstrated the most significant reductions in TPH with final concentrations being reported as 290 ± 400 mg/kg. Final TPH concentrations in the actively aerated system and passive system were 500 ± 400 and 1000 ± 1300 mg/kg, respectively (Sanscartier et al. 2009). Air humidification encouraged biodegradation in contaminated soil and minimized volatilization (Sanscartier et al. 2009). The final pH, NH_3 and PO_4^{3-} values were also lower in the humidified system indicating increased microbial activity (Sanscartier et al. 2009). Results from gas chromatography flame ionization detector analyses suggested that all TPH fractions were removed during treatment, with biodegradation representing the dominant process in the highest molecular weight fraction (Sanscartier et al. 2009).

Most recently, Akbari & Ghoshal (2014) demonstrated the potential of biopiles as a cost-effective solution for petroleum hydrocarbon contaminated soil in cold regions in a pilot trial that utilized crude-oil impacted soil from the Canadian Northwest Territories. Stainless steel tanks with perforated tubes installed to allow air injections were used as pilot-scale biopiles, each containing 300 kg of contaminated soil ($n = 4$; Akbari & Ghoshal 2014). Significant reductions in soil TPH (C_{14}–C_{34}) were observed in all biopile systems, except for the biopile with a high moisture content (23.5%) and high nutrient content (1340 mg N/kg), returning only an 11% reduction in TPH over 110 days (Akbari & Ghoshal 2014). As previously reported (Walworth et al. 2006), these results suggest that under high nitrogen concentrations, biodegradation of petroleum hydrocarbons was inhibited. However results from CO_2 analyses revealed sufficient levels of respiration, indicating that the biopile was still biologically active despite the lower levels of biodegradation (Akbari & Ghoshal 2014). The highest levels of biodegradation in biopiles were achieved by aeration and moisture amendment, or aeration with low doses of nitrogen amendment (Akbari & Ghoshal 2014). The study also demonstrated that aeration and moisture addition was sufficient for achieving 47% biodegradation with an end-point of 530 mg/kg for non-volatile (C_{16}–C_{34}) petroleum hydrocarbons under summer sub-Arctic conditions (Akbari & Ghoshal 2014).

Biopiles have also been implemented at a petroleum hydrocarbon contaminated site (Main Power House) at Casey Station, Antarctica (McWatters et al. 2014). However, because of the absence of published soil-TPH data or biodegradation analyses, additional discussion does not fit within the scope of this review.

These studies provide evidence of the potential of biopiles for the management of petroleum hydrocarbon contaminated sites in the Antarctic and Arctic. Biopiles require less space than other techniques (e.g., landfarming) to provide an environmentally sensitive approach to on-site remediation. However, they are more logistically demanding and are expensive to build, operate and maintain (Sanscartier et al. 2009). The logistical requirements, costs and environmental health concerns associated with operating biopiles represent important considerations in cold, remote environments where safety, space, time, expense, extreme weather and rough terrain can all impede remediation operations (Poland et al. 2003; Bolton 2012).

Phytoremediation

Phytoremediation relies on plant roots that encourage microbial activity through the release of metabolic products and improved aeration, subsequently facilitating the biodegradation of petroleum hydrocarbons through microbial degradation pathways or co-metabolism (Lin & Mendelssohn 2009; Leewis et al. 2013). The effectiveness of phytoremediation varies depending on the concentration of petroleum hydrocarbons, depth of contamination, climatic conditions and soil moisture characteristics at a site, all of which influence the growing potential of plants (Martin & Ruby 2004; Camenzuli et al. 2013). Siciliano et al. (2003) described in detail the mechanism by which phytoremediation degrades petroleum hydrocarbons in soil by increasing catabolic potential and altering the functional composition of the indigenous microbial community.

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Leewis et al. (2013) demonstrated the potential of phytoremediation in a long-term assessment of petroleum hydrocarbon contaminated soil in Fairbanks, Alaska. The study assessed three levels of rhizosphere enhancement, two nutrient levels and their combination at reducing TPH concentrations in soil contaminated with crude oil or diesel (Leewis et al. 2013). The three levels included unplanted plots, annual ryegrass (*Lolium multiflorum*) and Arctic red fescue (*Festuca rubra*) (Leewis et al. 2013). Results from one year after establishment indicated that the plots subjected to planting and nutrient addition showed significant decreases in soil TPH relative to the control plots. After 15 years without active site management, both native and non-native vegetation had colonized the site with higher vegetation density recorded in diesel contaminated soil plots (Leewis et al. 2013). Alaskan Department of Environmental Conservation clean-up targets for diesel range organics (1000 mg/kg) were achieved in all treatment groups with TPH levels declining by 80–95% over the 15-year study period (ADEC 2012; Leewis et al. 2013). The lowest TPH concentrations were recorded in plots with a greater density of woody vegetation (Leewis et al. 2013). The results also demonstrated significant changes in the plant community since the establishment of the site in 1995 (Leewis et al. 2013). The grasses originally planted were not observed on site; rather the plots had been colonized by native and non-native Alaskan plant species (Leewis et al. 2013). The diesel contaminated soils were more heavily colonized by plants than the crude oil contaminated soil, with larger woody plants more abundant in the diesel contaminated soil (Leewis et al. 2013). This was attributed to the differences in soil type. The crude oil contaminated soil was predominantly gravel, while the diesel contaminated soils were fine textured with higher organic matter content (Leewis et al. 2013). Coarse soils tend to have a lower cation exchange capacity and lower capacity for water and nutrient retention and represent non-optimal conditions for plant and microbial growth (Leewis et al. 2013).

Ferrera-Rodríguez et al. (2013) obtained rhizospheric soil from five plant species (*Eriophorum scheuchzeri*, *Potentilla* cf. *rubricaulis*, *Oxyria digyna*, *Salix arctica* and *Puccinella angustata*) and four soil samples from the Arctic and analysed them for comparisons of their microbial communities to detect appropriate plant species for phytoremediation (Ferrera-Rodríguez et al. 2013). The rhizosphere of *P. angustata* was revealed to have the highest abundance of hydrocarbon-degrading bacteria and highest prevalence of genes encoding hydrocarbon oxidizing enzymes (Ferrera-Rodríguez et al. 2013). The study successfully demonstrated the phytoremediation potential of *P. angustata* at petroleum hydrocarbon contaminated sites in the Arctic (Ferrera-Rodríguez et al. 2013). Similarly, native tussock grass (*Poa foliosa*) has been investigated for phytoremediation on sub-Antarctic Macquarie Island (Bramley-Alves et al. 2014). The tolerance of *P. foliosa* to increasing SAB concentrations (up to 10 000 mg/kg) was examined across an eight-month laboratory trial (Bramley-Alves et al. 2014). Results indicate significantly less SAB in soils at two months and a return to background concentrations after eight months (Bramley-Alves et al. 2014). As microbes were not observed to be the sole reason for the reduction in SAB concentrations, the study provides promise for the success of phytoremediation in sub-Antarctic climates.

Phillips et al. (2009) conducted a field assessment of petroleum hydrocarbon degradation by mixed and single plant treatments over two years in Saskatchewan, Canada. Tall wheat grass (*Thinopyrum ponticum*), Altai wild rye (*Leymus angustus*), alfalfa (*Medicago sativa*), a mix of all three plants and non-planted controls were assessed (Phillips et al. 2009). The presence of *L. angustus* resulted in 50% TPH removal in the first growing season and no cumulative degradation occurred in mixed plant or control treatments, although all treatments reached comparable TPH levels by the end of the study period (Phillips et al. 2009). The ability of *L. angustus* to increase and maintain microbial activity, even during periods of low water availability, was found to increase its performance relative to other treatments (Phillips et al. 2009). Since mixed plant treatments reported no cumulative TPH degradation over the first growing season, this study demonstrates that mixed plant treatments may lead to slower remediation and elucidates the importance of selective species coupling when establishing mixed plant treatments (Phillips et al. 2009).

Phytoremediation is an attractive technology for coupling with other technologies such as PRBs, biopiles and electrokinetic remediation (Poland et al. 2003; Filler et al. 2006; Camenzuli et al. 2013). Germaine et al. (2014) investigated the effectiveness of a combined phytoremediation–biopiling system, termed ecopiling, to remediate petroleum hydrocarbon contaminated soils (1613 mg/kg^{-1} TPH soil) from an industrial site in the Republic of Ireland. Contaminated soil was amended with nutrients, inoculated with hydrocarbon degrading bacteria and then used to construct passive biopiles (Germaine et al. 2014). Finally, perennial rye grass (*Lolium multiflorum*) and white clover (*Trifolium repens*) were sown on the soil surface to complete the ecopile. Results from soil TPH analyses indicated that after two years, TPH concentrations in eight out of the nine ecopiles were below detectable limits (Germaine et al. 2014). These plant–microbe interactions have also been the focus of other recent studies (Abhilash et al. 2012; Xu et al. 2014). Warmer temperatures and appropriate flora suggest that a phytoremediation-biopiling system may be feasible at petroleum hydrocarbon contaminated sites in the sub-Antarctic and sub-Arctic.

Phytoremediation is an attractive approach to remediation as it is environmentally sensitive, effective for a range of contaminants and can produce fertile, useable topsoil after treatment (Phillips et al. 2009; Leewis et al. 2013). Low immediate and ongoing costs, applicability to large sites, minimal energy, equipment and infrastructure requirements, strong public acceptance and capacity to prevent contaminant migration are also advantages of phytoremediation (Reynolds 2004; Camenzuli et al. 2013). A disadvantage of phytoremediation is that it typically requires multiple growing seasons before a significant reduction in contaminant concentration can be detected, potential requiring longer timeframes than other techniques to reach remedial targets (Khan et al. 2004; Leewis et al. 2013). Disposal of plant matter containing accumulated contaminants can also be problematic (Martin & Ruby 2004; US EPA 2006; Camenzuli et al. 2013). Phytoremediation is also limited by the depth of the water table and plant roots and is therefore less effective for contaminant plumes at depth and at dense non-aqueous phase liquid contaminated sites, where migration of contaminants to basal substrates often occurs (Loop & White 2001). Implementing phytoremediation is also less feasible in Antarctica because of the harsher climate, absence of native plants and soil conditions (SCAR 1993; Poland et al. 2003; Camenzuli et al. 2013). The quarantine requirements for operating in Antarctica are also stricter than the Arctic; for instance, Annex II to the Madrid Protocol prohibits the introduction of non-indigenous plant species without a permit (SCAR 1993; Poland et al. 2003; Camenzuli et al. 2013). When applying phytoremediation in cold regions, the principal considerations are determining the relevance and feasibility of this technique to the site and the availability of suitable plant species.

Electrokinetic remediation

Electrokinetic remediation of contaminated soil has attracted increasing interest among researchers in the last two decades and can be favourable in environments where techniques such as landfarming are not feasible (Virkutyte et al. 2002; Huang et al. 2012). The general principle of electrokinetic remediation relies on the application of an electrical potential gradient between appropriately spaced electrodes to stimulate the flow of water and contaminants from anode to cathode (Virkutyte et al. 2002; Lima et al. 2011). The subsurface response to the potential gradient results in an acidic solution at the anode (Virkutyte et al. 2002; US EPA 2006). Subsequently, soluble contaminants are transported towards the installed electrodes through the processes of electromigration and electro-osmosis (Virkutyte et al. 2002; Martin & Ruby 2004; US EPA 2006; Huang et al. 2012; Camenzuli et al. 2013). After treatment, contaminants are recovered in electrode chambers and can be treated accordingly (Martin & Ruby 2004). The performance of electrokinetic remediation is reduced when managing contaminants with low solubility (Virkutyte et al. 2002; Martin & Ruby 2004) or where the matrix of the contaminated material is relatively dry. In such circumstances, performance can be improved by applying solubilizing agents and processing fluids which enhance electro-osmotic flow (Virkutyte et al. 2002; Martin & Ruby 2004; US EPA 2006).

Electromigration and electrophoresis generate the movement of contaminants towards oppositely charged electrodes (Acuña et al. 2012). Alternatively, electro-osmosis arises from the migration of water towards the cathode and produces an electro-osmotic flow which facilitates the movement of petroleum hydrocarbons and microorganisms in the direction of the fluid (Bayer & Sloyer 1990; Acuña et al. 2012). The direction and magnitude of contaminant migration generated by electrokinetic remediation and electro-osmotic flow is influenced by the concentration and solubility of contaminants, soil type, heterogeneity, structure, surface charge, pH and grain size, and the mobility and conductivity of the soil pore water (Virkutyte et al. 2002). Electrokinetic remediation can be used in both saturated and unsaturated soils but performs particularly well in fine porous soils and soils characterized by low hydraulic permeability (Virkutyte et al. 2002; US EPA 2006; Camenzuli et al. 2013). Electrokinetic remediation is less effective at larger sites with near-surface contamination and at sites where soil moisture content is $<10\%$ (Virkutyte et al. 2002). Implementing electrokinetic remediation is also more challenging at sites characterized by extensive soil heterogeneity (Virkutyte et al. 2002; Martin & Ruby 2004; US EPA 2006).

In cold regions, further complications may arise as a result freezing, reduced migration potential on account of the low solubility of petroleum hydrocarbons in cold regions and slowed reaction kinetics (Acuña et al. 2012; Camenzuli et al. 2013). Similarly to bioremediation, biodegradation at sites treated with electrokinetic remediation is enhanced by a temperature induced increase in bioavailability (Suni & Romantschuk 2004).

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Electrokinetic remediation can also be associated with reduced soil moisture due to intense warming of the treatment passage by direct current or exothermic reactions that may occur in the soil as a result of temperature increases in the order of 1–3°C (Shapiro & Probstein 1993; Acuña et al. 2012). It is therefore important to maintain a balance electroosmotic migration, evaporation by warming or exothermic reactions and water supply at the anode (Acuña et al. 2012). These factors should be investigated as part of an initial site assessment and are important considerations when determining the site-specific appropriateness of this technique.

Electrokinetic remediation can be applied using several methods. For instance, non-uniform application of electrokinetic remediation can be achieved by implementing a non-uniform electric field over the distance between electrodes (Fan et al. 2007; Wang et al. 2007; Huang et al. 2012). This can increase contaminant removal rates and time efficiency (Luo et al. 2006; Huang et al. 2012). Alternatively, the Fenton technique can be applied by creating a pH3 environment near the anode. Simultaneously contaminants migrate by electro-osmotic flow and electromigration and become degraded by hydroxyl free radicals produced near the anode by Fenton reactions (Huang et al. 2012). Electrokinetic remediation can also be applied with surfactants or co-solvents to react with contaminants to form migratory compounds via physicochemical processes such as desorption, chelation, dissolution or complexation (Huang et al. 2012). The soluble contaminants then migrate towards electrode chambers for collection and further treatment (Huang et al. 2012). This technique can improve the performance of electrokinetic remediation substantially as petroleum hydrocarbons are typically strongly sorbed to soil. However, caution should be exercised when implementing this approach to co-contaminated soils as surfactants can mobilize heavy metals (Maini et al. 2000; Singh & Turner 2009; Huang et al. 2012; Camenzuli et al. 2013).

The efficiency of electrokinetic extraction can also be improved by coupling with bioremediation. This represents the application of electrokinetic remediation which has received the most substantial interest in cold regions (Suni & Romantschuk 2004; Acuña et al. 2012; Pucci et al. 2012). Harms & Wick (2006) discuss electro-bioremediation and its application to petroleum hydrocarbon contaminated sites. Electro-bioremediation utilizes the principles of electrokinetic remediation to encourage the movement of petroleum hydrocarbons and microorganisms through soil and bioremediation to subsequently biodegrade contaminants (Harms & Wick 2006; Acuña et al. 2012). Coupling electrokinetic and bioremediation is particularly advantageous in cold regions such as the Antarctic and Arctic where subsurface soil generally remains below 10°C (Suni & Romantschuk 2004). The performance of bioremediation and rate of biodegradation can become significantly reduced over prolonged periods at these temperatures (Suni & Romantschuk 2004). Heating the soil by applying an electric current can stimulate microbial activity and facilitate degradation, even during prolonged cold conditions (Suni & Romantschuk 2004).

Suni & Romantschuk (2004) performed an experiment using a horizontal gel electrophoresis apparatus with a direct current (constant voltage 2 V cm^{-1}) and used microcosms designed with electrodes to investigate the potential of electro-bioremediation in Finland under simulated field conditions. Three soil types were assessed (garden soil, fine sand and clay) in the study. The study results indicated that bacteria co-migrate with water towards the cathode when an electric current is applied (Suni & Romantschuk 2004). Bacterial migration was most effective in fine sand; however, migration occurred in all soil types, including the low-permeability soil (e.g., clayey soil; Suni & Romantschuk 2004). The study also indicated that degradation can be sustained over winter field conditions for four months; however, the rates of degradation appear to be unevenly distributed (Suni & Romantschuk 2004). Similarly, Pucci et al. (2012) remediated petroleum hydrocarbon contaminated soil from Patagonia, Argentina using electro-bioremediation. The soil material used in this laboratory experiment was an unsaturated, petroleum hydrocarbon contaminated soil which had previously been remediated using landfarming (Pucci et al. 2012). A direct current of 0.5 V cm^{-1} was applied to electro-remediation cells with installed phosphate bridges. Over 120 days, soil-TPH decreased from 4.2 to 3% (Pucci et al. 2012).

Acuña et al. (2012) also achieved electro-bioremediation of petroleum hydrocarbon contaminated soil excavated from a Patagonian landfill in a laboratory experiment. In this study, electrokinetic experiments were conducted using a constant electric field of 0.5 V/cm in an experimental apparatus that included three components: soil cells, electrode compartments and power supply (Acuña et al. 2012). The electrokinetic cells consisted of a glass cell divided into three compartments: two electrodes with phosphate buffers using platinum electrodes inside the buffers, and a soil compartment (Acuña et al. 2012). The experiments were conducted using three reactor cell designs. In the first design, the connections between compartments were made using a 1 cm NaCl agar bird channel for one month (Acuña et al. 2012). The second design used electrodes that were buried in soil for one month and the third design employed a 1 cm phosphate agar bird channel for 150 days (Acuña et al. 2012). The results indicated that salt bridges more effectively regulate pH, with the phosphate bridge being most effective (Acuña et al. 2012). The phosphate bridge also enhanced biodegradation rates by providing necessary nutrients (Acuña et al. 2012). Although TPH concentrations declined in all three parts of the electrokinetics cell, the largest reductions occurred around the anode (Acuña et al. 2012). Despite TPH reductions in the order of 50% in all designs, reduced soil moisture associated with electrokinetic treatment was problematic in all systems and required the addition of water on a weekly basis to maintain adequate soil moisture (Acuña et al. 2012).

There are currently no published in situ field trials of electrokinetic remediation systems at petroleum hydrocarbon contaminated sites in the Antarctic or Arctic. While laboratory studies and temperate field studies provide insight into the applicability of this technique in cold regions (Acar & Gale 1995; Baraud, Fourcade et al. 1997; Baraud, Tellier et al. 1997; Kim et al. 2002; Virkutyte et al. 2002; Kim et al. 2005; Camenzuli et al. 2013; Hansen et al. 2013), there is a need for further field-based research to corroborate the findings of models and controlled laboratory-based studies. The reviewed studies indicate that electrokinetic remediation has potential in cold regions and many of its limitations can be overcome by coupling technologies or using site-specific adaptations to factors such as electrode spacing (Acar & Gale 1995; Virkutyte et al. 2002). Pilot scale field trials prior to large-scale field implementation would be also advantageous in light of the remaining uncertainty associated with the application of this technology in cold regions (Virkutyte et al. 2002; Martin & Ruby 2004; Camenzuli et al. 2013). Finally, thermal desorption at sites undergoing electrokinetic treatment remains understudied (Acuña et al. 2012). As such, a thorough and long-term monitoring regime is recommended when undertaking electrokinetic treatment in remote, cold regions.

Remediation technologies applicable to groundwater

Permeable reactive barriers

PRBs are one of the most practical technologies for on-site or in situ groundwater remediation in cold regions on account of their minimal energy, monitoring and maintenance requirements (Snape et al. 2001; Mumford et al. 2013; Mumford et al. 2014). In a PRB, contaminated groundwater passively flows through a single or multiple compartments of reactive material wherein the contaminants are physically adsorbed or degraded by chemical or biological processes (Gore 2009; Yeh et al. 2010; Camenzuli et al. 2013).

Selecting the most appropriate material or sequence of materials for a PRB is vital for effective management of petroleum hydrocarbon contaminated groundwater (Gore 2009; Camenzuli et al. 2013; Gupta & Saleh 2013; Mumford et al. 2013). Mumford et al. (2013) demonstrated the removal of diesel-range light non-aqueous phase liquids by adsorption onto granular activated carbon (GAC) in a sequenced "funnel and gate" PRB at Casey Station, Antarctica. While not directly addressing petroleum hydrocarbons, Kalinovich et al. (2008) and Kalinovich et al. (2012) also successfully utilized GAC as an adsorbent for polychlorinated biphenyl contamination at Resolution Island, Canadian Arctic. However, Arora et al. (2011) demonstrated that breakthrough timeframes and saturation capacity values for toluene on GAC at 4°C were between 30 and 60% lower than at 20°C. Hornig et al. (2008) also reports reduced adsorption efficiency of toluene and *o*-xylene on GAC and surfactant modified zeolites at 4°C compared to 20°C. However, the reduction in adsorption capacity onto GAC due to low temperature was $<10\%$ of total adsorption (Hornig et al. 2008).

While maintaining PRB media reactivity is important for the retention of petroleum hydrocarbons from groundwater, the most critical aspect of PRB performance is the maintenance of permeability (Mumford et al. 2014). This is particularly relevant in the Antarctic and Arctic where materials are subject to freeze–thaw processes (Gore 2009). Gore et al. (2006) found that the grain size of coconut husk GAC was largely unchanged across 60 freeze–thaw cycles at a range of moisture contents below 40%. Coconut husk GAC is advantageous under freeze–thaw as these carbons are harder and more resistant to attrition (Gratuito et al. 2008). Alternatively, Mumford et al. (2014) reports a significant increase in the <63 μm fraction from GAC, indicating that freeze–thaw accelerates particle break up. Mumford et al. (2014) recommend the mixing of GAC with more robust materials (e.g., zeolites, sand) to ensure permeability and longevity of petroleum hydrocarbon capture in Antarctica and the Arctic.

While zeolites are typically applied for the adsorption of cations (e.g., transition metals, ammonium), natural surface properties can be modified with cationic surfactants to promote the removal petroleum hydrocarbons from groundwater (Northcott et al. 2010; Torabian et al. 2010; Misaelides 2011). Torabian et al. (2010) reports on the adsorption preference of benzene, toluene, ethylbenzene and xylene (BTEX) compounds on *N*-cetylpyridinium bromide modified zeolite. Results demonstrate high benzene adsorption (96.6% removal), followed by toluene

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(94.0%), xylenes (92.2%) and ethylbenzene (91.3%) (Torabian et al. 2010). A 60–70% increase in petroleum hydrocarbon sorption was also reported for hexadecyltrimethyl ammonium chloride modified zeolites (Torabian et al. 2010). Adsorption efficiency was found to be reduced on both surfactants from 93 to 10% at 20°C and 4°C, respectively (Torabian et al. 2010). Northcott et al. (2010) also report the potential of an octadecyltrichlorosilane surfactant on zeolite to facilitate petroleum hydrocarbon capture and nutrient delivery, thereby encouraging microbial activity within PRBs.

Colonization of GAC and zeolites by petroleum hydrocarbon degraders presents the potential for bioremediation within PRBs (Kubota et al. 2008; Yeh et al. 2010; Vignola, Bagatin, D'Aurisb, Flegoc et al. 2011; Vignola, Bagatin, D'Aurisb, Massara et al. 2011; Gibert et al. 2013), although this is yet to be trialled in the Antarctic or Arctic. Xin et al. (2013) investigated the coupling of bioaugmentation and PRBs by examining the response of *Mycobacterium* sp. on immobilized beads (polyvinyl alcohol and sodium alginate) to remediate BTEX contaminated groundwater (100 mg/L^{-1}). The bioaugmented PRB system achieved degradation rates of 97.8% for benzene, 94.2% for toluene, 84.7% for ethylbenzene and 87.4% for *p*-xylene, with the toxicity of the groundwater falling by 91% (Xin et al. 2013). Further investigation into the resilience of beads under freeze–thaw conditions will dictate the feasibility for this technology coupling in the Antarctic and Arctic.

The potential for permeable bioreactive barriers in Antarctica and the Arctic is hindered by extremely low temperatures, ephemeral groundwater flow and low nutrient delivery to reactive media (Gore 2009; Mumford et al. 2013). Mumford et al. (2013) describes the addition of commercial controlled release fertilizer (MaxBac™) and nutrient amended zeolites (Zeopro™ and ammonium conditioned zeolites) to promote microbial growth within a sequenced PRB at Casey Station, Antarctica. While MaxBac™ was found to be suitable for application in regions of freezing ground (Gore & Snape 2008), higher nutrient delivery was recorded than from nutrient amended zeolites (Mumford et al. 2013). Although optimal nutrient concentrations in sub-Antarctic soils have been investigated (Walworth et al. 2007), appropriate nutrient concentrations required for biodegradation of petroleum hydrocarbons within PRBs remains to be examined.

The development of permeable bioreactive barriers can have positive implications for the longevity of petroleum hydrocarbon adsorption material within a PRB; however, the promotion of biomass has the potential to reduce media permeability (Seki et al. 2006). The permeability of PRBs can be reduced by biomass accumulation or by microbial gas production, either of which can clog the reactive zone of a PRB (Seki et al. 2006; Yeh et al. 2010). Maintaining optimal biomass density is critical for PRBs, as the accumulation of a sufficient amount of biomass is necessary for bioremediation. Reduced permeability in PRBs can also occur by physical (e.g., particle deposition) and chemical (e.g., mineral precipitation, gas bubble formation) processes (Li & Benson 2010). Therefore, balancing nutrient release rates with the requirements of microorganisms is of critical importance to the development of bioreactive barriers in cold regions (Mumford et al. 2013; Walworth et al. 2013). A final advantage of PRBs is their capacity for coupling with all technologies reviewed here, providing the means to capture petroleum hydrocarbons entrained in groundwater following the construction and installation of infrastructure to address soil contamination. In the Antarctic and Arctic at present, this coupling is limited to the installation of biopiles and PRBs at the Main Power House site, Casey Station, Antarctica (Mumford et al. 2013; McWatters et al. 2014).

Conclusions

Managing petroleum hydrocarbon contaminated sites in the Antarctic and Arctic can be complicated by several environmental, logistical and engineering factors. Despite these obstacles, a range of potential techniques for the management of petroleum hydrocarbon contaminated sites in cold regions is available. No contaminated site is without its unique challenges and site-specific factors typically require multiple technologies for effective, long-term management. This is particularly so at sites co-contaminated with heavy metals and petroleum hydrocarbons and at heterogeneous contaminated sites. Selecting the most appropriate treatment strategy requires consideration of the contaminants present and their distribution, climate, soil characteristics, financial expenses, legislative considerations, logistics, equipment, required energy and infrastructure.

This article reports on the potential of the six technologies; however, a shortage of Antarctic or Arctic field-based studies and studies investigating the coupling potential of the reviewed technologies limits our ability to comprehensively discuss the potential of these technologies for application in cold regions. This is particularly true for electrokinetic remediation, which remains understudied in both Antarctic and the Arctic. Further, a lack of field trials makes validating models and laboratory studies difficult and limits our current capacity to manage contaminated sites on-site or in situ in the Antarctic and

Arctic. Because of the scarcity of research and remaining uncertainty associated with many of these technologies, remediation technologies should only be implemented on-site or in situ after a thorough site assessment and consideration of site-specific factors, and should be accompanied by a rigorous, ongoing monitoring regime. Finally, a common disadvantage of many of the technologies currently used in the Antarctic or Arctic is the absence of proven capability for treatment of soil co-contaminated with metals and petroleum hydrocarbons. This represents an important area for future research.

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