Development of orthophosphate and silica treatments for the management of environmental contaminants at Wilkes landfill, East Antarctica

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Submitted in fulfilment of the requirement for the degree of Doctor of Philosophy

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October, 2015

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A smooth sea never made for a skilled sailor

- ENGLISH PROVERB

Abstract

Wilkes Station is an abandoned research station located on Clark Peninsula, East Antarctica that was constructed by the United States of America during the International Geophysical Year (1957-1958). In 1961, exclusive control of Wilkes Station transferred to the Australian National Antarctic Research Expeditions. Wilkes Station was abandoned by Australia in 1969, but was not completely decommissioned due to logistical constraints. Consequently the majority of buildings, equipment and a landfill remain on-site. Annex III of the Madrid Protocol (1998) establishes the requirement for all past and present work sites in Antarctica to be cleaned up by the generators and users of sites. In response, various remediation technologies are being adapted or developed for use at contaminated sites in Antarctica and are effective, despite the challenges associated with operating in remote, cold regions. Orthophosphate and silica treatments are two technologies that demonstrate significant potential for use at Wilkes Station and other contaminated sites in Antarctica. However, their application in areas of freezing ground remains understudied.

This study assessed the performance of orthophosphate, silica and coupled orthophosphate-silica treatments on metal contaminated soil and soil co-contaminated with metals and petroleum hydrocarbons to evaluate their suitability for the management of environmental contaminants at Wilkes Station. The results of four experiments indicate that silica treatments are effective at immobilising Cr, Fe, Ni, Cu, Zn, Cd, Pb, while orthophosphate and coupled-orthophosphate treatments effectively immobilise Fe, Cu, Zn, Cd and Pb, but are ineffective at immobilising Cr and Ni. None of the assessed treatments were effective at immobilising As, and concentrations of P remained above environmentally safe levels in soils where treatments containing orthophosphoric acid or triple superphosphate were applied. The formation of brushite, cattite, hydroxylapatite, hydroxypyromorphite, sodium aluminosilicates and other calcium bearing minerals following treatment with orthophosphate, silica and coupled orthophosphate-silica provided further evidence of immobilisation.

Silica treatments were ineffective at reducing the mobility of petroleum hydrocarbons to environmentally safe levels in soil. Therefore, further research to optimise treatments is required before managing soil co-contaminated with metals and petroleum hydrocarbons using this technique can be considered viable. For effective management of environmental contamination at Wilkes Station, coupling the application of a chemical treatment with a downstream permeable reactive barrier capable of treating petroleum hydrocarbons, As and P contaminated water is recommended. A thorough monitoring program for detection of adverse effects of treatment and the potential for re-solubilisation of metals is also recommended.

Declaration

I hereby declare that this thesis titled 'Development of orthophosphate and silica treatments for the management of environmental contaminants at Wilkes landfill, East Antarctica' has not been previously submitted to any other institution or university for a higher degree. I certify that this thesis is an original piece of research that is comprised entirely of my own work. All of the information sources and literature used in the preparation of this thesis have been accurately cited and the contributions of others have been appropriately acknowledged.

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29 October 2015

Acknowledgements

Almost four years ago I started a PhD with almost no understanding of Antarctic science or environmental remediation, or how challenging it would be to obtain that understanding. It is no understatement to say that this thesis would not have been completed without the assistance of several individuals who deserve my gratitude and formal recognition.

Firstly, I wish to thank my supervisor Damian Gore for his integrity, courage, humility, loyalty and mentorship. No one goes more above and beyond than Damian, and my transition from a student to a scientist is owed almost entirely to his patience, enthusiasm, attention to detail and perseverance.

I also extend my thanks to my co-supervisor Kirstie Fryirs and adjunct supervisors Kathryn Mumford and Scott Stark for their advice, reviews, expertise and support. I owe particular thanks to Scott for his patience, humour and mentorship during my candidature at the 'Scott Stark Institute of Chemistry'. Laboratory and field work would not have been possible without the assistance of Lauren Wise who offered consistent, kind and not-patronising guidance throughout this journey and Johan Mets, Geoff Stevens, Greg Hince, Rebecca McWatters, Dan Wilkins, Dan Jones, Lachlan Mason and Russell Field.

I thank Ben Freidman for countless hours of assistance during field work, his endearing personality, patience and humour, and for frequently restoring my faith in humanity. I also wish to thank Tom Statham for helping me create some special memories in Austria and Antarctica, for field support, ongoing construction and chemical engineering guidance, and for teaching me the important difference between a 'big dog' and 'little dog'.

I thank my family for encouraging me to remain truthful to my authentic self, for enabling me with the drive and resilience to constantly challenge myself, and for believing in my capabilities during my time in the 'special needs' class. I also thank my future family (John and Sherry) and the people who became my surrogate Antarctic family at Casey for their compassion, humour and nurturing during some of my most and least triumphant moments.

My friends who shared this experience with me also deserve my gratitude for providing an unconditionally compassionate, tolerant, loyal, patient and colourful support network. In the spirit of tradition, I also wish to thank Chad Sanders. Finally, to my fiancé Reese (the most patient soul in my life), merci d'être mon co-pilote dans la vie, mon amour et ma muse.

Thesis structure

This thesis is structured into six sections and fifteen chapters and is an amalgamation of ten, peer-reviewed journal articles of which I am the sole, lead or co-author (Table I).

The first section of this thesis provides an introduction to the research topic. Section 2 includes an extensive review of literature surrounding orthophosphate and silica treatments. The research objectives outlined in Section 3 are addressed in Sections 4 and 5. Section 4 overviews the study area, discusses the issues surrounding the co-management of remediation operations and preservation of cultural heritage at Wilkes Station, and presents a less invasive method for delineating landfills concealed by ice. Section 5 includes a series of controlled, laboratory experiments which explore various aspects of orthophosphate and silica treatments. Section 6 provides a synthesis of the research included in this thesis and discusses the major research findings, study limitations and identifies topics which require further research. Two field trials were undertaken at Casey Station, East Antarctica to validate the results of laboratory studies. The experimental design of these two experiments are presented in Appendix I.

The formats of published manuscripts have been amended for inclusion in this thesis (Chapters 2, 3, 4, 5, 8, 9, 10, 11, 12 and 13); however, the content has been retained for bibliographic integrity. As such, there is some inevitable repetition of information; unfortunately this is essential as the articles must be independently comprehensive for publication. The individual contribution of authors on the publications submitted as part of this thesis are summarised in Table II.

Table I: Thesis structure.

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Chapter 3: On-site and in situ remediation technologies applicable to petroleum hydrocarbon contaminated sites in the Antarctic and Arctic
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Table II: Contribution of authors on publications included in this thesis.

Title	Author	Conception (%)	Research (%)	Writing (%)
On-site and in situ remediation technologies applicable to metal contaminated sites in Antarctica and the Arctic	D. Camenzuli	80	80	70
	B.L Freidman	10	10	20
	T. Statham	2.5	2.5	2.5
	K. Mumford	2.5	2.5	2.5
	D. Gore	5	5	5
On-site and in situ remediation technologies applicable to petroleum hydrocarbon contaminated sites in Antarctica and the Arctic	D. Camenzuli	80	60	65
	B. Freidman	20	40	35
Fixation of metals using orthophosphate solutions	E.G. Hafsteinsdóttir	40	60	50
	D. Camenzuli	5	10	20
	A. Rocavert	10	5	5
	J. Walworth	5	5	5
	D. Gore	40	20	20
Immobilisation and encapsulation of contaminants using silica treatments: A review	D. Camenzuli	80	90	85
	D. Gore	20	10	15
Managing legacy waste in the presence of cultural heritage at Wilkes Station, East Antarctica	D. Camenzuli	70	70	80
	K. Fryirs	10	5	5
	B. Freidman	20	25	15
Locating an Antarctic ice-covered landfill using ground magnetometry	B. Freidman	60	55	50
	D. Camenzuli	30	30	40
	M. Lackie	10	15	10
Immobilisation of metals in contaminated landfill material using orthophosphate and silica amendments: A pilot study	D. Camenzuli	80	75	80
	S. Stark	10	15	10
	D. Gore	10	10	10
Minerals formed by treatment of heavy metals with orthophosphate, silica or a coupled orthophosphate-silica treatment under cold conditions: Implications for remediation	D. Camenzuli	100	100	100
Treatment of low-level metal contaminated soil with orthophosphate and silica at sites with a heterogeneous distribution of contaminants	D. Camenzuli	80	75	85
	S. Stark	10	15	5
	D. Gore	10	10	10
Treatment of soil co-contaminated with inorganics and petroleum hydrocarbons with silica: Implications for remediation in cold regions	D. Camenzuli	80	75	80
	L. Wise	10	10	5
	S.C. Stark	5	5	5
	A. Stokes	0	5	5
	D. Gore	5	5	5

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Section 1: Introduction

Chapter 1: Research introduction

1.1: Study introduction

Metal and petroleum hydrocarbon contaminated soil associated with activities including resource exploration and extraction, mining and smelting, landfilling, tourism and transport can present a serious environmental and human health risks (Snape et al. 2001a; Poland et al. 2003; Juhasz et al. 2006; Smith et al. 2011; Taylor et al. 2013). Environmental contamination exists globally, but the majority of research relating to the management and remediation of contaminated sites is concentrated in industrialised, temperate regions (Poland et al. 2003; Filler et al. 2006). Research specific to temperate regions offers limited relevance to Antarctica, which has different environmental conditions, attracts additional environmental and logistical challenges, and operates according to the unique regulatory framework provided by the Antarctic Treaty System (Poland et al. 2003).

Assessment and management of contaminated sites in Antarctica can be challenged by the presence of ice cover (Fryirs et al. 2013, 2015). Financial constraints, limited infrastructure, logistical challenges and environmental factors such as slow rates of petroleum hydrocarbon degradation, higher vulnerability to disturbance, extreme weather and freeze-thaw cycling can also confound remediation operations in Antarctica (Snape et al. 2001a; Poland et al. 2003; Filler et al. 2006; Chapters 2 and 3). Traditional approaches to remediation (e.g. extraction, transport and disposal of bulk material at a secure landfill) can be beneficial in the presence of highly hazardous compounds (Tomei and Daugulis 2013). However, such approaches are expensive, logistically inefficient and the potential for environmental harm during excavation can be significant (Aislabie et al. 2004; Filler et al. 2006; White et al. 2012). For instance, excavation can result in the re-suspension of contaminants or instigate permafrost melt which may result in altered groundwater flow, soil shrinkage, land slumping or salinisation (Aislabie et al. 2004; Martin and Ruby 2004; White et al. 2012). This warrants particular concern in Antarctica, where the Madrid Protocol (1998) stipulates that remediation must not generate additional adverse environmental impacts (SCAR 1993; Fryirs et al. 2013, 2015).

Practical, safe and effective remediation technologies are being developed for application in Antarctica in response to the challenges of operating in remote, cold locations (Rutter et al. 2003; Filler et al. 2006; Statham et al. 2015; Chapters 2 and 3). In situ treatments are generally preferred as they are less disruptive to the environment, prevent contaminant migration and reduce demand for commissioning additional waste disposal sites (Martin and Ruby 2004; Filler et al. 2006; White et al. 2012; Denyes et al. 2013; Statham et al. 2015). Orthophosphate and silica treatments display significant potential for the management of contaminated soil, but remain understudied and underutilised in cold regions (Chapters 4 and 5).

Orthophosphate treatments immobilise metals by reactions which convert target ions into sparingly soluble, metal-phosphate minerals (Crannell et al. 2000; Porter et al. 2004; Hafsteinsdóttir et al. 2011, 2013, 2014; Chapter 4). Unlike many commonly used remediation technologies, the objective of orthophosphate treatments is not to remove a contaminant, but to decrease the solubility, mobility and bioavailability of metal contaminants (Hettiarachchi et al. 2000; Scheckel and Ryan 2004; Zhu et al. 2004; Sonmez and Pierzynski 2005; Hafsteinsdóttir et al. 2011, 2013; Chapter 4). By reducing the solubility, mobility and bioavailability of contaminants, orthophosphate treatments reduce the potential impact of metal contaminants on the environment and human health (Chapter 4). Orthophosphate treatments have been successfully applied in temperate environments (Hettiarachchi et al. 2000, 2001; Porter at al. 2004; Sonmez and Pierzynski 2005). However, research describing their application in cold regions is limited to a small number of laboratory and field based studies (Hafsteinsdóttir et al. 2011, 2013, 2014; White et al. 2012).

Silica treatments immobilise metals by forming hydroxides, or precipitating metal-silicate minerals (Mbhele 2007; Chapter 5). Encapsulation of petroleum hydrocarbons can also occur following treatment with silica due to the polymerisation of soluble silicates (Chapter 5). As silica treatments can also be applied in situ, they offer many of the same benefits as orthophosphate treatments. However, an important additional advantage of silica treatments is their applicability to soil co-contaminated with metals and petroleum hydrocarbons (Mitchell and Atkinson 1994; Arocha et al. 1996; Chapter 5). Silica treatments remain in their early developmental stages, with only a few published studies in temperate regions reporting on the application of this technology (Mitchell and Atkinson 1994; Arocha et al. 1996; Fytas et al. 1999; Vandiviere and Evangelou 1998; Chapter 5). Prior to this research, there were no published studies demonstrating the potential of silica treatments in low temperature environments.

This research investigates the suitability of orthophosphate and silica treatments for the management of environmental contaminants at the abandoned landfill at Wilkes Station, East Antarctica (Wilkes). As Wilkes is predominantly buried by ice, this research also required the application of a safe, non-invasive method for delineating the geometry of the landfill material concealed by ice. Although the research included in this thesis is largely specific to Wilkes, the reported research outcomes extend beyond Wilkes and are applicable to similarly contaminated sites in other remote, cold locations (Poland et al. 2001, 2003; Ubugunov 2014; Ficko et al. 2015).

1.2: Background to the study

This study began in 2012 as part of a large collaborative research project involving Macquarie University, the University of Melbourne and the Australian Antarctic Division (AAD). The broad objective of the project was to investigate and implement innovative remediation technologies capable

of managing metal contaminants in situ at Wilkes. Specifically, the aim of the project was to develop and implement an orthophosphate treatment capable of managing metal contaminated soil, coupled with a permeable reactive barrier capable of managing metal contaminated groundwater. My role in the project was to assess the suitability of orthophosphate treatments for the management of metal contaminant soil at the abandoned landfill at Wilkes, which required me to first delineate the ice-covered landfill using geophysical techniques.

An extensive review of relevant literature prior to my first Antarctic field season revealed the hazards associated with orthophosphate based remedial techniques, primarily the high risk for arsenic mobilisation and eutrophication of receiving waters due to the release of unreacted orthophosphate. This resulted in the identification of silica treatments as a potential alternative to orthophosphate treatments. Literature review also revealed an additional benefit of silica treatments in their ability to remediate petroleum hydrocarbon contaminated soil and soil co-contaminated with metals and petroleum hydrocarbons. Consequently the scope of my research increased to assessing the suitability of orthophosphate, silica and coupled orthophosphate-silica treatments for the management of metal contaminated soil and soil co-contaminated with metals and petroleum hydrocarbons at Wilkes.

Two field-based experiments were undertaken as part of this research at Casey Station, East Antarctica using soil material excavated from the abandoned landfill at Wilkes. The experimental design of these experiments are presented in Appendix I. Unfortunately, negligence by AAD staff during the transfer of samples from Antarctica to Australia resulted in the destruction of more than 30% of the samples collected during these experiments. The remaining samples were damaged or compromised beyond analytical use, the experimental design was irreversibly compromised and no data resulted from these experiments. Subsequently, Federal Government budget cuts resulted in significant reductions in financial allocations for Antarctic science, making a return visit to Casey Station to repeat these experiments impossible.

The remaining part of my candidature was invested into undertaking laboratory-based experiments which assessed the performance of orthophosphate, silica and coupled orthophosphate-silica treatments at managing metal contaminated soil and soil co-contaminated with metals and petroleum hydrocarbons. The majority of these experiments were undertaken under cold conditions to simulate an Antarctic summer climate and are presented in section 5 of this thesis.

Evidently the objectives and research strategy of this research has changed significantly since 2012. However, the focus on developing innovative technologies capable of managing environmental contaminants at Wilkes has been retained, despite the aforementioned obstacles and unanticipated complications.

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Section 2: Literature Review

Chapter 2: On-site and in situ remediation technologies applicable to metal-contaminated sites in Antarctica and the Arctic

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Citation: Camenzuli D., Freidman B.L., Statham T.M., Mumford K.A. and Gore D.B. 2014. On-site and in situ remediation technologies applicable to metal-contaminated sites in Antarctica and the Arctic: A review. *Polar Research 33*, 21522, http://dx.doi.org/10.3402/polar.v33.21522.

Submitted: 23 May 2013; *Accepted for publication:* 09 October 2013; *Published*: 01 January 2014

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 industrialised, 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.

Keywords: Polar; Heavy Metals; Remediation; Contaminants; In situ.

2.1: Introduction

Environmental metal contamination from human activities is an on-going problem in temperate and polar environments (Snape et al. 2001a; 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 and 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 et al. 2001a; 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 and 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 et al. 2001a, b; 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 technique is highly expensive and there are several technical issues associated with this approach. For instance, excavation may re-suspend or re-mobilise 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 and 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 onsite 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.

2.1.1: 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 years (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 et al. 2001a, b; Duquesne and 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 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 largescale 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).

2.1.2: 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 summarise 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.

2.1.3: 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 et al. 2001a). The majority of research activities and contaminated material in Antarctica is also situated on these coastal ice-free areas (Snape et al. 2001a, b). 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 et al. 2001a; 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 and Korner 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).

2.1.4: 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 et al. 2001a; 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 et al. 2001a; 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 et al. 2001a; 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 utilisation (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.

2.1.5: 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 et al. 2001a; 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 industrialised 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.

2.2: 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 et al. 2001 a, b; 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).

2.2.1: 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 et al. 2001b; Gore 2009; Higgins and 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 immobilised by precipitation. Barriers can be customised according to site-specific requirements and a wide range of effective barrier designs have been described (e.g. Snape et al. 2001b; Babel and Kurniawan 2003; Henderson and Demond 2007; Fu and 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 et al. 2001b; 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 et al. 2001b; 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).

2.2.2: Chemical fixation

Chemical fixation treatments immobilise 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 immobilised and their potential for environmental harm is significantly reduced (Zhu et al. 2004; Sonmez and Pierzynski 2005). Fixation is relatively cost-effective, fast and can be used at multi-metal-contaminated sites. Knox et al. (2003) reported successful immobilisation 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 2.1). 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).

Table 2.1: Organic and inorganic resources available for metal immobilisation.

Material	Metal	References
Lime and quicklime	Ni, Cu, Zn, Cd, Hg, Pb	Dermatas and Meng 1996; Bolan et al. 2003; Kostarelos et al. 2006.
Phosphate	Cu, Zn, Cd, Pb	Ma et al. 1993; Cao et al. 2003; Basta and 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.

While an extensive literature database demonstrates the effectiveness of chemical fixation, published in situ field trials are almost absent (Hettiarachchi et al. 2000; Scheckel and Ryan 2004; Zhu et al. 2004; Sonmez and 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 and Ruby

2004). Treatments can be applied to soils on-site or in situ using conventional earth-moving equipment, augers and injection grouting (Martin and 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 and 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).

2.2.3: 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 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 immobilise 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 et al. 2008). However, caution should be used when undertaking bioleaching as it can prompt the solubilisation 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 pre-served 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, fertilisation and irrigation, respectively (Powell et al. 2006). Although nitrogen and phosphorus fertilisers 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 optimise 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 authorisation 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).

2.2.4: Phytoremediation

Phytoremediation refers to the use of crops or plants that accumulate and immobilise metals, or grow in and stabilise metal-contaminated soil, for the remediation of contaminated land (Brown et al. 1994; Martin and Ruby 2004). There are several types of phytoremediation techniques applicable to metal-contaminated sites; the two most common types are phytoextraction and phytostabilisation (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, phytostabilisation 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 phytostabilisation 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 phytostabilisation techniques and can significantly influence remediation outcomes. Ideally, plants used for stabilisation 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 characterised 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 and 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 phytostabilisation 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 and 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 phytostabilisation 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).

2.2.5: 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 and 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 and 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 mobilise metals, which in the absence of a pump and treat system or permeable reactive barrier could be potentially damaging to the environment (Martin and 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 characterised by extensive soil heterogeneity or significantly varying concentrations of several metal contaminants (Virkutyte et al. 2002; Martin and 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 ionised 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 and 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 and 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).

2.2.6: 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 and Jones-Lee 1996; McGowen et al. 1996). LCLs are widely used due to their ability to contain a contaminant source and minimise the exposure impacts of contaminants in a timely and cost effective manner (Lee and 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 and 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 and 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.

2.2.7: Pump and treat

Pump and treat systems are one of the most common technologies used for metal-contaminated groundwater extraction (Higgins and 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 and Olsen 2009). These systems operate by extracting contaminated groundwater via extraction wells, typically with submersible pumps (Higgins and 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 and 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 mobilise 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 2003, 2009; Higgins and 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).

2.3: Conclusion

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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Chapter 3: On-site and in situ remediation technologies applicable to petroleum hydrocarbon contaminated sites in the Antarctic and Arctic

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Citation: Camenzuli D. and Freidman B.L. 2015. On-site and in situ remediation technologies applicable to petroleum hydrocarbon contaminated sites in the Antarctic and Arctic. *Polar Research 34*, 24492, http://dx.doi.org/10.3402/polar.v34.24492

Submitted: 30 March 2014; *Accepted for publication:* 10 March 2015; *Published:* 7 September 2015

Abstract

Petroleum hydrocarbon contaminated sites, associated with the contemporary and legacy effects of human activities, remains 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 paper 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 emphasised, 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.

Keywords: Petroleum Hydrocarbons; Remediation; Antarctica; Arctic; Cold Regions; Contaminated Site.

3.1: Introduction

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; Camenzuli et al. 2014 for detailed reviews). The financial expense associated with implementing traditional remediation approaches in remote, cold regions can also be significant (Poland et al. 2003; Leewis et al. 2013; Camenzuli et al. 2014). 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. 2014).

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 and Ruby 2004; Harms and Wick 2006; Camenzuli et al. 2014). Ex situ remediation approaches can be advantageous in the presence of severe contamination of highly hazardous compounds (Tomei and 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 salinisation (Aislabie et al. 2004; Martin and Ruby 2004; Perelo 2010; White et al. 2012; Camenzuli et al. 2014). 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. 2014). 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 minimises the need for transporting contaminated material or generating additional waste disposal sites (Martin and 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 and 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 and Obuekwe 2005; Alisi et al. 2009; Dong et al. 2013). Technology coupling may also be required at highly heterogeneous sites, (i.e., characterised by variable subsurface flow rates, soil types or an uneven distribution of contamination) (Filler et al. 2006; Camenzuli et al. 2014). 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. 2014).

This paper 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; Leewis. Et al. 2013; Mair et al. 2013; Mumford et al. 2013; Camenzuli et al. 2014). 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.

3.1.1: Petroleum hydrocarbon contaminated soil in the Antarctic and Arctic

Petroleum hydrocarbon contamination in Antarctica is typically concentrated around active and abandoned 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). Whereas exploration, extraction and transport of petroleum reserves are the primary sources of petroleum hydrocarbon contamination in the Arctic (Poland et al. 2003; Aislabie et al. 2004; Fritt-Rasmussen et al. 2012; Akbari and 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 and 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. Firstly, 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 and 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).

Secondly, 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 and 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 mobilised upon thawing and have the potential to migrate to offshore marine environments (Kennicutt and 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 (1958) (Aislabie et al. 2004; Klein et al. 2012; Fryirs et al. 2013; Fryirs et al. 2015). Detailed descriptions on the impact of petroleum hydrocarbon contamination on natural thermal and moisture regimes, soil pH and nutrient activity in cold regions is reported elsewhere (Atlas 1981; Grechishchev et al. 2001; Balks et al. 2002; Filler et al. 2006).

3.2: Remediation technologies applicable to soil

3.2.1: 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 and Daugulis 2013). Bioremediation aims to accelerate the rate of natural attenuation of petroleum hydrocarbons by optimising 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 optimisation 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 and 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, 2006; Revill et al. 2007; Dias et al. 2012). However, the addition of nitrogen, peaking in the range 1,000-1,600 mg N kg-soil-H_2O^{-1} enhanced the mineralisation 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 maximised 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 were 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 has 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, 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 and 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 mineralisation 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 et al. (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 et al. 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 and Schiewer 2009). Results at 6 °C indicate < 5% mineralisation of diesel fuel while synthetic diesel reported consistent degradation across a 4 week study (Horel and Schiewer 2009). Furthermore, biodegradation of synthetic diesel was accelerated by 50% following nutrient addition over unamended soils spiked with synthetic diesel (Horel and Scheiwer 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 utilisation 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 7,000 mg/kg TPH, concentrations of ~ 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 indicate that oxygen levels of 10.4% maximised 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 SAB (Special Antarctic Blend) 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 2,020 ± 340 mg/kg to 800 ± 190 mg/kg, after 5 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 recognised 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 mineralisation 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). Characterisation of hydrocarbon-degrading microorganisms in Antarctic soils demonstrates that isolation of psychrotolerant bacteria capable of metabolising 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. Additionally, microbial gene abundance has also been recently investigated for the development of remediation guidelines in polar soils (Richardson et al. 2015). 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. 2015). However the response of genes to weathered hydrocarbons requires further investigation (Richardson et al. 2015).

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 utilise the principles of bioremediation for petroleum hydrocarbon remediation.

3.2.2: 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 volatilisation 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 fertiliser addition, and an unmodified control plot. Enhanced bioremediation with fertiliser saw a decrease in mean soil TPH concentrations to 200 mg/kg from an initial concentration of 2,800 mg/kg (Paudyn et al. 2008). Significant petroleum hydrocarbon losses associated with rototilling was 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 1,000 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). Analogueous with the findings of Paudyn et al. (2008), nutrient amendments and periodic 10-day tilling reduced TPH concentrations by > 60% over a 2 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 and Hinchee 1994; Reynolds et al. 1994, 1998; Chatham 2003) where summer temperatures are warmer than the Canadian Arctic, but where rates of biodegradation and volatilisation 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 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 volatilisation from tilling rather than biodegradation (Filler et al. 2006).

Landfarming has several advantages. Firstly, 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 volatilisation 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; FCSAP 2013). This can increase operating costs and emphasises the advantages of soil stabilisation 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; FCSAP 2013; Hosney and 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).

3.2.3: 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 optimise 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 volatilisation of low molecular weight organic compounds, generating concerns for environmental health (van Loon and Duffy 2000; Sanscartier et al. 2009). Similar to landfarms, air filtration systems can be implemented to reduce contamination by volatilisation (Sanscartier et al. 2009; FCSAP 2013). Air humidification systems can reduce volatilisation 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). Volatilisation 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 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 mg/kg to 10 mg/kg at the first site and from 2,109 mg/kg 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 5,000 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 (ESG 2001). In this study, soil TPH was reduced from approximately 7,000 mg/kg to 800 mg/kg over a two year period. Similarly, McCarthy et al. (2004) used this technique to reduce soil TPH levels from 1,400 mg/kg to 430 mg/kg in 3,600 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 unfertilised 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 ± 5,000 mg/kg soil TPH) was actively heated with an aeration system, the second biopile (9,600 ± 4,400 mg/kg soil TPH) was aerated, heated and received water by humidification, and the third biopile (13,000 ± 9,000 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 1,000 ± 1,300 mg/kg, respectively (Sanscartier et al. 2009). Air humidification encouraged biodegradation in contaminated soil and minimised volatilisation (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 Ionisation 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 and 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 utilised crude-oil impacted soil from the Canadian Northwest Territories. Stainless steel tanks with perforated tubes installed to allow air injection were used as pilot-scale biopiles, each containing 300 kg of contaminated soil (n=4) (Akbari and Ghoshal 2014). Significant reductions in soil TPH (C_{14}-C_{34}) was observed in all biopile systems, except for the biopile with a high moisture content (23.5%) and high nutrient content (1,340 mg-N/kg), returning only an 11% reduction in TPH over 110 days (Akbari and 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 and 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 and 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 and 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).

3.2.4: 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 and 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 and Ruby 2004; Camenzuli et al. 2013). Siciliano et al. (2003) describes 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.

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 colonised 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 (1,000 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 colonised by native and non-native Alaskan plant species (Leewis et al. 2013). The diesel contaminated soils were more heavily colonised 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 oxidising 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 8 month laboratory trial (Bramley-Alves et al. 2014). Results indicate significantly less SAB in soils at 2 months and a return to background concentrations after 8 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. 2014). Germaine et al. (2014) investigated the effectiveness of a combined phytoremediation-biopiling system, termed Ecopiling, to remediate petroleum hydrocarbon contaminated soils (1,613 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*) was 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 and Ruby 2004; US EPA 2006; Camenzuli et al. 2014). 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 sites contaminated with dense non aqueous phase liquids, where migration of contaminants to basal substrates often occurs (Loop and 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. 2014). 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. 2014). 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.

3.2.5: 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 electroosmosis (Virkutyte et al. 2002; Martin and Ruby 2004; US EPA 2006; Huang et al. 2012; Camenzuli et al. 2014).

After treatment, contaminants are recovered in electrode chambers and can be treated accordingly (Martin and Ruby 2004). The performance of electrokinetic remediation is reduced when managing contaminants with low solubility (Virkutyte et al. 2002; Martin and Ruby 2004) or where the matrix of the contaminated material is relatively dry. In such circumstances, performance can be improved by applying optimisation agents and processing fluids which enhance electroosmotic flow (Virkutyte et al. 2002; Martin and Ruby 2004; US EPA 2006).

Electromigration and electrophoresis generate the movement of contaminants towards oppositely charged electrodes (Acuña et al. 2012). Alternatively, electroosmosis arises from the migration of water towards the cathode and produces an electroosmotic flow which facilitates the movement of petroleum hydrocarbons and microorganisms in the direction of the fluid (Bayer and Sloyer 1990; Acuña et al. 2012). The direction and magnitude of contaminant migration generated by electrokinetic remediation and electroosmotic 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 characterised by low hydraulic permeability (Virkutyte et al. 2002; US EPA 2006; Camenzuli et al. 2014). 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 characterised by extensive soil heterogeneity (Virkutyte et al. 2002; Martin and 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. 2014). Similarly to bioremediation, biodegradation at sites treated with electrokinetic remediation is enhanced by a temperature induced increase in bioavailability (Suni and Romantschuk 2004). 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 to 3 ºC (Shapiro and 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 pH 3 environment near the anode. Simultaneously contaminants migrate by electroosmotic 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 mobilise heavy metals (Maini et al. 2000; Singh and Turner 2009; Huang et al. 2012; Camenzuli et al. 2014).

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 and Romantschuk 2004; Acuña et al. 2012; Pucci et al. 2012). Harms and Wick (2006) discuss electro-bioremediation and its application to petroleum hydrocarbon contaminated sites. Electro-bioremediation utilises the principles of electrokinetic remediation to encourage the movement of petroleum hydrocarbons and microorganisms through soil and bioremediation to subsequently biodegrade contaminants (Harms and 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 and Romantschuk 2004). The performance of bioremediation and rate of biodegradation can become significantly reduced over prolonged periods at these temperatures (Suni and Romantschuk 2004). Heating the soil by applying an electric current can stimulate microbial activity and facilitate degradation, even during prolonged cold conditions (Suni and Romantschuk 2004).

Suni and 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 and 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 and 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 and 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 and Gale 1995; Baraud et al. 1997b, 1997a; Virkutyte et al. 2002; Kim et al. 2002, 2005; Hansen et al. 2013; Camenzuli et al. 2014), there is a need for further field based research to corroborate the findings of models and controlled laboratory-based studies. The reviewed studies indicate 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 and 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 and Ruby 2004; Camenzuli et al. 2014). 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.

3.3: Remediation technologies applicable to groundwater

3.3.1: Permeable Reactive Barriers

Permeable reactive barriers (PRB) 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, 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. 2014).

Selecting the most appropriate material or sequence of materials for a PRB is vital for effective management of petroleum hydrocarbon contaminated groundwater (Gore 2009; Gupta and Saleh 2013; Mumford et al. 2013; Camenzuli et al. 2014). 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, 2012) also successfully utilised 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 30-60% 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 (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 reports the potential of an octadecyltrichlorosilane surfactant on zeolite to facilitate petroleum hydrocarbon capture and nutrient delivery, thereby encouraging microbial activity within PRBs.

Colonisation of GAC and zeolites by petroleum hydrocarbon degraders presents the potential for bioremediation within PRBs (Kubota et al. 2008; Yeh et al. 2010; Vignola et al. 2011a, 2011b; 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 immobilised 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 fertiliser (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 and 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 and 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).

3.4: Conclusion

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 are 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 paper 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. Due to 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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Chapter 4: Chemical immobilisation of metals and metalloids by phosphates

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Citation: Hafsteinsdóttir E.G., Camenzuli D., Rocavert A., Walworth J. and Gore D.B. 2015. Chemical immobilisation of metals and metalloids by phosphates. *Applied Geochemistry 59*, 47-62.

Submitted: 23 May 2014; *Accepted for publication:* 21 March 2015; *Published*: 27 March 2015

Abstract

Remediation of metal contaminated media using orthophosphate fixation forms insoluble and nonbioavailable salts from metal and phosphate sources. The main focus has been on fixation of Pb, where the formation of pyromorphite, the most insoluble lead phosphate, has shown the great potential of this remediation technique. Other metals (Ba, Cd, Co, Cu, Eu, Ni, U, Zn) also have potential for effective fixation by orthophosphate. We review the applicability of the treatment across wider environmental conditions, particularly in surface soil, its use with elements other than Pb, product stability and efficiency with mixed contaminants.

4.1: Introduction

Remediation of metal-contaminated soil can be achieved by amendments which reduce metal bioavailability and minimise environmental impacts (Pierzynski et al. 2005). Ex situ and in situ treatments are used; however, in situ (in ground) treatments cause less environmental disturbance and are more cost-effective (Pierzynski et al. 2005; Matusik et al. 2008).

Chemical fixation converts metals to insoluble, non-bioavailable compounds under pH and oxidising conditions found in soil (Porter et al. 2004), reducing or eliminating risk to humans and the environment. Fixation can be achieved by the addition of anion(s) to form inert minerals or salts. Compounds with the potential to form inert minerals with metals include oxides, hydroxides, chlorides, sulphates, sulphides, phosphates, molybdites and carbonates (Porter et al. 2004). Orthophosphate (PO_4^{3-}) is a powerful and cost effective tool for metal fixation in soil and water (Ma et al. 1993; Xu et al. 1994; Ayati and Lundager Madsen 2000; Crannell et al. 2000; Liu and Zhao 2007; Cao et al. 2008). Reagents are readily available and safe for transport.

Orthophosphate fixation does not remove the contaminant from soil, but alters it to insoluble and non-bioavailable forms (Hettiarachchi et al. 2000; Scheckel and Ryan 2004; Zhu et al. 2004; Sonmez and Pierzynski 2005). Mechanisms of orthophosphate fixation include sorption onto inorganic and organic surfaces, ion exchange, and dissolution and precipitation (McKenzie 1980; Xu et al. 1994; Ma et al. 1995; Hettiarachchi et al. 2000; Melamed et al. 2003; Basta and McGowen 2004; Cao et al. 2004; Chen et al. 2007; Matusik et al. 2008; Smičiklas et al. 2008). Metal fixation using PO_4^{3-} forms salts or solid solutions (Eighmy et al. 1997; Crannell et al. 2000; Sugiyama et al. 2002; Melamed et al. 2003). An example is the conversion of Pb-minerals to pyromorphite ($Pb_5(PO_4)_3$(Cl K_{sp} $10^{-84.4}$, Br K_{sp} $10^{-78.1}$, F K_{sp} $^{10-71.6}$,OH K_{sp} $10^{-76.8}$)) which is orders of magnitude less soluble than other Pb-minerals (Ruby et al. 1994; Zhang et al. 1997; Zhang and Ryan 1998, 1999a,b; Porter et al. 2004; Cao et al. 2008). Phosphates of Cu (e.g. $Cu_5(PO_4)_3OH$, K_{sp} $10^{-51.62}$, $Cu_5(PO_4)_3Cl$, Ksp $10^{-53.96}$) and Cd (e.g. $Cd_5(PO_4)_3OH$, Ksp $10^{-42.49}$, $Cd_5(PO_4)_3Cl$, K_{sp} $10^{-49.66}$) are less soluble than other Cd and Cu compounds (Eighmy et al. 1997).

At least 49 elements can combine with PO_4^{3-} (Figure 4.1), forming ~300 minerals (Nriagu 1984b). A minority of minerals form with ions regarded as environmental contaminants, or are stable enough for fixation. Metal phosphate compounds are commonly in oxidised metal sulphide deposits, soils and sediments, and some are stable with respect to pH, Eh, and mineral diagenesis (Nriagu 1974, 1984a). Isomorphic substitution of divalent cations and oxyanions often occurs within minerals; Pb^{2+} for example can substitute for Ca^{2+}, and AsO_4^{3-} for $PO^4{}_{3-}$ (Nriagu 1984b).

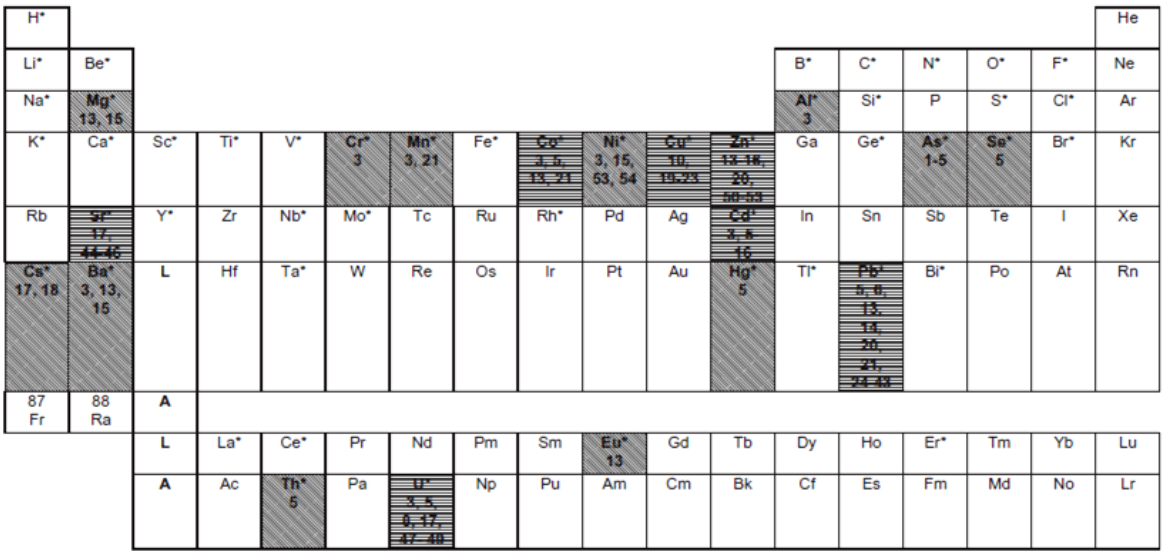

Figure 4.1: Efficiency of orthophosphate fixation. Asterisks indicate that PO_4^{3-} forms phosphate minerals with that element (Nriagu, 1984b). Elements with horizontally lined backgrounds are remediated by orthophosphate; diagonal lines indicate potential for remediation and clear backgrounds (where studied) are not remediated by orthophosphate fixation. 1-Peryea and Kammereck (1997), 2-Peryea (1991), 3-Seaman et al. (2001a), 4-Basta and McGowen (2004), 5-Kaplan and Knox (2004), 6-Porter et al. (2004), 7-Bolan et al. (1999), 8-Raicevic et al. (2005), 9-Matusik et al. (2008), 10-Ayati and Lundager Madsen (2000), 11-Thawornchaisit and Polprasert (2009), 12-Liao et al. (2008), 13-Knox et al. (2003), 14-Zwonitzer et al. (2003), 15-Suzuki et al. (1981), 16-Xu et al. (1994), 17-Seaman et al. (2001b), 18-Asabina et al. (2008), 19-Liu and Zhao (2007), 20-Cao et al. (2004), 21-Suzuki et al. (1982), 22-Bes and Mench (2008), 23-Qian et al. (2009), 24-Nriagu (1973a), 25-Nriagu (1973b), 26-Nriagu (1974), 27-Ma et al. (1995), 28-Ryan et al. (2001), 29-Cao et al. (2002), 30-Scheckel and Ryan (2002), 31-Hettiarachchi et al. (2000), 32-Zhang et al. (1997), 33-Zhang and Ryan (1998), 34-Zhang and Ryan (1999a), 35-Zhang and Ryan (1999b), 36-Cao et al. (2008), 37-Nriagu (1972), 38-Ma et al. (1993), 39-Hashimoto et al. (2009), 40-Rijkenberg and Depree (2010), 41-Martínez et al. (2004), 42-Shevade et al. (2001), 43-Melamed et al. (2003), 44-Moore et al. (2004), 45-Vukovic et al. (1998), 46-Smičiklas et al. (2000), 47-Arey et al. (1999), 48-El-Arabi and Khalifa (2002), 49-Jerden and Sinha (2003), 50-Maenpaa et al. (2002), 51-Brown et al. (2005), 52-Saxena and D'Souza (2006), 53-Boisson et al. (1999), 54-Zupančič et al. (2006).

Orthophosphate fixation is more effective for some metals and different phosphate sources are better for treating contaminated materials (Basta et al. 2001; Melamed et al. 2003; Zwonitzer et al. 2003; Basta and McGowen 2004). Fixation has focused on Pb (Ma et al. 1995; Laperche et al. 1997; Hettiarachchi et al. 2000; Zhu et al. 2004; Cao et al. 2008), however fixation is also effective for Ca, Cu, Zn, Cd and U contaminated soils and waters (Crannell et al. 2000; Seaman et al. 2001b; Hamon et al. 2002; Cao et al. 2004; Liu and Zhao 2007; Matusik et al. 2008). Major elements (e.g. Mg, Al, Ca, Mn, Fe), co-occuring with more toxic elements, can interfere with the precipitation of As, Cd, Hg and Pb (Ma et al. 1994b; Porter et al. 2004). Cu, Zn, Ni and Cd co-occur commonly with Pb (Ma et al. 1994b; Zwonitzer et al. 2003; Chen et al. 2007) due to common geological sources (Pierzynski et al. 2005) or co-disposal. This creates the need and opportunity to treat multiple contaminants in one material. Mobility, retention, and transformation of metals in soil is influenced by pH, redox potential, cation exchange capacity, organic matter, mineralogy and metal concentrations (Calace et al. 2002). Although orthophosphate is powerful and cost effective for metal fixation, the range of metals which

orthophosphate fixes effectively, the environmental conditions under which new minerals form and remain stable, and the identity and role of interfering ions, remain poorly understood. This paper focuses on orthophosphate fixation of metals and metalloids including Co, Ni, Cu, Zn, As, Cd, Ba, Eu and U. It addresses the types and influences of orthophosphate source, controls on reaction rate, factors influencing fixation efficiency and successful treatment preparation and application.

4.2: Influential factors

4.2.1: Type and influence of the orthophosphate source

Orthophosphate occurs mainly as phosphate rock (PR), which consists mostly of calcium phosphate ($Ca_3(PO_4)_2$) and fluoroapatite ($Ca_5(PO_4)_3F$) (Chang 2007). Calcium phosphate minerals are common in unweathered to moderately weathered soils, however with increased weathering Ca leaches from the soil and precipitates of Al and Fe phosphates form (Pierzynski et al. 2005). Phosphate sources vary in their potential for metal fixation and both liquid PO_4^{3-} and PO_4^{3-} containing solids are considered for fixation of metals (Table 4.1).

A challenge for chemical fixation-based management strategies is the need to keep orthophosphate solutions in contact with metal-contaminated materials long enough for reactions to occur. When reaction kinetics are slow due to either intrinsically slow reactions or very cold temperatures, it might be necessary to have controlled release nutrient sources to ensure a slow, steady supply of orthophosphate solution (e.g. Knox et al. 2006; Prasad et al. 2008). Mined PR has a low solubility (K_{sp} $10^{-57.0}$) and might be a good source for long term treatment of contaminated materials (Knox et al. 2006). Processed phosphate (fertiliser created from PR) and biogenic phosphate (ground fish bones) are more soluble (K_{sp} $10^{-48.0}$ and $10^{-45.2}$ respectively) and are suitable for faster treatments (Knox et al. 2006). Both Single and Triple Superphosphate ($Ca(H_2PO_4)_2 \cdot H_2O$) and ($Ca(H_2PO_4)_2$) have an advantage over liquid forms of phosphate, such as phosphoric acid (PA [H_3PO_4]) (Brown et al. 2005), in that the solid phase remains in the soil longer than a liquid, which may leach rapidly from the treatment area. Superphosphate is soluble in water and has a low pH (<4.68), forming brushite ($CaHPO_4 \cdot 2H_2O$) and then monetite ($CaHPO_4$) as it dissolves over days, with the two solids and solution system persisting for up to 17 days as the solution reaches equilibrium with respect to superphosphate and monetite (Lindsay 1979; Porter et al. 2004).

Table 4.1: Summary of orthophosphate fixation studies and phosphate sources.

Phosphate source	References
Phosphate rock (PR) • natural and activated • fluoroapatite ($Ca_5(PO_4)_3F$ or $Ca_{10}(PO_4)_6F_2$) • carbonated fluoroapatite ($Ca_{10}(PO_4, CO_3)_6F_2$) • 12.4% P- carbonated fluoroapatite • combined with manganese oxide (cryptomelane [MnO_2])	Ma et al. (1995), Hettiarachchi et al. (2000), Basta et al. (2001), Hettiarachchi and Pierzynski (2002), Melamed et al. (2003), Zwonitzer et al. (2003), Basta and McGowen (2004), Cao et al. (2004), Zhu et al. (2004), Mouflih et al. (2005), Sonmez and Pierzynski (2005), Aboulroos et al. (2006), Chen et al. (2007)
Phosphoric acid (PA [H_3PO_4]) • combined with $Ca(H_2PO_4)_2$ or PR (PR mainly $Ca_{10}(PO_4)_6F_2$ with substantial CO_3^{2-}) • fertiliser grade, 85% P_2O_5 • combined with KCl and $CaCl_2$	Cao et al. (2002), Melamed et al. (2003), Yang and Mosby (2006)
Hydroxyapatite (HA [$Ca_5(PO_4)_3OH$]) • synthetic hydroxyapatite • natural hydroxyapatite	Ma et al. (1993), Ma et al. (1994a), Ma et al. (1994b), Ryan et al. (2001), Mavropoulos et al. (2002), Knox et al. (2003), Zhu et al. (2004), Chen et al. (2007)
Phosphatic clay • apatite, smectite	Singh et al. (2001)
Biogenic phosphate • ground fishbone	Knox et al. (2006)
Phosphate bearing slags	Bes and Mench (2008)
Potassium phosphate • monopotassium phosphate (MPP [KH_2PO_4]) • dipotassium phosphate (DPP [K_2HPO_4])	Hamon et al. (2002), Maenpaa et al. (2002), Zwonitzer et al. (2003), Matusik et al. (2008)
Single superphosphate (SSP [$Ca(H_2PO_4)_2.2H_2O$])	Zhu et al. (2004)
Triple superphosphate (TSP [$Ca(H_2PO_4)_2$]) • combined with iron-rich material • combined with manganese oxide (cryptomelane [MnO_2])	Hettiarachchi et al. (2000), Hettiarachchi et al. (2001), Hettiarachchi and Pierzynski (2002), Maenpaa et al. (2002), Scheckel and Ryan (2004), Sonmez and Pierzynski (2005), Chen et al. (2007), Cao et al. (2008)
Ammonium phosphate ($(NH_4)_3PO_4$)	Bes and Mench (2008)
Monoammonium phosphate (MAP [$NH_4H_2PO_4$]) • combined with DAP	Levi-Minzi and Petruzzelli (1984), Peryea (1991), Peryea and Kammereck (1997), Ayati and Lundager Madsen (2000)
Diammonium phosphate (DAP [$(NH_4)_2HPO_4$])	Basta and McGowen (2004), Chen et al. (2007)
Iron phosphate nanoparticles • vivianite ($Fe_3(PO_4)_2 \cdot H_2O$)	Liu aand Zhao (2007)
Sodium phosphate (Na_3PO_4)	Moore et al. (2004)
Monosodium phosphate monohydrate ($NaH_2PO_4 \cdot H_2O$)	Ma et al. (1993)
Calcium magnesium phosphate ($(Ca, Mg)_3(PO_4)_2$)	Liao et al. (2008)

The greater the solubility of the phosphate source the more effective it is at immobilising the contaminant (Ma et al. 1995). Apatite (e.g. $Ca_5(PO_4)_3OH$ and $Ca_5(PO_4)_3Cl$) is the best phosphate source to immobilise Pb in Pb-contaminated soils, as the more stable pyromorphite forms after dissolution of the apatite (Ma et al. 1993; Ma et al. 1995; Zhu et al. 2004). Apatite can reduce aqueous concentrations of Co^{2+}, Ba^{2+}, Eu^{3+}, Pb^{2+}, and UO_2^{2+} in one week (Knox et al. 2003). Higher solubility and greater purity of hydroxyapatite (HA [$Ca_5(PO_4)_3OH$]) than, for example PR, can explain the

greater immobilising efficiency of HA (Ma et al. 1995). Fluoropyromorphite ($Pb_{10}(PO_4)_6F_2$) forms after 24 h using PR (mainly as fluoroapatite) (Cao et al. 2004), whereas chloropyromorphite ($Pb_5(PO_4)_3Cl$) forms and reaches equilibrium in 60 min using triple superphosphate (TSP [$Ca(H_2PO_4)_2$]) (Cao et al. 2008). A mix of solubilities of the phosphate source and the contaminated material is useful for successful immobilisation (Zhang and Ryan 1999a, b).

Chen et al. (2007) examined the effect of phosphate amendments on bioavailability and of Zn, Cd and Pb in soil with pH 5.42 and found the order from most to least effective was HA > PR > diammonium phosphate (DAP [$(NH_4)_2HPO_4$]) > TSP. Hydroxyapatite and PR immobilised metals while impacting less on soil pH than alternative phosphate amendments. Monopotassium phosphate (MPP [KH_2PO_4]) affected soil pH less than TSP but both P sources can reduce bioavailable Pb, Zn and Cd within 13 days and with higher amendment levels showing even more reduction (Maenpaa et al. 2002). Zwonitzer et al. (2003) found P source and level of P addition had no influence on Cd or Pb concentrations in plant tissue. Hettiarachchi et al. (2000) found TSP more effective in immobilising Pb in a smelter slag with 18.3% bioavailable Pb than PR, but PR proved as or more effective in soils which were collected from two repository storage areas and a vacant lot, with 22.6-36.6% bioavailable Pb. Basta and McGowen (2004) reported ineffective reduction in leachable Zn, Cd and Pb (<27%) when low solubility PR (12.4% P, carbonated fluoroapatite [$Ca_{10}(PO_4, CO_3)_6F_2$]), with P/total metal (M_{total}) molar ratios of 3:5 and 1:5, was mixed with smelter contaminated sandy loam. However, when it was used as a reactive barrier underneath the contaminated material (3:5 ratio) Cd, Zn and Pb transport reduced by 53%, 24% and 99.9% respectively. Apatite has been suggested for use in reactive barriers (Fedoroff et al. 1999).

PR is an efficient P source for the treatment of Cu, Zn and Pb contamination, with adsorption efficiency after 24 h increasing in the order Pb (60-68%) > Cu (42-56%) > Zn (<10%) (Cao et al. 2004). However, PR is a naturally occurring rock and its composition and fixation efficiency can vary depending on its place of origin. Ma et al. (1995) examined PR from Florida, Idaho, Utah, North Carolina and Montana (USA), that originated from calcined rock, raw ore, wash plant product, phosphate acid plant, pipeline slurry and fertilisers. All phosphate sources reduced Pb concentrations (as $Pb(NO_3)_2$) in aqueous solutions with efficiencies ranging from 39-100%. All PR types removed Pb when the initial concentration was 4.82 μmol L^{-1} but when the concentration was increased to 48.2 μmol L^{-1}, only PR from Florida showed acceptable removal levels of 0.02 g Pb/g PR. Oxalic-acid activated PRs more effectively immobilise Pb when compared to raw PRs (Jiang et al. 2012). All types of PR more effectively reduce Pb concentration with greater P addition.

Competing ions can reduce the efficiency of the phosphate source. Calcium and P are common in soil and water (Pierzynski et al. 2005), with Ca usually in excess of P (Porter et al. 2004). Calcium competes

with other metals for sorption sites and may consume much of the P to form apatite (Maenpaa et al. 2002; Porter et al. 2004). Where formation of apatites and metal phosphates might occur (Nriagu 1974), higher doses of phosphate might be needed for precipitation of both the Ca and the metal (Ayati and Lundager Madsen 2000).

Phosphate can be used in conjunction with amendments which provide additional reactants. Iron-rich material can serve as potential sorbents for both P and Pb. Scheckel and Ryan (2004) found adding 1% or 2.5% iron-rich material to 1% TSP resulted in 31% or 41% more pyromorphite formation, respectively. KCl and $CaCl_2$ have been applied with PA, supplying chloride to optimise formation of chloropyromorphite (Melamed et al. 2003; Yang and Mosby 2006). Hettiarachchi et al. (2000) found a combination of phosphorus (PR or TSP) and manganese oxide (cryptomelane [MnO_2]) stabilised soil Pb more effectively than either reagent used separately. Sonmez and Pierzynski (2005) found interactions between the Pb-mineral, Mn oxides, P and soil components reduced metal bioaccessibility, consistent with Mn(IV) (hydr)oxide (birnessite and cryptomelane) being a strong metal adsorbent, especially for Pb (McKenzie 1980). Manganese oxide use in conjunction with phosphorus fertiliser may reduce P lost to the environment, lessening the risk of eutrophication (Hettiarachchi and Pierzynski 2002).

4.2.2: Reaction rate and stability

The rate of metal PO_4 fixation reactions is influenced by the mineralogy, particle size and ionic radius, solubility of reactants, the concentration of all components of the reaction, pH, Eh and temperature (Hermann and Neumann-Mahlkau 1985; Ayati and Lundager Madsen 2000; Jerden and Sinha 2003; Knox et al. 2006; Prasad et al. 2008; Unuabonah et al. 2007; Xu et al. 2008). Once a metal phosphate salt is formed, its stability becomes crucial for the long term efficiency of fixation. Most of the factors that affect reaction rate control the stability of the formed P minerals: pH, Eh, temperature, moisture and soil-solution concentrations of Al, Ca, Fe and Mg (Pierzynski et al. 2005).Here we discuss factors that influence reaction rate, and due to the importance of pH and Eh, their effects will be discussed later.

PO_4-fixation occurs by dissolution-precipitation (Xu et al. 2008), so the metal and phosphate need to be in solution to react with each other. Dissolution kinetics for pure anglesite solutions ($PbSO_4$) and Pb contaminated soils (mainly anglesite and galena [PbS]) followed first-order (k_1) and parabolic (k_3) diffusion equations respectively (Ruby et al. 1992). The first-order reaction was pH dependent, with increasing pH increasing the dissolution and reaching equilibrium more quickly. However, parabolic diffusion patterns resulted in decreased reaction rates as pH increased (Ruby et al. 1992). Although Ruby et al. (1992) showed that dissolution of anglesite is pH dependent, Zhang and Ryan (1998) observed that dissolution of anglesite in a simple system is independent of pH over the pH range 2-

7, while the dissolution rate for the phosphate source (HA) is pH dependent. Dissolution increased with decreasing pH and was too fast at pH <4 and 37 °C to be accurately measured. Lead adsorption on low-grade PR followed either a first-order or a pseudo-first-order kinetic reaction, where equilibrium was reached in 2 hours at 25 °C (Keleş et al. 2010) and the rate of adsorption decreased with increasing initial concentrations of Pb (Prasad et al. 2000). Alam et al. (2001) showed that As extraction from contaminated soils by potassium phosphate followed first-order reaction kinetics. The extraction at 20 °C and an initial pH 6, was rapid for the first 2.5 hours; equilibrium was reached within 5 hours. Smičiklas et al. (2008), observed pseudo second-order reaction kinetics (k_2) when poorly crystalline synthetic HA (Ca/P ratio 1.60:1) reached sorption equilibrium at room temperature (20 °C) in 30 mins for aqueous Pb, and in 24 hours for aqueous Zn, Sr and Cd. Increasing initial Pb concentrations increased the sorption rate on phosphate-modified kaolinite clay in a process that followed a pseudo-second-order kinetic reaction (Unuabonah et al. 2007).

Metal removal by orthophosphate occurs in two stages. Two-step kinetics were observed for Cd sorption on synthetic HA, whereby most of the metal was fixed in 2 min,and after which the kinetics slowed considerably (Fedoroff et al. 1999). Mouflih et al. (2005) observed very rapid adsorption of Pb onto natural and activated PR in the first 30 min, then adsorption slowed and reached equilibrium in 1 h for natural PR and 3 h for activated PR. This difference in equilibrium rate can be related to almost doubling in surface area after activation of the PR (13.89 $m^2 g^{-1}$ for natural PR and 22.22 $m^2 g^{-1}$ for activated PR). Xu et al. (2008) studied the sorption of aqueous Pb by poorly crystalline synthetic carbonate-HA (Ca/P ratio 1.60:1) at room temperature (25 °C), and found that the reaction rate could be described in two kinetic stages. For the first 10 min the reaction was fast, with hydroxypyromorphite forming in 1 min, possibly involving a dissolution-precipitation mechanism. After 10 min the reaction rate slowed and followed a first-order kinetic equation (k_1), with surface sorption suggested as the fixation mechanism. The first-order rate constant (k_1) (Xu et al. 2008) relates to the simpler second reaction stage. While temperature dependence is described by the Arrhenius equation, its value is also influenced by the conditions under which the more complicated first reaction stage occurs (initial [Pb], pH, and the HA dose.) Varying the conditions under which the first reaction stage occurs brings about different starting conditions for the second reaction stage. The second stage cannot be considered in isolation from the first unless a constant set of conditions is used, which is the case when examining temperature dependence. This supports the concept that the reaction rate of a multiphase reaction is controlled by the rate of the slowest process (Xu et al. 2008).

4.2.3: Mineralogy, particle size and ionic radius

Mineralogy, particle size and ionic radius can significantly control phosphate fixation efficiency in terms of the reaction rate and the type of metal contaminant that is preferentially fixed. Electronegativity and the ionic radius of cations control to what extent metal cations are removed by

apatite, i.e. cations with ionic radii close to or higher than the Ca^{2+} range (90-130 pm) and high electronegativity are exchanged more into the apatite lattice (Suzuki et al. 1982; Unuabonah et al. 2007). The ionic radius of Pb^{2+} (120 pm) and Cd^{2+} (100 pm) in comparison to Zn^{2+} (75 pm), Cu^{2+} (75-79 pm) and Co^{2+} (65 pm) makes them preferred cations for the substitution of Ca^{2+} released from PR or other calcium phosphates (e.g. β-$Ca_3(PO_4)_2$, $CaHPO_4 \cdot 2H_2O$, $Ca(H_2PO_4)_2 \cdot H_2O$) (Suzuki et al. 1982; Sugiyama et al. 2003; Saxena and D'Souza 2006). Due to this preferred radius size of Pb, the initial reaction rate has shown to be fastest for Pb compared to Cu and Zn when fixed by low-grade sedimentary PR, with 95% of the Pb reaching equilibrium in 25 min (Prasad and Saxena 2004). Similarly, since Cd^{2+} and Pb^{2+} are preferred cations for the substitution of Ca^{2+} they might compete with each other, as has been observed with the presence of Cd slowing the initial adsorption rate for Pb onto phosphate-modified kaolinite clay (Unuabonah et al. 2007). Crystalline compounds may be created from the fixation of cations that are larger than Ca^{2+}, like Cd^{2+} and Pb^{2+}, while amorphous compounds are obtained from smaller cations (e.g. Cu^{2+} and Co^{2+}) (Sugiyama et al. 2003). Amorphous phases are typically less stable than crystalline, like poorly crystalline carbonate HA that diffuses very rapidly in acidic aqueous solutions (Xu et al. 2008).

Metal-phosphate precipitation is affected by the particle size of the phosphate source, which controls dissolution rate due to surface area and thus availability of P for fixation (Knox et al. 2006). Dissolution rates of orthosilicate minerals span several orders of magnitude (Casey and Westrich 1992), and the solubilities of other mineral salts such as carbonates and sulphides can vary even more. Smaller (<90 μm) Pb bearing mineral particles dissolve faster than coarser particles (Ruby et al. 1992). Decreasing PR particle size from 210-420 μm to 75-105 μm in a Pb, Zn and Cu solution increased the efficiency of metal removal (Prasad et al. 2008), but decreasing the size of PR particles further did not improve sorption efficiency. Similarly, the efficiency of PR in reducing Pb uptake by sudan grass (*Sorghum bicolour* L. Moench) increased with decreasing particle size, with PR <250 μm diameter twice as effective as PR 0.5- 2 mm diameter (Laperche et al. 1997).

4.2.4: Solubility

Solubility of both the contaminant- and phosphate-bearing reactants controls the success of fixation. Solubility of P-minerals is greatest at pH 6.0-6.5 (Pierzynski et al. 2005). Formation of metastable phosphate minerals controls PO_4^{3-} solubility (Peryea 1991). Dissolution of phosphate fertilisers such as superphosphate results in precipitation of brushite and monetite due to supersaturation. Brushite is the metastable mineral, eventually dissolving and forming monetite. Equilibrium is reached in 7-17 days when both superphosphate and monetite are stable (Lindsay 1979).

A mix of P-sources with different solubilities can result in more successful fixation (Knox et al. 2006); higher solubility P-sources (e.g. biogenic apatite and HA) can provide PO_4 faster in the beginning of

the fixation and be appropriate when a fast fixation is required, whereas lower solubility P-sources that dissolve more slowly (e.g. PR) can provide longer term treatment (Laperche et al. 1997; Knox et al. 2006). Dissolution of cerussite ($PbCO_3$) and HA and precipitation of pyromorphite is near complete and far more rapid at pH <5 than pH >5, due to greater solubility of cerussite at pH <5, with slower reaction rates as pH increases (Zhang et al. 1998).

4.2.5: Concentration of reactants

Pb immobilisation in a $PbHAsO_4$ insecticide-contaminated alkaline soil from an old apple orchard was tested with PR from two chemical companies in Florida that had previously proved effective in aqueous solutions. Available Pb reduced from 56.8% to 98.5%, with greater soil Pb fixation achieved by larger additions of PR (Ma et al. 1995). Increasing initial concentrations of aqueous Pb reacted for 30 min with 5 g/L of synthetic carbonate-HA at pH 2 and 25 °C slowed the reaction rate. Higher concentrations of phosphate increased reaction rate (Xu et al. 2008). This could be explained by increased availability of active sites for sorption of Pb on HA or the P source lowering pH and hence increasing dissolution. For fixation of Cd by synthetic-HA, diffusion slowed as the concentration of Cd increased (Fedoroff et al. 1999). Equilibrium for low-grade PR fixation of Pb, Cu, and Zn respectively in solution at different concentrations was reached in 30 min, whereas equilibrium for low-grade PR fixation of Co was reached in 84 h. The faster equilibrium of Pb, Cu and Zn compared to Co can be explained by availability of active sites on adsorbent surfaces (Prasad and Saxena 2004; Saxena and D'Souza 2006). By increasing adsorbent dosage (low-grade PR; from 0.15 to 0.50 g/L) equilibrium for Pb fixation was reached faster (<50 min compared to >200 min), which can be explained by increased numbers of adsorption sites. Increasing initial Pb concentrations increases the amount that is adsorbed, with rapid adsorption to begin and reaching an asymptotic value with time (Keleş et al. 2010). These findings show how important sufficient characterisation of the contaminated material is prior to fixation, as the concentration of the contaminant-bearing reactant present in the solution and the phosphate-bearing reactant to be added to the solution for fixation, are both crucial factors for successful fixation.

4.2.6: Soil conditions

Equilibrium in soil is rare due to microbial activity, plant uptake, weathering, and leaching (Pierzynski et al. 2005). There can be great differences in dissolution rate for metals and P-sources in real soils compared to simple systems, due to interactions with soil particles and availability of reactive surfaces (Ruby et al. 1992).

Adsorption and desorption of Cu(II), Zn(II), Pb(II) and Cd(II) were studied on two soils that were amended with nanoscale HA. Increasing initial concentrations of metals increased adsorption efficiency on both soils. Fewer metals adsorbed on one soil than the other, due to lower CEC and pH

in that soil. A Freundlich model described the adsorption isotherms for the metals well for both soils, with the adsorption affinity in the order $Cu^{2+} > Pb^{2+} > Cd^{2+} > Zn^{2+}$ (Chen et al. 2010). Sorption kinetics of P by soils commonly occurs in two stages, where the initial reaction is fast (1 day or less) while the second stage lasts for weeks. Once P is sorbed it does not easily desorb due to hysteresis (Pierzynski et al. 2005). However, this can be overcome and the availability of P for metal fixation increased by either liming acid soils, and preventing the formation of Al or Fe phosphates, or adding organic matter which inhibits P sorption (Pierzynski et al. 2005).

Phosphate fixation (using MAP or MAP and DAP) in Cu, Cd and Pb systems, with and without Ca^{2+}, showed that co-precipitation of Ca can consume phosphate needed for precipitation of the metals (Ayati and Lundager Madsen 2000). The Ca ion inhibits the growth of Cu and Cd phosphates, especially at high pH. However, Ca did not affect the formation of lead hydrogen phosphate ($PbHPO_4$), either in solution or in minerals. Although Ca inhibits crystal growth of Cu and Cd phosphates, Ca-containing Cd and Cu phosphates are less soluble than the pure metal phosphates. Where substitution occurs, as is the case with Cd by Ca, the degree of substitution may be so large that greater doses of phosphate are needed for precipitation of both Ca and Cd than would be required without Ca (Ayati and Lundager Madsen 2000). This Ca competing ion effect can explain the difference in phosphate fixation efficiency in soils with different mineral composition, acidity or weathering stage (Pierzynski et al. 2005). PR did not form chloropyromorphite 220 days after application to Pb-contaminated soil with a pH of 6.95 ± 0.19, however chloropyromorphite was detected via X-ray diffractometry 330 - 480 days after P application (Melamed et al. 2003). This longer time for pyromorphite formation could reflect soil characteristics affecting the fixation efficiency. Soil organic acids in the rhizosphere could liberate Pb from pyromorphite (Debela et al. 2010). Organic carbon can constrain reactions rates strongly, probably via blocking of crystal growth surfaces (Lang and Kaupenjohann 2003).

Soil microorganisms help decompose phosphorus-bearing minerals, releasing P for immobilisation of metals, metalloids and uptake by plants (Park et al. 2011a; 2011b; 2011c; 2011d; Walpola and Yoon 2012). Some bacteria increase the solubility of sparingly soluble P compounds by changing soil pH through the production of organic acids and phosphatases (Rodríguez and Fraga 1999; Park et al. 2011a; Park et al. 2011b). These microbes, including *Pseudomonas, Bacillus, Rhizobium* and *Enterobacter*, can increase the bioavailability and effectiveness of PR treatments. Park et al. (2011a) compared Pb leaching in contaminated soil treated by soluble and insoluble P sources with the phosphate solubilising bacteria *Enterobacter cloacae*. Leachability of metals increased in soils treated with soluble P as the treatment increased dissolved organic carbon concentrations in soil, thereby increasing Pb mobility (Park et al. 2011a). Leachability of metals reduced by up to 36% in soil treated with PR and phosphate solubilising bacteria (Park et al. 2011a). *Enterobacter sp.*, a solubilising phosphate bacteria,

increased PR bioavailability and the immobilisation of Pb by up to 32% (Park et al. 2011b). Immobilisation of Pb in solutions did not increase due to acidification of the bacterial medium (Park et al. 2011b).

4.2.7: Temperature

Greater temperature imparts faster reaction rates (Lo et al. 2009). Lower temperatures usually result in slower reaction rates and slower phosphate fixation efficiency. Increased ion-exchange between Zn^{2+} in solution and Ca^{2+} in apatite was observed with temperature increase from 20 °C to 40 °C (Suzuki et al. 1981). Sorption of Cd by synthetic-HA increased with time and temperature (18, 28, 75 °C), however equilibrium was not reached in 12 days (Fedoroff et al. 1999). Adsorption of Pb onto natural and activated PR increased as temperature was elevated (25, 35, 45 °C) (Mouflih et al. 2005). As extraction efficiency by potassium phosphate increased significantly from 10-40 °C and was optimised at 40 °C with approximately 60% As extraction; extraction was not greatly improved with temperatures >40 °C (Alam et al. 2001). Adsorption of Pb by low-grade PR increased with increasing temperature (25-50 °C) and reached equilibrium faster at higher temperatures (Keleş et al. 2010). The reaction was endothermic due to increased adsorption of Pb^{2+} ions onto PR with increasing temperature. Adsorption of Pb onto phosphate-modified kaolinite clay and natural and activated PR is endothermic and is more effective at high temperatures (Mouflih et al. 2005; Unuabonah et al. 2007). However, sorption of Pb on low grade (<15% P_2O_5) carbonated PR (105-150 μm grain size) was exothermic since the percentage of adsorption decreased with increasing temperature (30-60 °C).

Mineral formation and crystallite size is affected by temperature, as fewer and bigger crystals form at higher temperatures (Ayati and Lundager Madsen 2000). Ayati and Lundager Madsen (2000) investigated phosphate crystallisation of metal- and calcium nitrates (0.02 M and 0.01 M respectively) at 5 °C and 37 °C after 35 days of reaction time, using MAP or MAP and DAP. Smaller Cd phosphate crystals ($Cd_5H_2(PO_4)_4,4H_2O$) formed at 5 °C than at 37 °C. However, temperature had little effect on size of hydroxypyromorphite and $PbHPO_4$ crystals. Hydroxypyromorphite crystals formed at 37 °C were small but more crystalline than HA at the same temperature. Chloropyromorphite is the most thermodynamically stable low temperature lead phosphate compared to $Pb_4O(PO_4)_2$, $Pb_3(PO_4)_2$, $PbHPO_4$, $Pb_5(PO_4)_3OH$ and $Pb(H_2PO_4)_2$ (Nriagu 1974). Ayati and Lundager Madsen (2000) found at 5 °C Cu phosphate crystals contained both cornetite ($Cu_3(OH)_3PO_4$) and copper ammonium phosphate ($CuNH_4PO_4$), whereas at 37 °C they consisted of libethenite (Cu_2OHPO_4). Copper phosphate crystals were smaller than those of the other metals. Nearly complete formation of Cd and Pb phosphates occurred quickly compared to a pure copper phosphate system where it may take several months to reach equilibrium, even at 37 °C.

White et al. (2012) demonstrated fixation of metals in cold temperatures using orthophosphate, but showed that conversation rates to metal-orthophosphate mineral phases is temperature dependent. Cu reacted faster with orthophosphate at 2 °C than 22 °C due to enhanced exothermic reactions in cold conditions; however, Pb and Zn reactions were faster and more complete at 22 °C than 2 °C.

Low temperatures affect mineral solubility and hydration; while freezing desiccates particles, increasing the concentrations of soluble metals (Dietzel 2005; Hafsteinsdóttir et al. 2011). This can influence reaction rates and the formation and stability of metal-orthophosphate minerals formed during fixation. Hafsteinsdóttir et al. (2011, 2013) examined the effects of 240 freeze thaw cycles from -20 °C to +10 °C in laboratory experiments. In single metal systems Cu, Pb and Zn phosphates formed and were stable, while Cu and Zn minerals reduced in multi-metal systems. Competing ions, concentration of the phosphate treatment and amount of available water were factors for reduced fixation efficiency (Hafsteinsdóttir et al. 2011, 2013).

4.2.8: pH

In unweathered and moderately weathered soils, dominant P-minerals are apatites; Ca phosphates with the general formula $Ca_{10}(PO_4)_6X_2$. In strongly weathered soils, Ca eventually leaches from the soil, pH decreases and precipitates of Fe and Al phosphates become the main mineral forms of P (Pierzynski et al. 2005). Release of P from soils is enhanced at low and high pH. Acidic conditions dissolve inorganic cements such as Al oxides and clays, whereas high pH can degrade organic coatings, releasing P in colloids (Liang et al. 2010).

The pH range of contaminated environments is very broad; some acid-sulphate soils can have pH <2 (Liu et al. 2009), mine tailings can range from being alkaline to strongly acidic (Gore et al. 2007; Hamon et al. 2002; Praharaj and Fortin 2008), some household and industrial waste landfill material has pH 8-9 (Östman et al. 2008), leachates from bottom ash of combusted municipal solid waste can have pH 11 (Crannell et al. 2000) and pH 13 for strongly alkaline fly ashes (Izquierdo and Querol 2012).

Phosphate additions can raise or lower soil pH. Dissolution of the orthophosphate source and the contaminated material, and the consequent formation of a stable metal-phosphate mineral, is largely controlled by pH (Ma et al. 1993), particularly for reactants which are poorly water soluble, such as Pb bearing solids (cerussite [$PbCO_3$] and galena [PbS]) (Zhang and Ryan 1999a, b). P compounds typically used as amendments can be grouped into highly, moderately or low solubility, but are commonly either water soluble (fast release) or water insoluble (slow-release). Water soluble forms of P include TSP, MAP and DAP and insoluble forms include PR, HA and biogenic forms (Bolan et al.

2003). Understanding reactions of different sources of P in soil allows prediction of their relative effectiveness at immobilising metals and metalloids.

Water soluble forms of superphosphate P applied to soil, create monocalcium phosphate (MCP) by dissolution, forming dicalcium phosphate with the release of phosphoric acid (Bolan et al. 2003). The acid dissociates into $H_2PO_4^-$ and hydrogen ions and soil pH drops substantially; $Ca(H_2PO_4)_2 + H_2O \rightarrow CaHPO_4\ H_2O + H_3PO_4$ (Bolan et al. 2003). Alternatively, when ammonium-based P sources are applied to soil, they dissociate into ammonium and $H_2PO_4^-$ ions, instigating oxidation of ammonium to nitrate. This releases protons; $NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$ (Bolan et al. 2003). Soil treated with ammonium P has generally higher pH than soils treated with superphosphate fertilisers (Bolan et al. 2003). Acidity generated by soluble P sources (TSP, phosphoric acid, HA, DAP and MPP) can increase metal and metalloid mobility and should be used with a pH buffer.

Sparingly soluble P forms such as PR must be dissolved in soil prior to becoming available for immobilisation of metals. Insoluble forms of P are typically dissolved by soil acid: $Ca_{10}(PO_4)_6F_2 + 12H^+ \rightarrow 10Ca^{2+} + 6H_2PO_4^- + 2F^-$ (Bolan et al. 2003). PR dissolution rates are variable, depending on the chemical nature and particle size of the PR, as dissolution rates increase with decreasing particle size (Bolan et al. 2003; Soltan et al. 2012). Once sparingly soluble forms of P are dissolved they undergo similar adsorption and precipitation reactions to that of more soluble P forms. pH also controls reaction rates in aqueous solutions (Ma et al. 1995).

Removal of Pb from solution is pH independent. Apatites (HA, PR) fix Pb^{2+} over pH 3-12, with almost complete removal of Pb over that entire range (Ma et al. 1993; Chen et al. 1997; Crannell et al. 2000; Cao et al. 2004; Smičiklas et al. 2008). However, dissolution of the phosphate source and lead-bearing contaminant, and formation of lead-phosphates is pH dependent. Under neutral to acidic conditions, dissolution of HA and precipitation of various pyromorphite-like minerals occurs. The formation of chloropyromorphite, using superphosphate as a phosphate source and by dissolution of Pb from cerussite, anglesite and litharge (PbO), is greatly influenced by pH, with more acidic conditions (pH 3-5) favouring formation of chloropyromorphite (Cao et al. 2008). Without superphosphate added to the soils the dissolution of cerussite, anglesite and litharge, at room temperature (~25 °C), took 180 min to reach equilibrium but with superphosphate addition the dissolution reached equilibrium within 60 min (Cao et al. 2008), as superphosphate lowers pH and reactions occur faster. HA can reach near complete dissolution in 5 min at pH 2 and 3, with barely any cerussite left in the solids at pH 2-4. Almost 100% conversion of cerussite to chloropyromorphite has been achieved in 60 min (Zhang and Ryan 1999b). With dynamic pH, from initial pH of 2.1-2.4, the solubility of chloropyromorphite can control the amount of soluble Pb throughout the reaction (Zhang and Ryan 1999b). Lower pH enhances dissolution of Pb minerals and provides more Pb for

the formation of chloropyromorphite. Without P addition at pH 3 and 5, Pb solubility followed the order of litharge > cerussite > anglesite but at pH 7 the order was anglesite > litharge > cerussite. With P additions at pH 7, solubility was in the order of anglesite > cerussite > litharge but at pH 3 and 5 the order was cerussite > litharge > anglesite (Cao et al. 2008). Under alkaline conditions the dissolution of the apatite reduces, leaving less PO_4 to react with Pb, forming hydrocerussite ($(Pb_3(CO_3)_2(OH)_2)$ or $Pb(OH)_2$) and lead oxide fluoride (Pb_2OF_2) (Chen et al. 1997; Smičiklas et al. 2008). Using HA or aqueous P (monosodium phosphate monohydrate [$NaH_2PO_4 \cdot H_2O$]) as a P source, with lead nitrate ($Pb(NO_3)_2$) as the aqueous Pb source, forms hydroxypyromorphite throughout pH values of 3 to 7 (Ma et al. 1993). The strongest X-ray diffraction peaks for hydroxypyromorphite were at pH 5 when HA was used as the treatment. Little HA was detected at pH 3, indicating most of that mineral had dissolved. In addition to hydroxypyromorphite, $PbHPO_4$ formed at pH 3. Maximum removal of Pb as $Pb(NO_3)_2$ occurs at pH 2 and 3 for natural PR and at pH 3 and 4 for activated PR; at higher pH values the efficiency of phosphate fixation diminishes (Mouflih et al. 2005).

Mobility of Cd, Cu, Sr and Zn in soils decreases with increasing pH. Decreasing pH enhances desorption and solubility of adsorbed Cu and Zn from PR (fluoroapatite) due to weakly bound complexation of these metals onto the PR surface (Cao et al. 2004). In an effort to stabilise Cu and Zn in bottom ash from combusted solid municipal waste, formation of $(Cu, Ca_2)(PO_4)_2$ occurred after PO_4^{3-} addition at pH 4 and reduced copper leaching (Crannell et al. 2000). At pH 4 and 6, Zn^{2+} solubility reduced by 1 to 2 orders of magnitude due to $(Zn,Ca_2)(PO_4)_2$ and $(Zn_3,Ca_2)(PO_4)_3OH$ formation, and at pH 8 there was no detectable Zn in the aqueous phase. Matusik et al. (2008) used potassium phosphate (K_2HPO_4), MAP and "Polifoska 15" fertiliser in a Cd immobilisation study at three initial pH levels (5, 7, 9). All phosphate sources had the most effective Cd reduction at an initial pH of 7. Aqueous Cd reduction by potassium phosphate resulted in pH changes, dropping from pH 5 to 3.99 and from pH 9 to 7.65. Where initial pH was 7, it stayed stable (6.91 ± 0.01) for 720 h, although pH after 1440 h was slightly elevated (pH 7.38). When MAP was used as a P source, no Cd phosphate formation was observed at pH 5. When pH increased to pH 5.5 a gradual decrease in Cd concentration was observed for the two months of the experiment. Faster decreases in Cd concentration were observed when initial pH was either 7 or 9. Addition of MAP to the solution lowered pH (from 5.5 to 4.62, from 7 to 6.83, and from 9 to 8.71). "Polifoska 15" fertiliser changed pH over the two month experiment; pH 5 and 9 decreased to 4.07 and 8.84, respectively, but pH 7, which showed the most efficient Cd reduction, increased to 7.55. Smičiklas et al. (2008) adjusted initial solution pH to 5.0 ± 0.1 when using HA to fix Zn^{2+}, Sr^{2+}, and Cd^{2+}. Sorption capacity of Zn, Sr and Cd onto the HA surface increased with an increase in pH. A rapid decrease in Cd and Zn aqueous concentrations at higher pH was caused by the sorption of hydrolytic species and precipitation of insoluble hydroxides. Since Sr does not hydrolyse, the decrease in Sr can be explained by the apatite

surface becoming negatively charged and attracting Sr^{2+}. These findings support identification of the dominant mechanisms of cation removal as sorption of hydrolytic species, precipitation of insoluble hydroxides or attractive electrostatic forces at higher pH, rather than ion-exchange and dissolution/precipitation mechanisms, which dominate at lower pH (Smičiklas et al. 2008).Acidity can determine the success of metal-orthophosphate fixation strategies (Cao et al. 2008; Zhang and Ryan 1998). The ability to form new metal phosphate minerals relies on the initial liberation of metal ions. The duration and magnitude of a pH drop is critical for contaminant dissolution and new mineral formation, and pH control is a critical aspect of contaminated site fixation. If the success of phosphate treatments depend on a specific pH, then a buffer could help achieving the required pH conditions.

Dissolution of superphosphate fertiliser ($Ca(H_2PO_4)_2 \cdot H_2O$) into Ca^{2+} and $H_2PO_4^-$ ions results in a pH of 4.68, with the formation of brushite ($CaHPO_4 \cdot 2H_2O$) giving a pH of 1.48, and then the formation of monetite ($CaHPO_4$) dropping pH to 1.01 (Figure 4.2) (Lindsay 1979). This low pH helps form chloropyromorphite (Porter et al. 2004). Brown et al. (2004) reported 3.2% TSP was the most successful treatment, reducing bioaccessibility of soil Pb by 89%. Soil pH reduced to 3.42 by this amount of TSP, and liming (200 t ha^{-1} $CaCO_3$) was suggested to return pH to an acceptable range. Calcium carbonate ($CaCO_3$) and burnt lime (CaO) could counteract the decrease in pH which MPP causes (Hamon et al. 2002; Zwonitzer et al. 2003). Hydrated quicklime ($Ca(OH)_2$) has been used as a buffer to raise soil pH (Yang and Mosby 2006). Application of quicklime to Pb-contaminated soils and mine spoils 24 h after addition of TSP (5000 mg P/kg soil) was insufficient to restore soil pH to pre-treatment levels, although Pb fixation was successful (Hettiarachchi et al. 2001). Thermodynamic modelling indicates that the stability of chloropyromorphite cannot be ensured if hydrated quicklime is mixed with the material and alternatives, such as a combination of potassium and ammonium phosphates, have been suggested (Porter et al. 2004). When used as a treatment for a scrubber residue, PA (1.2 moles PA/kg of residue) did not alter pH greatly. The slight reduction in pH, from 12.36-12.54 to 12.10-12.33, was due to the high buffering capacity of excess CaO in the residue. Alternatively, the PA may have dissolved minerals containing Ca, Cu, Zn, Cd and Pb in the residue, forming chlorapatite ($Ca_5(PO_4)_3Cl$), zinc phosphate ($Zn_3(PO_4)_2$), cadmium chlorapatite ($Cd_5(PO_4)_3Cl$), and chloropyromorphite ($Pb_5(PO_4)_3Cl$) (Eighmy et al. 1997). Hydroxyapatite can have a relatively high $CaCO_3$ content (Knox et al. 2003) and potentially is a buffer (Smičiklas et al. 2008). Manganese oxides, often used as buffers, can be dissolved by naturally occurring reducing compounds in the soil, releasing metal ions (Godtfredsen and Stone 1994). Synthetic Mn oxides combined with TSP or PR can reduce bioaccessibility of Pb and Cd more than TSP or PR alone.

Soil pH can vary considerably depending on soil type and local conditions (including degree of contamination), and chemical characterisation of the matrix and contaminant before designing

treatment solutions is important. Co-application of a buffer and P treatment (Thawornchaisit and Polprasert 2009) is a practical approach for managing acidification of treated material.

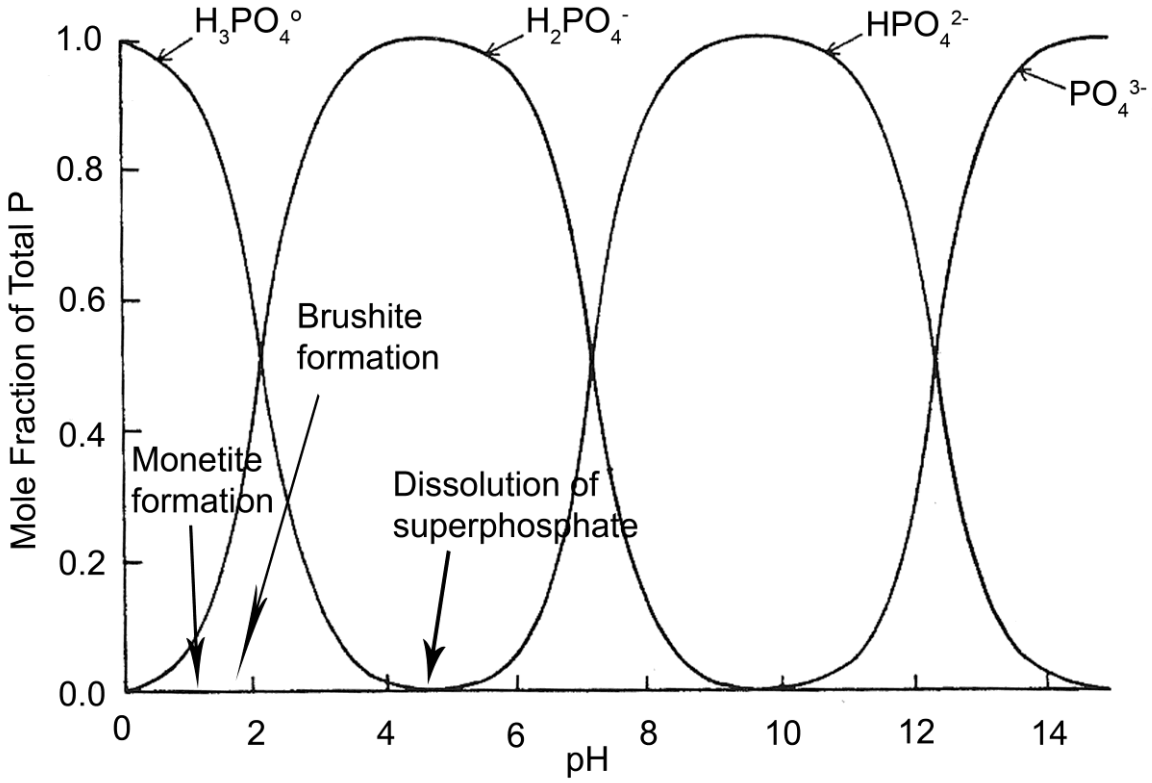

Figure 4.2: pH dependence of phosphate speciation (after Lindsay 1979).

4.2.9: Oxidation-reduction potential

Physical, chemical and biological changes occur as soil becomes water saturated. Changes to Eh can be pronounced, where bacterial catalysts or abiotic processes reduce some elements to a lower oxidation state (Manahan 2005; Pierzynski et al. 2005). Changes in redox potential can make some elements more mobile and toxic to the environment. Groundwater usually lowers soil redox potential. Redox potential ranges from +49 mV in the more reducing environment of the lower horizon of the soil to +347 mV in the oxidising environment of the upper horizon (Hermann and Neumann-Mahlkau 1985). Redox potential can vary seasonally, being higher in the wet season (Eh = +150 to +562 mV) compared to the dry season (Eh = +22 to +531 mV) and always oxidising. Eh is often higher in contaminated waters (Eh = +287 to +562 mV) compared to pristine waters (Eh = +22 to +438 mV), during both dry and wet seasons (Salvarredy-Aranguren et al. 2008).

When uncontaminated natural waters enter mined areas and interact with mine wastes, water chemistry may change from the Ca-Mg-HCO_3 dominance to Ca-Mg-SO_4, due to sulphide oxidation (Salvarredy-Aranguren et al. 2008; Frau et al. 2009). Sulphidic mine waste oxidises to form secondary

sulphides, oxides, hydroxides, arsenates and sulphates (Harris et al. 2003). Galena is commonly found in mine wastes (Harris and Lottermoser 2006; Frau et al. 2009). Under oxidising conditions galena (K_{sp} 3.4 x 10^{-28} (Chang 2007)) weathers to anglesite (K_{sp} 2.0 x 10^{-8} (Cao et al. 2008)), its first oxidation product (Blowes et al. 2003; Frau et al. 2009), becoming more soluble. Abundance of anglesite as an oxidation product of galena accounts for Pb bound to the exchangeable fraction (Frau et al. 2009). Lead release to streams in mining areas has been observed to be initially due to dissolution of anglesite and probably cerussite (Frau et al. 2009).

Redox potential can affect the fate, concentration and mobility of contaminants. A mixed municipal and industrial landfill had a redox potential from -300 mV to +780 mV. With predominantly organic matter, redox potential was 0 mV. Table 14.2 summarises the phases of the metals in relation to redox potential (Östman et al. 2008). Acidic (pH 2.44-3.22) mine contaminated waters results from the oxidation of sulphide minerals including sphalerite (ZnS), arsenopyrite (FeAsS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and galena (Salvarredy-Aranguren et al. 2008). Chemical oxidation of sulphides increased mobility of potentially harmful elements, with their availability in the order: As > Fe > Pb > Cd > Zn ~ Cu > Sn. In oxidising groundwater, Zn, Cd and Cu concentrations increased, although no significant difference was identified for Pb concentrations in relation to Eh values, and As and Fe concentrations increased under reducing conditions (Hermann and Neumann-Mahlkau 1985). This highlights the importance of determining redox potential to understand the contaminated material and to achieve successful fixation.

The stability and speciation of P varies according to pH and Eh (Figure 4.2). Few studies report changes in Eh during orthophosphate fixation or the effects that changing redox conditions can have on fixation efficiency. The following studies show that Eh is important for phosphate fixation.

Table 14.2: Fate of metals within a landfill (Östman et al. 2008).

Element	Reducing conditions (Eh<0)	Eh = 0	Oxidising conditions (Eh>0)
Zn	Sulphide (ZnS), bound to organic matter, $Zn_5(OH)_6(CO_3)_2$ (only at high Zn conc.)		Bound to organic matter (low Zn conc.), hydroxide-carbonate complex (high Zn conc.)
Fe	Sulphides, soluble ferrous irons		Ferric iron oxyhydroxide
Cu	Sulphides, stable at high Cu conc.	Copper oxide	Bound to organic matter (low Cu conc.), carbonates or hydroxyl-carbonates (high Cu conc.), stable at high Cu conc.
Cd	Sulphide	Bound to organic matter, carbonate	Bound to organic matter (low Cd conc.), carbonate
Pb	Sulphide (high S conc.), carbonate (low S conc.)		Carbonate (high Pb conc.)
Ni	Sulphide	Bound to organic matter	
Co	Bound to organic matter		Bound to organic matter

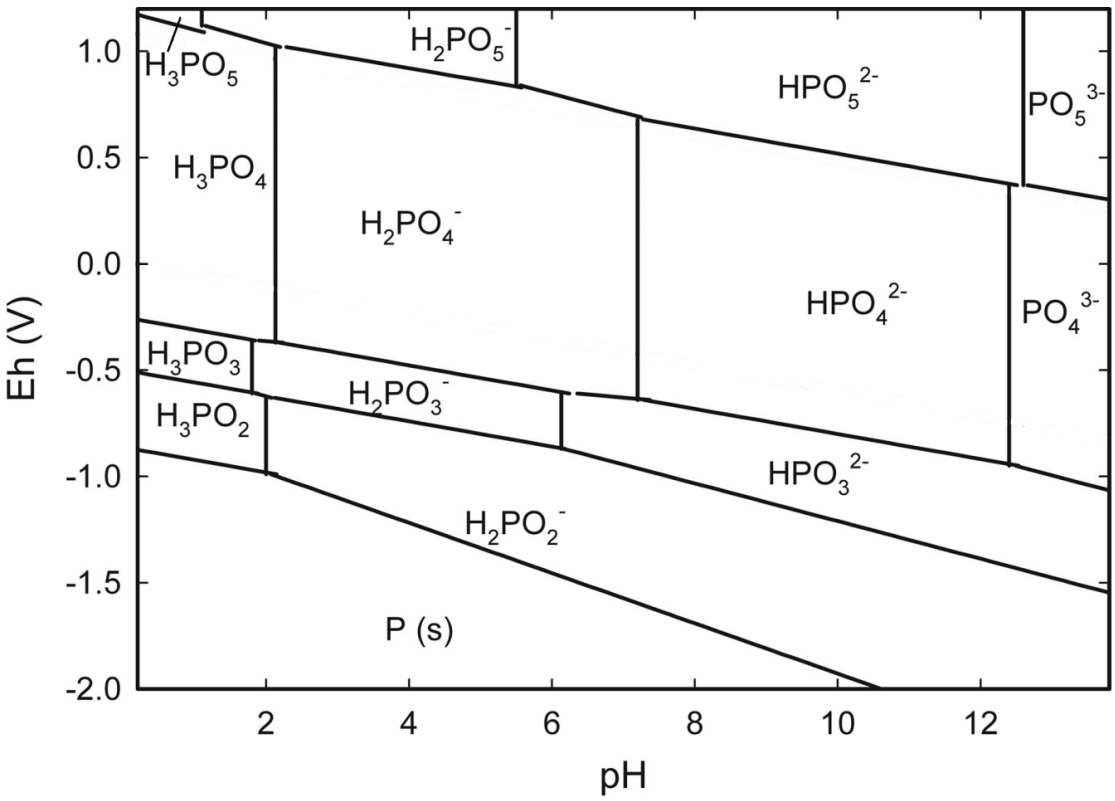

Figure 4.2: Eh-pH diagram showing the stability and speciation of P at 25 °C and 10^{-6} M (after Pasek 2008).

Uranium (U) rich (<1000 mg kg^{-1}) deposits in an oxidising bedrock aquifer exhibited natural phosphate fixation, with Eh as one of the factors responsible for the fixation. Oxidation of U(IV) to

U(VI) and the precipitation of uranyl phosphate ($Ba[(UO_2)(PO_4)]_2(6\text{-}8H_2O)$) occurs within weeks, with U(IV) assemblages (coffinite [$USiO_4{:}nH_2O$] and uraninite [UO_{2+x}]) on the reducing side and U(VI) assemblages on the oxidising side (Jerden and Sinha 2003).

Material from a site where Th was the main contaminant was treated with either apatite or Fe(0), or both. Samples underwent wet-dry cycles to determine the effect of different redox conditions on the material. During the investigation redox potential ranged from +24 mV in the material that was kept saturated, to +501 mV in the wet-dry cycled material. When the material was treated with apatite under oxidising conditions (wet-dry cycles) an increase in Th concentrations was observed, probably due to concurrent increases in aqueous organic matter concentrations. Under reducing conditions (saturated material), apatite reduced Th concentrations (Kaplan and Knox 2004).

Five soils with textures ranging from silt to coarse sandy loams were contaminated with AsO_4 pesticide residues and tested for immobilisation efficiency using MAP or superphosphate (Peryea 1991). Redox potential was >+500 mV in all soil suspensions, indicating the main form of dissolved As was AsO_4^3. An Eh-pH diagram suggested that $Pb_3(AsO_4)_2$ was stable in these soils. However, these soils were probably not at equilibrium and after reacting in the soil, Pb and As were likely to separate into different solid phases and the study demonstrated ineffective PO_4-fixation of As.

Harris and Lottermoser (2006) studied the efficiency of changing sulphide oxidation and metal and metalloid mobility by applying bulk chemicals (potassium permanganate [$KMnO_4$] and water-soluble phosphate fertilisers [superphosphate and MPP]) to polymineralic, partly oxidised, acid producing, sulphide-rich mine wastes. The abundance of metal-phosphate phases depended on the phosphate source and the availability of metal and alkali cations in solution. The release of cations was dependent on the amount of sulphide oxidation induced by $KMnO_4$ and the dissolution of soluble sulphates. Application of 0.2 M $KMnO_4$ and superphosphate decreased sulphide oxidation, as well as reducing Cu, Pb, Zn and Sb mobility by metal/metalloid-phosphate formation (phosphate coatings or phosphate precipitates). Chalcopyrite and galena were the most abundantly coated sulphides. The technique was ineffective in decreasing oxidation of arsenopyrite by phosphate coating and did not reduce As leaching. Galena is unstable under oxidising conditions and the Eh required to convert galena to pyromorphite (or vice versa) is ~-270 mV (Nriagu 1974). The rate limiting factor, reacting galena with synthetic HA under varying pH conditions to form chloropyromorphite, is the dissolution of galena (Zhang and Ryan 1999a). The importance of Eh has been understood for some time, and it is surprising how little attention it has received in relation to orthophosphate fixation. It would help our understanding if future studies monitored and reported Eh as routinely as they do pH.

4.3 Applicability of phosphate-based immobilisation

A review of the effectiveness of orthophosphate fixation for various elements follows, with examples from published studies (Figure 4.1). Most studies here were carried out in the laboratory.

4.3.1: Arsenic (As)

Arsenic contamination occurs with mining, smelting, fertilisers, pesticides, wood treatment, manures and poultry litter (Pierzynski et al. 2005). Lead arsenate ($Pb_3(AsO_4)_2$) was common in pesticides before the mid 20th century (Manahan 2005) and has accumulated in soils (Peryea and Kammereck 1997). The solubility of arsenate-containing compounds is enhanced by orthophosphate, except in volcanic soils that are high in anion-adsorbing allophane minerals (Peryea 1991). An increase in As concentration with depth and a downward leaching of As from the topsoil to the subsoil resulted from the addition of a MAP amendment (Peryea and Kammereck 1997). Peryea (1991) treated five AsO_4 pesticide contaminated silt to coarse sandy loam soils, with MAP or superphosphate. MAP enhanced As solubility, mobility, phytoavailability and phytotoxicity through a competitive phosphate-arsenate (PO_4^{3-}-AsO_4^{3-}) interaction. Arsenic release was positively related to PO_4^{3-} concentration but not to PO_4^{3-} source or the cation (Ca^{2+} or NH_4^+) accompanying the PO_4^{3-} (Peryea 1991). Phosphate applications induced phosphate-arsenate ligand exchange and mobilised As (Seaman et al. 2001a; Basta and McGowen 2004; Kaplan and Knox 2004; Munksgaard and Lottermoser 2013). This competitive exchange can be used to enhance extraction efficiency for alternative types of site remediation, such as pump and treat remediation of aquifers (Wovkulich et al. 2010). Orthophosphate can immobilise As when combined with Ca, or when applied to soils with a high Ca content (Neupane and Donahoe 2013). In Ca deficient soils, orthophosphate increased HNO_{3-} digestible As mobility by up to 55% (Neupane and Donahoe 2013). Either orthophosphate should not be used to treat As contamination or to treat materials where As co-exists, or it should be used only with additional Ca.

4.3.2: Cadmium (Cd)

Cadmium from batteries, fertilisers, diesel emissions, tire attrition and mining can contaminate soil and groundwater (Pierzynski et al. 2005). Cadmium compounds have two forms generally immobile from pH 3-12: cadmium sulphide (CdS) and cadmium phosphate ($Cd_3(PO_4)_2$) (Porter et al. 2004). As CdS oxidises to cadmium sulphate ($CdSO_4$) it becomes soluble, leaving the phosphate form as the preferred salt for stabilisation. At pH >8 however, Cd carbonate becomes less soluble than Cd phosphate (Porter et al. 2004). Phosphate minerals sorb Cd more effectively than sulphate, nitrate or chloride minerals (Bolan et al. 1999).

Multiple forms of phosphate application have been trialled to determine the effectiveness of Cd adsorption. Calcium magnesium phosphate ($(Ca,Mg)_3(PO_4)_2$) reduced bioavailability of Cd in agricultural soils (Liao et al. 2008). Hydroxyapatite reduced the solubility of Cd (Seaman et al. 2001a)

and apatite reduced Cd concentrations in pore water and plants (Knox et al. 2003; Kaplan and Knox 2004). However, PR and MPP did not reduce Cd bioavailability sufficiently to reduce Cd concentrations in plants (Zwonitzer et al. 2003). Hong et al. (2009) trialled seven P treatments (fused phosphate, fused and superphosphate, PR, $Ca[H_2PO_4]_2 \cdot H_2O$ $[NH_4]_2HPO_4$, KH_2PO_4 and K_2HPO_4) and reported that K_2HPO_4 was most effective at reducing NH_4OAc-extractable Cd. This was attributed to the negative charge increase created by soil pH and P adsorption, which suggests that alkaline P materials are effective immobilisers of soil Cd.

Assessment of the efficiency of phosphate sources MPP, MAP and "Polifoska 15" fertiliser [N 15 wt%, P_2O_5 15 wt%, K_2O 15 wt%, MgO 2 wt%, S 5 wt%] on the removal of Cd from aqueous solutions with pH 5-9 and over reaction times 2-1440 h, indicated that the formation of $Cd_3(PO_4)_2$ was mainly controlled by pH rather than the type of phosphate source. Fixation was most effective at pH 6.75-9.00 (Matusik et al. 2008). Fixation by MAP and DAP at 5 °C and 37 °C over 35 days yielded the same mineral, $Cd_5H_2(PO_4)_4 \cdot 4H_2O$. However, smaller crystals formed at 5 °C compared with 37 °C (Ayati and Lundager Madsen 2000). Phosphate source can control reaction pH, and in so doing control the leachability of the Cd source and the amount of Cd available for stabilisation (Thawornchaisit and Polprasert 2009). Cadmium phosphates may form via initial precipitation of pyromorphite, followed by gradual substitution of Pb by Cd (Raicevic et al. 2005). The main mechanism for reduction of Cd concentrations by HA is thought to be ion exchange (Suzuki et al. 1981), or surface complexation and co-precipitation primarily, with some ion exchange and solid diffusion (Xu et al. 1994). Diffusion and ion exchange are possible mechanisms for the fixation of Cd by synthetic-HA, as there is a linear relationship between the sorbed Cd and released Ca, indicating that the metal is incorporated into the HA lattice, substituting for Ca^{2+} (Fedoroff et al. 1999). Fixation of Cd by orthophosphate can be recommended for remediation, as long as the phosphate source will help achieve the most effective pH.

4.3.3: Caesium (^{137}Cs)

^{137}Caesium is of concern following nuclear incidents (Pierzynski et al. 2005). The use of HA alone or with illitic clays ($(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$) or zeolites (clinoptilolite; $(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36} \cdot 12(H_2O)$) to immobilise Cs in sediments has been tested in batch and column studies (Seaman et al. 2001b). Amendments were combined in equal mass fractions (e.g. 50 g kg^{-1} HA + 50 g kg^{-1} illite). In batch study, amendments were ineffective at immobilising Cs, however immobilisation increased with greater amounts of amendment. Amendments were also ineffective in reducing Cs leaching in the column studies (Seaman et al. 2001b). Using MAP as a phosphate source, caesium-magnesium monophosphate ($CsMgPO_4$) is a prospective candidate for the immobilisation of ^{137}caesium from nuclear waste (Asabina et al. 2008), although its thermodynamic stability is undetermined. Further research is required before phosphate is recommended for Cs.

4.3.4: Cobalt (Co)

Cobalt contamination follows from mining or metal refining (Manahan 2005; Pierzynski et al. 2005). Knox et al. (2003) reported significant reductions in aqueous concentrations of Co^{2+} in one week by apatite ($Ca_5(PO_4)_3(F,Cl,OH)$) (from 50.7 μg L^{-1} to 10.2 μg L^{-1}). Apatite reduced Co concentrations in pore water (Kaplan and Knox 2004). Hydroxyapatite reduced Co solubility in sediments (Seaman et al. 2001a). Although the radius of Co ions falls out of the preferred 90-130 pm range for removal by HA, synthetic HA shows potential for Co immobilisation due to the high electronegativity of this transition metal (Suzuki et al. 1982).

4.3.5: Copper (Cu)

Copper contamination occurs via mining and smelting (Pierzynski et al. 2005), metal recycling, wood treatment, plumbing and biosolids (Pierzynski et al. 2005; Bes and Mench 2008). Iron phosphate (vivianite) nanoparticles can immobilise soil-bound Cu in alkaline, neutral, and acidic soils (Liu and Zhao 2007). No Cu-phosphate minerals formed from copper nitrate ($Cu(NO_3)_2$) reacted with PR in a mono-metal aqueous solution for 24 h at pH 5.5 and 25 °C. Instead, copper was probably immobilised via surface adsorption or complexation (Cao et al. 2004). Immobilisation increased with increasing initial metal concentration (0-0.6 mM Cu). Suzuki et al. (1982) suggested adsorption and ion exchange as mechanisms for Cu removal by HA. In a pure system it may take two months for Cu-PO_4 to reach equilibrium via formation of cornetite and copper ammonium phosphate at 5 °C and libethenite at 37 °C (Ayati and Lundager Madsen 2000). Bes and Mench (2008) reported poor stabilisation of Cu over four weeks in contaminated topsoil following application of HA, ammonium phosphate ($(NH_4)_3PO_4$) and TSP, and modest performance using phosphate-bearing slags. Qian et al. (2009) immobilised 90% of the Cu^{2+} in a contaminated soil over five months using a mixture of apatite and ferrihydrite. Reports of effective immobilisation of Cu using orthophosphate include Ma et al. (2012), Mignardi et al. (2012), Soltan et al. (2012) and Zupančič et al. (2012), however successful formation of copper phosphates requires a lengthy reaction time.

4.3.6: Lead (Pb)

Lead contamination occurs from batteries, petrol, fertilisers, paint, industrial sites and mining (Pierzynski et al. 2005). The use of orthophosphate for the fixation of Pb in contaminated soils and waters via dissolution of solid phase Pb and the P-source, and precipitation of pyromorphite-like minerals ($Pb_5(PO_4)_3(Cl,Br,F,OH)$) (Nriagu 1973a, b, 1974; Ma et al. 1995; Ryan et al. 2001; Cao et al. 2002; Scheckel and Ryan 2002) is effective because of the low solubility of these minerals (Nriagu 1973b, 1974; Hettiarachchi et al. 2000). Dissolution-precipitation in conjunction with surface sorption are the main mechanisms for Pb removal by carbonate-HA (Xu et al. 2008). Fixation can also occur by adsorption of Pb on materials such as the manganese oxides birnessite ($(Na,Ca,K)_x(Mn^{4+},Mn^{3+})_2O_4 \cdot 1.5(H_2O)$) and cryptomelane ($K(Mn^{4+},Mn^{2+})_8O_{16}$), or by simultaneous ion

adsorption and new mineral formation (Hettiarachchi et al. 2000; Sonmez and Pierzynski 2005). Pyromorphite can form when lead is present as cerussite, galena, anglesite, and litharge, or as a sorbed phase on goethite (α-FeOOH) (Zhang et al. 1997; Zhang and Ryan 1998, 1999a, b; Cao et al. 2008). Lead adsorbed on goethite is however readily desorbed due to its large ionic size (≈120 pm) (Padmanabham 1983).

Pyromorphite is the most stable group of Pb minerals in soils (Nriagu 1974; Hettiarachchi et al. 2000) and in situ stabilisation of Pb can occur through the formation of insoluble Pb compounds. In the presence of chloride ions, secondary lead orthophosphates transform readily into chloropyromorphite, making it the most stable lead phosphate across pH 3-8 under both aerobic and anaerobic environments (Nriagu (1972, 1973a, b, 1974)). K_{sp} values for fluoropyromorphite ($Pb_5(PO_4)_3F$), bromopyromorphite ($Pb_5(PO_4)_3Br$) and hydroxypyromorphite ($Pb_5(PO_4)_3OH$) are $10^{-71.6}$, $10^{-78.1}$ and $10^{-76.8}$ respectively, compared to $10^{-84.4}$ for chloropyromorphite (Nriagu 1972, 1973a, b), which gives the following stability sequence; $Pb_5(PO_4)_3Cl$ > $Pb_5(PO_4)_3Br$ > $Pb_5(PO_4)_3OH$ > $Pb_5(PO_4)_3F$. Due to the common occurrence of Cl^- in natural environments, bromo- and hydroxypyromorphite will transform into chloropyromorphite under most natural environments (Nriagu 1973a, b; Porter et al. 2004) and fluoropyromorphite, the least stable of the pyromorphites, will only form if the concentration of chloride ions is low and at pH <6.0 (Nriagu 1973b). Formation of fluoropyromorphite is the primary mechanism for the immobilisation of Pb by PR (fluoroapatite or carbonated fluoroapatite) in aqueous solutions and contaminated soils (Ma et al. 1995). Cao et al. (2004) suggested surface adsorption or complexation as the main mechanism for fluoropyromorphite formation by PR, with up to 78% of Pb immobilised. Dissolution of PR and precipitation of carbonated fluoropyromorphite-like minerals can be expressed, assuming equal amounts of PO_4^{3-} and CO_3^{2-}, F^- and OH^-, as:

$$Ca_{10}(PO_4)_3(CO_3)_3FOH(c) + 6H^+ \rightarrow 10Ca^{2+} + 3H_2PO^{4-} + 3CO_3^{2-} + F^- + OH^-$$

$$10Pb^{2+} + 3H_2PO^{4-} + 3CO_3^{2-} + F^- + OH^- \rightarrow Pb_{10}(PO_4)_3(CO_3)_3FOH(c) + 6H^+ \text{ (Ma et al. 1995).}$$

Removal of Pb^{2+} ions from 100-1000 mg kg^{-1} HA solutions is 99.6-100% effective (Suzuki et al. 1982). Pb concentrations in aqueous solutions and contaminated soils are reduced through the application of HA and the dissolution of HA leads to precipitation of the more stable hydroxypyromorphite (Ma et al. 1993). Apatite reduces Pb in plants (maize (*Zea mays* L.), oats (*Avena sativa* L.)) and pore water (Knox et al. 2003; Kaplan and Knox 2004). Although synthetic HA and natural PR reduced Pb concentrations in sudax tissue (*Sorghum bicolour* L. Moench) (Laperche et al. 1997), PR and MPP addition did not affect Pb concentrations in sorghum-sudangrass, a different variety of *S. bicolour* (Zwonitzer et al. 2003). This could be explained by the low solubility of PR and although no direct

evidence of insoluble Pb phosphate formation was observed in the latter study, the slight acidifying effect of MPP may have offset potential reduction in Pb uptake (Pierzynski, written communication, 14 Jan 2011).

Cao et al. (2008) tested cerussite, anglesite and litharge at pH 3-7, and confirmed that chloropyromorphite formation was greatly influenced by pH and the type of Pb mineral reactants. Lower pH resulted in chloropyromorphite, followed by anglesite, then cerussite and finally litharge. Insoluble pyromorphites can form rapidly, with cerussite and HA in a saturated solution forming pyromorphite in only a few seconds (Zhang and Ryan 1999b). Chloropyromorphite can form within 24 h and stay stable in acid conditions (pH 2.0, 4.0, 6.0) for at least one year (Scheckel and Ryan 2002). Although soils with high organic matter, clay and oxide content adsorb the most amount of metals (Covelo et al. 2004), the presence of organic Pb complexes can slow the transformation of Pb into chloropyromorphite, preventing reactions going to completion over 380 days (Hashimoto et al. 2009). Rijkenberg and Depree (2010) reported a linear increase in leached Pb and Zn (in some samples) with increasing phosphate, probably due to increased dissolved organic carbon induced by the phosphate. Similarly, if soluble ligands are present in soils or waters, lead may be leached from lead phosphate minerals in a pH dependent manner (Martínez et al. 2004). Competing cations can destabilise some lead phosphate minerals. Chloropyromorphite can be degraded by competing Cd^{2+} and Zn^{2+} (Martínez et al. 2004; Shevade et al. 2001).

Pb fixation using orthophosphate is an effective long-term solution for Pb management. Pb contaminated mill tailings treated with phosphoric acid (Tang and Yang 2012), reduced bioaccessible and leachable Pb by up to 89% and 86% respectively; these reductions were sustained over 6 years (Tang and Yang 2012).

4.3.7: Nickel (Ni)

Nickel contamination follows from mining, smelting, steel corrosion and batteries (Pierzynski et al. 2005). Zupančič et al. (2006) showed that Ni-rich slightly alkaline (pH 7.7 ± 0.1) sewage sludge that was added to sandy, peaty or clay soils, and then treated with HA was not effectively immobilised although amendment levels were large (0.5 kg of HA per 1 kg of sewage sludge). Hydroxyapatite reduced leachable Ni in sandy soil from 1.9% to 1.7%. In clay, leachable Ni reduced by 1.4-1.2% and in peat leachable Ni was reduced from 1.2% to 0.9%. Boisson et al. (1999) reported soil dependent decrease in Ni mobility when treated with HA; immobilisation was effective in poor sandy soil contaminated by atmospheric deposition from a former Zn smelter and contaminated soil from a former As refinery respectively, however HA did not influence Ni mobility in soil containing waste materials and ore from a former Zn smelter. A decrease in Ni solubility by HA was reported (Seaman et al. 2001a) although Ni concentrations were still high (>1 mg L^{-1}). Competing ion effects from Ca

ions in the HA could explain the high levels of Ni (Seaman et al. 2001a). Hydroxyapatite has not proved very successful for the treatment of Ni contamination, however, adsorption and ion-exchange have been suggested as possible immobilisation mechanisms (Suzuki et al. 1981). Although these findings show the potential of fixing Ni, further research is required where higher doses of phosphate might improve fixation efficiency.

4.3.8: Strontium (^{90}Sr)

^{90}Strontium can be of concern following nuclear incidents (Pierzynski et al. 2005). It enters food chains via cows passing on ^{90}Sr in their milk after ingesting contaminated water or grass, and due to the chemical similarity of strontium and calcium it is interchangeable with Ca^{2+} in bones (Manahan 2005; Chang 2007). ^{90}Sr is fixed by orthophosphate; it is strongly sorbed by both sodium phosphate (Na_3PO_4) and HA, with average uptake of 77.0% and 94.7% respectively (Moore et al. 2004). The main mechanisms for sorption is isomorphous substitution of calcium by Sr into HA (Vukovic et al. 1998). Strontium(II) ions sorbed by HA increase in sorption as final pH increased (4.5-11.5), which can be explained by electrostatic forces as the final pH in the solution rises higher than the pH_{PZC} (pH at the point of zero charge) (Smičiklas et al. 2000). HA applied at 0-50 g kg^{-1} of sediment immobilised ^{88}Sr (as a surrogate for the prediction of ^{90}Sr behaviour) in a batch experiment (Seaman et al. 2001b).

4.3.9: Uranium (U)

Uranium mining and smelting, nuclear incidents and depleted uranium in ordnance, contaminate groundwater (Pierzynski et al. 2005). Uranium can be immobilised by apatite (Seaman et al. 2001a; Kaplan and Knox 2004) and by HA where the main controls were pH and dissolved organic carbon through complexation (Arey et al. 1999). Uranium immobilisation by HA was observed in batch and column tests on sediments, with immobilisation within 2 days in a batch test (Seaman et al. 2001b). The lowest amount of HA added in a batch test (5 g kg^{-1}, compared to 20 and 50 g kg^{-1}) decreased the solubility and extractability of U (Knox et al. 2003). When leached with 1.0 mol L^{-1} NH_4Cl in a column test the total U leachate dropped from ~1.7% in the unamended columns to ~0.01% in the amended columns, due to the formation of sparingly soluble phosphates (Knox et al. 2003).

4.3.10: Zinc (Zn)

Zinc contamination can be derived from mining and smelting, fertilisers and galvanized metal (Boisson et al. 1999; Pierzynski et al. 2005). Fixation of Zn using P occurs but the efficiency of Zn-PO_4 mineral formation is variable (Debela et al. 2013). The presence of other metal contaminants with Zn and competing ions reduce stabilisation efficiency. Soils with high concentrations of Fe or Mn oxides contain numerous sorption sites which compete for available P, reducing the efficiency of Zn-PO_4 formation (Debela et al. 2013). Low molecular weight organic acids in soil may also impact Zn-PO_4 mineral formation. Only 17% of available Zn was transformed into Zn-PO_4 minerals by

phosphoric acid in the presence of oxalic, citric and diethylene triamine pentaacetic acids, due to the formation of oxalates which do not react readily with soluble P (Debela et al. 2013). Organic acids, abundant in the rhizosphere, should be considered prior to treatment of Zn contaminated soil (Debela et al. 2013).

Hydroxyapatite reduced Zn concentrations by ion exchange with Ca ions in apatite (Suzuki et al. 1981), with >99% of Zn^{2+} being removed from solution through sorption by HA, from pH 5.64 to 7.22 (Xu et al. 1994). Surface complexation and co-precipitation occurred, with ion exchange and solid diffusion. Saxena and D'Souza (2006) reported precipitation as the main mechanism for Zn removal by PR. Zinc reactivity can change with phosphate source due to acidifying effects (Zwonitzer et al. 2003). In such instances alkalizing and insoluble P sources such as PR decreased Zn solubility and acidifying sources such as MPP and phosphoric acid increased Zn solubility (Zwonitzer et al. 2003; Baker et al. 2012).

Reduction in earthworm (*Eisenia fetida*) Zn was reported for MPP and TSP as soil amendments (Maenpaa et al. 2002). Apatite reduced Zn concentrations in plants (Knox et al. 2003). Plant Zn can be reduced by TSP and liquid P (PA) although final Zn concentrations remained at toxic concentrations (406±41 mg kg^{-1}) (Brown et al. 2005). Significant changes in Ca and PO_4 concentrations during sorption in a Zn-Cd-HA system imply the occurrence of co-precipitation of Zn^{2+} and Cd^{2+} with Ca^{2+} onto HA (Xu et al. 1994). Desorption experiments in the same Zn-Cd system, using 0.5 M KNO_3 or 0.5 M $CaCl_2$, indicate Zn^{2+} being held more strongly to the mineral surface than Cd^{2+} (Xu et al. 1994). Zn mobility reduced using 5% w/w HA in a multi-element system (Cd, Cu, Ni, Pb, Zn, As), although arsenic mobility increased in the system due to phosphate-arsenate (PO_4^{3-}-AsO_4^{3-}) competition (Boisson et al. 1999). Adsorption of aqueous Zn by PR at pH 5.5 was 75% less in a multi-metal (Zn, Pb, Cu) compared to a mono-metal system (Cao et al. 2004).

4.3.11: Other elements (Al, Ba, Cr, Eu, Hg, Mg, Mn, Se, Th)

Phosphate has potential to immobilise Al, Hg, Mg, Mn, Ba and Eu (Suzuki et al. 1981; Suzuki et al. 1982; Seaman et al. 2001a; Knox et al. 2003; Kaplan and Knox 2004). Apatite can reduce aqueous concentrations of Ba^{2+} and Eu^{3+} in one week (Knox et al. 2003). However, the solubility of Cr, Se and Th can be increased by apatite (Seaman et al. 2001a; Kaplan and Knox 2004). Further work needs to be carried out to characterise fixation effectiveness.

4.4: Field treatment methods

The total amount of P required for treating metal contaminated material can be determined in various ways. One way is to base the amount of P on the stoichiometric ratio of the metal and phosphate or phosphorus in the resulting metal-phosphate mineral, e.g. Pb:PO_4 in chloropyromorphite and Cd:PO_4

in cadmium phosphate ($Cd_3(PO_4)_2$) (Cao et al. 2008; Matusik et al. 2008). The calculation can be based on the P content of the phosphate amendments used (Hettiarachchi et al. 2001; Hettiarachchi and Pierzynski 2002; Zhu et al. 2004) or on the molar ratio of the soil contaminant and the amount of P released from the phosphate source (Knox et al. 2003). Treatments could be added to the contaminated material on the basis of soil dry weight (Ryan et al. 2001 ;Hamon et al. 2002; Liu and Zhao, 2007; Bes and Mench 2008). For example, Porter et al. (2004) suggested 34-174 g superphosphate kg^{-1} dry soil will convert Pb minerals in contaminated soil to chloropyromorphite. For conversion of all Pb forms in soil into chloropyromorphite ($Pb_5(PO_4)_3Cl$), the phosphate to calcium ratio should be >3:5 to first convert all Ca in the soil to HA (Porter et al. 2004).

Laboratory studies commonly apply deionised (e.g. Liu and Zhao 2007) or doubly distilled (Zupančič et al. 2006) water to experiments. However, it is not critical in the field whether tap or deionised water is used (L.Q. Ma, written communication, 01 Nov 2008). No studies have reported the use of surfactants or other wetting agents. It is common to add potassium chloride (KCl) or calcium chloride ($CaCl_2$) to encourage the formation of chloropyromorphite in Pb contaminated soils (Melamed et al. 2003; Yang and Mosby, 2006; Zhu et al. 2004) and liming agents (e.g. $CaCO_3$, $Ca(OH)_2$, CaO) to restore pH (Wang et al. 2001; Hamon et al. 2002; Yang and Mosby 2006).

Dynamic and complex natural environments can be more problematic than controlled laboratory counterparts, and few in situ or in ground studies have been carried out. Field application methods include spraying, rototilling, surface application, pressure injection, excavation and backfilling, and mixing by backhoe or shovel (Wang et al. 2001; Cao et al. 2002; Melamed et al. 2003; Yang and Mosby 2006). Thorough distribution by mixing or tilling is important when adding superphosphate to natural soils, as they are heterogeneous and uneven application of superphosphate can result in pockets of high concentration of phosphoric acid solution (Porter et al. 2004).

In an ex situ field experiment, Pb contaminated soil was treated with superphosphate and lime (Wang et al. 2001). The contaminated material (3.5 m^3) was excavated with a backhoe into a 6 m^3 container where the treatments were incorporated with a backhoe for ~10 min. After 30 days the contaminated material passed the TCLP (USEPA 1992) test, the material was backfilled to the site and the surface was layered with concrete.

As ex situ treatments may not be appropriate or cost effective for metal immobilisation, some studies have evaluated in ground methods for treating contaminated material. Yang and Mosby (2006) applied PA at the rate of 10 g P kg^{-1} of soil with KCl to 2 x 4 m plots with three application methods: rototilling, surface application and pressure injection. For the rototilling treatment the soil was rototilled prior to P application, then again following application of half of the reactants (PA + KCl) and again after application of the remainder. Surface application consisted of disturbing the surface of the soil with a

garden aerator prior to treatment, then adding half the PA + KCl to the surface and aerating, and then applying the remaining half of the treatment and aerating again. Pressure injected plots were amended with KCl prior to the application of PA, which was then injected by a pressure injector 15 cm depth in the soil at 15 cm spacings. Pressure injection did not distribute P uniformly to the surrounding soil. Although rototilling and surface application were not very successful at mixing the PA vertically into the soil, rototilling maximized homogeneity and reduced bioaccessible Pb more effectively than surface application or pressure injection for treating surface soil (Yang and Mosby 2006).

Melamed et al. (2003) used four experimental plots with Pb contaminated material (mainly cerussite) and used four treatments: an untreated control (T0), PA (T1), superphosphate (T2), or PR (T3). Treatments were applied at a molar ratio of 4.0 P/Pb for PA and superphosphate but 4.5 P/Pb for PR due to its low solubility. The total amount of P added was based on the Pb content of the upper 20 cm of soil. To pre-acidify the soil and enhance the formation of chloropyromorphite a mixture of PA and $CaCl_2$ in 25 L tap water was sprayed evenly in each of three experimental plots (T1, T2, T3). Forty days later the treatments were applied to each plot and mixed with a shovel to 20 cm depth. Sampling was carried out at different depth intervals 220 days after the first P application. The greatest concentration of total Pb and the P applied was at 10-20 cm and at 0-10 cm depth respectively. Chloropyromorphite formed in plots T1 and T2 but not in plot T3 until 330 to 480 days after the first P application, which might reflect insufficient time for the PR to dissolve prior to the formation of pyromorphite (Hettiarachchi et al. 2001). Lead immobilisation became less effective with soil depth, which could be related to difficulty in distributing the phosphate source as the P concentrations declined sharply with soil depth (0-80 cm), especially when using PR and PA together as treatment (Melamed et al. 2003).

4.5: Potential environmental risks

Eutrophication, an oversupply of nutrients and organic matter in the environment, can occur should excessive orthophosphate be released from the remediation site. Soluble phosphates (e.g. TSP, PA, MPP) are more likely to pose environmental hazards from eutrophication than less soluble phosphates (e.g. PR) (Hettiarachchi et al. 2001; Hettiarachchi and Pierzynski 2002; Melamed et al. 2003; Liu and Zhao 2007).

Melamed et al. (2003) used soluble PA with either TSP or PR as their phosphate source since PA would dissolve cerussite ($PbCO_3$) (the main form of Pb in their soil), then the PR or TSP would gradually add orthophosphate to complex Pb, while minimising soil pH reduction which could solubilise P and increase the chance of eutrophication.

Basta and McGowen (2004) examined the solubility and transport of Zn, Cd and Pb in a smelter contaminated sandy loam with elevated concentrations of Zn, As, Cd and Pb. Diammonium phosphate (23% P), with 1:15 P:total metal ratio reduced Zn, Pb and Cd by 95.8%, 98.9% and 94.6% respectively. DAP at 3:5 ratio resulted in high concentrations of soluble phosphate in the soil and increased the release of As(V). Also, 10.5% of the total P added (for the 3:5 DAP ratio) was eluted compared to <1% using 1:15 DAP. Increases in other contaminants can be derived from impurities in the phosphate. Zinc and cadmium are common in P fertilisers (Mann et al. 2002) and elevated concentrations of Cd can be in some PR and water-soluble phosphate fertilisers, including superphosphate (Pierzynski et al. 2005). Cadmium concentrations in phosphate fertilisers from the USA range from 0.15 to 250 mg kg^{-1} (USEPA 1999). Application of Cd-bearing fertiliser may elevate soil Cd over time (Gray et al. 1999; Mann et al. 2002). Kuo et al. (2007) found 50% of TSP Cd and 32.7% of PR Cd remained water soluble after 210 days. The solubility of Cd in water is lower than for Zn and P in TSP, so it is possible to reduce Cd input from TSP into the soil by dissolving the TSP prior to application, facilitating removal of the less soluble Cd prior to TSP-solution soil application (Kuo et al. 2007). Although soil Cd from P fertilisers accumulates, increased Cd-soil contact time will render the Cd less mobile as it sorbs onto soil particles (Gray et al. 1999).

Since Ca can consume P needed for precipitation of metals (Maenpaa et al. 2002; Porter et al. 2004), higher doses of P might be needed for successful fixation of metals, which in return could lead to eutrophication. Liu and Zhao (2007) used iron phosphate nanoparticles (8.4 ± 2.9 nm vivianite [$Fe_3(PO_4)_2 \cdot H_2O$]) to immobilise Cu in soils. Iron showed great potential as a stabilising agent, possibly reducing the amount of phosphate needed for immobilisation and therefore lessening the potential of environmental problems. Two amendment levels (Case 1, Case 2) were used, with 1 mL and 5 mL of nanoparticle solution to 0.5 g soil respectively. Amendments were added to Cu-spiked acidic, neutral and calcareous soils (pH 4.36, 6.93 and 7.85). Case 1 reduced TCLP Cu leachability by 39% (from 58% to 35%) in an acidic soil after 1 day of amendment. Reduction was 58% after 56 days of amendment. For a neutral soil Cu leachability reduced by 33% after 1 day with a reduction of 50% after 56 days of amendment. Calcareous soil decreased Cu leachability by 23% (from ~5% to 4%) after 1 day of amendment and further 78% (1% leachability) after 14 days of amendment. Increasing amendment levels 5 fold (Case 2) changed immobilisation efficiency relative to Case 1: Cu leachability decreased by 48% in acidic soil, 32% in neutral soil, and 30% in calcareous soil after 1 day, further reductions after 56 days of amendment were 81% in acidic soil, 63% in neutral soil, and 87% in calcareous soil. These reductions in Cu leachability are similar to studies where the more commonly used phosphate sources TSP and PA were tested (Eighmy et al. 1997; Wang et al. 2001), supporting the utility of using phosphate nanoparticles.

4.6: Conclusion

Orthophosphate fixation works well with metal ions such as Pb, not as well with others such as Ni, and very poorly with some metalloids, leading to desorption of As in some cases. Fixation behaviour of many elements remains poorly constrained. Competitive ion effects, particularly regarding Ca^{2+} (Ayati and Lundager Madsen 2000; Seaman et al. 2001a), and organic matter (Hashimoto et al. 2009; Rijkenberg and Depree 2010), especially at pH <4 (Lang and Kaupenjohann 2003), contribute to complexity in the behaviour of many cations reacting with orthophosphate solutions (Shevade et al. 2001; Martínez et al. 2004). Eh in orthophosphate fixation experiments is underreported. Many applications of orthophosphate stabilisation consist of a small number of contaminants and future research should seek to understand the complexity associated with multi-element contamination. Field validation experiments will always be required in order to confirm that fixation, observed in vitro, works in the field given the variability intrinsic to natural environments.

4.7: Acknowledgements

We thank the Australian Research Council, PANalytical, Veolia Environmental Services and the Australian Antarctic Division for financial support (grants LP0776373, AAS2937, AAS4029), and Kirstie Fryirs, Duanne White, Scott Stark and anonymous reviewers for helpful comments.

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Chapter 5: Immobilisation and encapsulation of contaminants using silica treatments

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Citation: Camenzuli D. and Gore D.B. 2013. Immobilisation and Encapsulation of Contaminants Using Silica Treatments: A Review. *Remediation 24*, 49-67.

Submitted: 15 August 2013; *Accepted for publication*: 10 September 2013; *Published*: 19 December 2013

Abstract

The immobilisation and encapsulation of contaminants using silica treatments is an emerging technique for the management of contaminated land. This paper reviews the potential of silica treatments for the management of metals, hydrocarbons and acid mine drainage at contaminated sites; and evaluates the effects of environmental conditions on silica treatment performance. The review demonstrates the potential of silica treatments for managing contaminated land; however, a paucity of research offers only a limited understanding of this technique. Further development of this technique will require additional research evaluating its long-term performance under a range of environmental conditions. Field based experiments and studies investigating potential adverse effects of silica treatments are also necessary to demonstrate the safety, efficacy and reliability of silica treatments.

Keywords: Silica; Microencapsulation; Immobilisation; Remediation; Stabilisation.

5.1: Introduction

Environmental contamination from human activities remains unresolved in many parts of the world, despite the legacy and exposure effects of metal and hydrocarbon contaminants being studied extensively (Hiroki 1992; Järup 2003; Poland et al. 2003; Filler et al. 2006; Taylor et al. 2010; Taylor et al. 2013). Various new, innovative and cost-effective technologies are being developed to more efficiently manage contaminated land (for example phytoremediation, bioremediation and electrokinetic remediation); however, there remains a shortage of techniques suitable for soils contaminated with metals and hydrocarbons (Martin and Ruby 2004; US EPA 2004; Filler et al. 2006). Immobilisation and encapsulation by silica-based chemical treatments (hereafter silica treatments) is one technique applicable to land contaminated with both metals and hydrocarbons (Mitchell et al. 2000a, b; Mbhele 2007).

Silica treatments do not remove contamination from an environment, but either alters contaminants into less hazardous forms or entraps them. Treatment of contaminated soil with silica treatments is similar to phosphate or cement based fixation and encapsulation techniques, in that the application of a chemical treatment to contaminated soil is required (Arocha et al. 1996; Fytas et al. 1999; Mbhele 2007). Chemical reactions stimulate metal-silicate mineral formation or prompt the encapsulation of hydrocarbons occur once the treatment is applied and mixed with contaminated soil (McDowell 1994; Arocha et al. 1996; Mitchell et al. 2000a, b; Li et al. 2012). Once contaminants are transformed into metal-silicate minerals or become encapsulated by microscopic silica shells, they are considered to be immobilised or encapsulated (McDowell 1994; Zhu et al. 2004; Sonmez and Pierzynski 2005; Li et al. 2012). Effective immobilisation or encapsulation prevents contaminant migration and reduces the potential negative impacts of contaminants on the environment (Mitchell et al. 2000a, b; Mbhele 2007).

The earliest research describing the application of silica treatments to the management of contaminated land was by McDowell (1994), with few relevant studies published since then (Arocha et al. 1996; Fytas et al. 1999; Mitchell et al. 2000a, b; Abdel-Hamid et al. 2012). This paucity of research limits the understanding of the performance of silica treatments under a range of environmental conditions (Arocha et al. 1996; Fytas et al. 1999; Li et al. 2012). Therefore, this paper reviews the literature on silica treatments and their application to contaminated soil, to provide a knowledge base and help direct future research. This review provides an overview of silica treatments, describes their composition, and reviews techniques used for their application into the environment. The effects of environmental parameters such as temperature, solubility, oxidation-reduction potential and soil character on treatment performance are also considered. Case studies reporting on the application of silica treatments for the management of metal and hydrocarbon contaminated sites and prevention of

Acid Mine Drainage (AMD) are also reviewed. Finally, areas which require further investigation are identified to aid in the development of this remediation technique.

5.2: Silica treatments

Silica treatments react rapidly with multivalent metal cations such as Mg^{2+}, Ca^{2+}, Fe^{3+}, Cu^{2+}, $Zn^{2+}$and Pb^{2+} to immobilise metals and precipitate insoluble, metal-silicate minerals (Mitchell et al. 2000a, b; Naja and Volesky 2009; Abdel-Hamid et al. 2012). Silica treatments can also be used to prevent pyrite oxidation (Vandiviere and Evangelou 1998; Fytas et al. 1999; Mitchell et al. 2000a, b).

Encapsulation of petroleum hydrocarbons by silica treatments occurs during a two-stage reaction (McDowell 1994; Hill and Ross 2012). The first stage typically involves the application of an emulsifier to desorb hydrocarbons from the soil, followed by the application of an alkaline silica solution (McDowell 1994). An acid-base reaction occurs between the silica solution and the emulsifier micelle and is neutralised, resulting in the formation of microscopic silica shells which encapsulate hydrocarbons (McDowell 1994). Alternatively, a strongly alkaline-based silicate solution can be applied first, followed by a weakly acidic polymer-based solution (Billings and Burns 1997). The application of an acidic solution following the addition of a silicate solution will rapidly reduce pH and prompt faster immobilisation or encapsulation of contaminants (Billings and Burns 1997). Hydrocarbons encapsulated by silica treatments are environmentally benign and resistant to degradation, even in low pH environments (i.e. pH ≤ 4) (Mitchell et al. 2000b; Kargbo and Chatterjee 2005). Remediation of contaminated soil using silica treatments generally does not require a pre-treatment; however, pH buffering in highly acidic soils may be required to prevent the polymerisation of silica treatments prior to immobilisation or encapsulation (Mitchell et al. 2000a; Pham et al. 2007).

The processes responsible for the formation of insoluble metal-silicate minerals and encapsulation of hydrocarbons using silica treatments are hydration and dehydration reactions, precipitation reactions and polymerisation or gelation (Xu and Deventer 2000; Nalaskowski et al. 2003; Pham et al. 2007; Prasad et al. 2008). Hydration and dehydration reactions involve the loss or gain of a water molecule from the reacting molecule (Nalaskowski et al. 2003). Precipitation refers to the growth of a new mineral product as a result of a chemical reaction (Saxena and D'Souza 2006; Prasad et al. 2008); and polymerisation or gelation is a more complicated process, due to the complex surface nature of silicates (Vigil et al. 1994; Pham et al. 2007). Particle size is a critical component of the dispersion and aggregation behaviours of dissolved silicates which form most silica treatments, with smaller particles (diameter ~30 nm) typically consisting of isolated silanol groups which improve the absorption capacity of silicates and their ability to agglomerate (Vigil et al. 1994; Kamiya et al. 2000; Kneuer et al. 2000; Pham et al. 2007). Depending on the nature and strength of interparticle forces, small silicate particles in unstable suspensions can flocculate together to form open, fractal-like networks of

colloidal silica gel (Pham et al. 2007). The formation of colloidal silica gels is often regarded as the onset of polymerisation or gelation (Pham et al. 2007). Polymerisation can range from fragile gels in dilute colloidal systems to strong polymer gels (Shibayama 2006; Pham et al. 2007). In some cases the reactions responsible for immobilisation or encapsulation occur simultaneously, making it difficult to determine the dominant process for remediation (Hettiarachchi et al. 2000; Sonmez and Pierzynski 2005).

5.3: Composition of silica treatments

Sodium metasilicate (Na_2SiO_3) is the principal component of silica treatments (Arocha et al. 1996; Fytas et al. 1999; Mbhele 2007). A significant variation in the composition of trialled silica treatments is apparent, despite the small number of relevant published field and laboratory trials (Table 5.1). Treatments vary substantially depending on the contaminants being treated; for instance, treatments tailored for hydrocarbon contaminated sites commonly contain surfactants such as sodium laurel sulphate or acetic acid (Arocha et al. 1996; Billings and Burns 1997; Mbhele 2007).) The addition of a surfactant or acid can significantly improve the effectiveness of encapsulation due to the amphiphilic structure of surfactants which furnish an acidic medium on contaminated soil that encourages silica precipitation (Arocha et al. 1996; Mbhele 2007). While surfactants can improve hydrocarbon encapsulation efficiency, they should only be used with extreme caution due to their toxicity for aquatic biota and capacity to mobilise metal contaminants (Martin and Ruby 2004).

Table 5.1: Summary table of silica based treatments used for the immobilisation or encapsulation of contaminants.

Reference	Composition	Starting pH	Contaminant treated
Arocha et al. (1996)	SiO_2, Na_20 and H_20	11.3	Hydrocarbons
Billings and Burns (1997)	Two-step treatment Solution 1: Na_2SiO_3, $C_6H_{15}NO_3$, $C_8H_{17}NaO_4S$, $C_{2n}H_{4n+2}O_{n+1}$, $C_8H_{17}C_6H_4$ $(OCH_2CH_2)_nOH$ and H_2O. Solution 2: H_3PO_4, $C_2H_2O_4$, acrylic polymer and H_2O.	≥8	Hydrocarbons and metals
Fytas et al. (1999)	Various treatments consisting of Na_2SiO_3, H_2O, NaOAc, $CaCO_3$, H_2O_2, and CaS04	Treatments ranged in pH from 5.75 to 12.6	Pyrite oxidation
Vandiviere and Evangelou (1998)	NaOAc, H_2O, $Ca(OCl)_2)$ and Na_2SiO_3	Not reported	Pyrite oxidation
Hill and Ross (2012)	Na_2SiO_3, surfactant (e.g. sodium laurel sulphate), ethylene glycol and H_2O.	10.5-11.9	Hydrocarbons, metals and pesticides

The addition of calcium carbonate ($CaCO_3$) to silica treatments aimed at immobilising metals is beneficial as it can encourages metal-silicate and calcium-silicate mineral formation, thereby increasing immobilisation efficiency (Mitchell et al. 2000a, b; Will Gates pers.comm 2012). When selecting the most appropriate silica treatment composition, it is important to consider the types of contaminants present and the impact of environmental parameters such as temperature, solubility, oxidation state, pH and soil character on treatment performance. This is particularly the case in instances where treatments are applied in situ.

5.4: On-site and in situ techniques for the application of silica treatments

In situ application of silica treatments is preferable; however, natural environments are highly heterogeneous and consequently difficult to control (Martin and Ruby 2004). The majority of existing research on silica treatments has been undertaken in controlled, laboratory environments (Arocha et al. 1996; Fytas et al. 1999).

Silica treatments are typically applied as a solution, but can be applied as a powder (Mitchell et al. 2000a, b). In laboratory experiments, treatment solutions are usually prepared with deionised water

(Arocha et al. 1996; Fytas et al. 1999; Mitchell et al. 2000a, b). It is less critical for deionised water to be used when preparing treatments for in situ remediation; however, an analysis of metal concentrations in the water source should be undertaken before the treatment is prepared to prevent contamination of the treatment with residual metals (Hovsepyan and Bonzongo 2009).

Application techniques for silica treatments are similar to those used for phosphate, fly ash or lime based fixation and encapsulation treatments (McDowell 1994). Spraying, rototilling, pug mills, ribbon blenders, surface application and excavation with subsequent mixing have all been used to successfully achieve in situ or on-site application of chemical treatments (McDowell 1994; Mulligan et al. 2001; Wang et al. 2001; Cao et al. 2002; Melamed et al. 2003; Yang and Mosby 2006). Pressure injection using hollow augers (ranging in length from 3-42 ft) have also been successfully used to inject and mix treatment reagents with waste materials to depths of up to 13 m (McDowell 1994; Mulligan et al. 2001). Larger augers (6-12 ft diameter) are used for shallow (10- 40 ft) drilling and can treat 500-1000 cubic yards of soil per day (Wuana and Okieimen 2011). Treatment of deeper soils (depths of up to 150 ft) can be achieved using ganged augers (typically 3 ft in diameter) to treat up to 150-400 cubic yards of soil per day (Wuana and Okieimen 2011). Natural soil systems are highly heterogeneous, making uniform treatment of the contaminated material difficult but essential (Wuana and Okieimen 2011). Mixing the soil and treatment, as with augers and grouting equipment, can help reduce heterogeneity and improve mixing, but in such soils post-treatment sampling and testing of treatment viability assumes even greater importance than usual.

Only a few field trials of silica immobilisation or encapsulation have been published (McDowell 1994; US EPA 2004). McDowell (1994) reported on on-site and in situ techniques used for silica treatment delivery and concluded that that pug mills and ribbon blenders are the most effective techniques for the application of silica treatments in contaminated soils and sludges, respectively. Application of a silica treatment on-site has also been achieved using concrete mixers in portable enclosed structures to allow controlled treatment in batches and subsequent backfilling (US EPA 2004). Yang and Mosby (2006) undertook in situ remediation using phosphate based fixation treatments and found that rototilling was the most effective technique for treatment delivery in shallow soils when compared with surface application or pressure injection.

5.5: Controls on treatment performance

5.5.1: Temperature

Contaminated land is a problem in both temperate and polar environments; as a consequence low temperatures can affect the rate and efficiency of remediation operations (Mulligan et al. 2001; Filler et al. 2006; Taylor et al. 2013). Higher temperatures are typically associated with a greater average kinetic energy of molecules, faster chemical reaction rates and subsequently faster rates of

immobilisation or encapsulation (Irifune et al. 2004; Lo et al. 2009). Minerals formed during treatment can be affected by temperature, with smaller crystals often forming in soil treated at low temperatures (Ayati and Lundager Madsen 2000). There are currently no published studies which describe the impact of temperature on silica immobilisation or encapsulation; however, studies of alternative chemical treatments and their application in cold environments can provide insight into the performance of chemical treatments in cold climates.

White et al. (2012) demonstrated the potential for fixation of metals in cold temperatures using orthophosphate. Both the efficacy and rate of conversion to metal-orthophosphate phases were found to be heavily influenced by temperature (White et al. 2012). For instance, Cu reacted faster with orthophosphate at 2 °C than 22 °C, but reactions involving Pb and Zn were typically faster and more complete at 22 °C than 2 °C (White et al. 2012). Natural freeze-thaw cycling also influences reactions and mineral formation in cold climates and its effects must be considered if applying silica treatments in cold environments (Hafsteinsdóttir et al. 2011, 2012). Temperature changes also affect mineral solubility, hydration and dehydration reactions (Doner and Lynn 1989; Ayati and Lundager Madsen 2000; Dietzel 2005; Hafsteinsdóttir et al. 2011). Freezing can also desiccate particles, thereby increasing the soluble concentrations of metals in the soil water (Blackwell et al. 2010; Hafsteinsdóttir et al. 2011). Thus, temperature can influence reaction rates and the formation and stability of minerals formed during immobilisation (Hafsteinsdóttir et al. 2011).

5.5.2: Solubility

The majority of dissolved silica occurs in monomeric form; however, the precipitation of silica in solution is determined by the solubility and dissolution of amorphous silica (White et al. 1956; Krauskopf 1956; Chen 1989). The solubility and dissolution of mineral and amorphous forms of silica is influenced by environmental temperature, pH, salinity and particle size, and is governed by hydration and dehydration reactions catalysed by OH^- ions formed by the chemisorptions of H_2O molecules on an oxide surface where: $(SiO_2)_x + 2H_2O$ hydration $\leftrightarrow$ dehydration $(SiO_2)_{x-1} + Si(OH)_4$ (Chen 1989; Pokrovsky et al. 2006). The concentration of $SiOH^+$ and SiO^- species in solution is influenced by pH, with concentrations of $SiOH^+$ increasing at pH<7, and SiO^- species increasing at pH>7 (Pokrovsky et al. 2006).

The solubility of both mineral and amorphous forms of silica in the environment increases with temperature (Rimstidt and Barnes 1980; Chen 1989; Brady and Walther 1990; Mitra 2008), however, the relationship between silica solubility and pH is more complicated. The solubility of silica in solution increases at pH is <3 or ≥8, reaches a minimum at pH 7-8 and maximum at pH 12 (Ller 1979; Chen 1989). The solubility of silica increases when pH is ≥8 due to an increase in the concentration of negatively charged species in solution (Brady and Walther 1990). Where pH is ≥ 8

dissolution rates are controlled by the nucleophilic attack of OH^- ligands on silica, with the rate of dissolution increasing with pH (Mitra 2008). The solubility of silica increases when pH < 3, with several conflicting mechanisms and explanations for this trend being provided in previous studies (Wollast and Chou 1989; Hiemstra and van Riemsdijk 1990; Pokrovsky et al. 2006). Wollast and Chou (1989) suggested that the faster dissolution rates of silica observed at pH <3 are proportional to the concentrations of positively charged $SiOH_2$ surface species (e.g. silanols) which increase in concentration with decreasing pH. Hiemstra and van Riemsdijk (1990) attributed the faster dissolution rates of silica and surface silanol groups (>Si-OH° ↔ Si- O^- H^-) at low pH to the polarisation of Si-O bonds. Pokrovsky et al. (2006) argued that at pH near 0, silicon hydroxide exists on up to 50% of surface sites, with the observed dissolution rates at low pH having a reaction order of 1 with respect to the concentration of silicon hydroxide. While the reaction mechanisms explaining silica solubility at low pH remain unclear; the trend for increasing silica solubility at < 3 or ≥ 8 appears to be agreed upon in the literature (Wollast and Chou 1989; Hiemstra and van Riemsdijk 1990; Pokrovsky et al. 2006). This has important implications for the composition and application of silica treatments, as prepared silica treatment solutions must be highly alkaline (pH ≥ 8) to prevent polymerisation of the treatment prior to immobilisation or encapsulation of contaminants (Mitchell et al. 2000a, b; John Provis, University of Sheffield, written comm. 2013).

The effect of salinity on the solubility of amorphous silica is minimal when salts such as NaCl, Na_2SO_4, MgCl and $MgSO_4$ are in moderately low concentration (Krauskopf 1956; Siever 1962). However, the solubility of mineral and amorphous forms of silica in aqueous solutions decreases with increasing concentrations of salts (Jorgensen 1968; Ler 1979; Rimstidt and Barnes 1980; Chen and Marshall 1982).

Particle size and surface area effects also influence the solubility of silica, with particles < 0.1 μm being more soluble than macroscopic grains (Siever 1962; Rimstidt and Barnes 1980; Sommer et al. 2006). Surface impurities can also reduce the solubility of silica in water by encouraging adsorption onto the surface of crystal or amorphous forms of silica which inhibits dissolution (Ler 1979). The overall concentration of soluble silica in solution depends largely on the relative rates of dissolution and adsorption (Ler 1979).

5.5.3: Oxidation-reduction potential

Soil water content has important implications for immobilisation and encapsulation efficiency as physical, chemical and biological changes in soil occur as it becomes saturated (Manahan 2005). Changes in oxidation-reduction (redox) potential due to biotic or abiotic processes are critical as they can increase the mobility and toxicity of contaminants (Manahan 2005; Pierzynski et al. 2005).

Redox potential can vary substantially and has been reported to range from -300 in reducing wetland soils to +700 mV in oxidising aerobic soils (Hermann and Neumann-Mahlkau 1985; Delaune and Reddy 2005). Redox potential is typically higher in wet environments (Eh ~ +150 to +562 mV), compared to dry environments (Eh ~ +22 to +531 mV) and is often higher in contaminated waters (Eh ~ +287 to +562 mV) when compared to pristine waters (Eh ~ +22 to +438 mV) (Salvarredy-Aranguren et al. 2008).

Oxidation can change water chemistry by transforming sulphides into secondary sulphides, oxides, hydroxides, arsenates and sulphates (Harris et al. 2003), which can increase the concentration, solubility and mobility of metals and metalloids such as Cu, Zn, As, Cd and Pb and subsequently their potential threat to the environment (Hermann and Neumann-Mahlkau 1985; Salvarredy-Aranguren et al. 2008). Acidification of groundwater can also occur as a result of the oxidation of sulphide minerals and AMD (e.g. sphalerite, arsenopyrite, pyrite, chalcopyrite and galena) (Hermann and Neumann-Mahlkau 1985; Salvarredy-Aranguren et al. 2008).

Redox potential also promotes additional releases of silica during cyclic patterns of water-logging and drying in batch experiments (Rückert 1992), due to H^+ production during oxidation of ferrous to ferric compounds and subsequent dissolution of clay minerals during the pedogenic process ferrolysis (Brinkman 1970, 1979; Rückert 1992; Sommer et al. 2006). Similarly, the release of silica increased following the oxidation of ferrous-silicate surface coatings (Morris and Fletcher 1987). While a shortage of direct analyses of the effect of redox potential on silica treatments exists, these studies highlight the importance of understanding the effect of environmental chemical changes on contaminated materials, and indicate that reactions between contaminants and silica may be more easily facilitated in oxidising environments which encourage silica dissolution.

5.5.4: Soil character

Natural soils are typically heterogeneous and are constantly influenced by factors such as particle deposition or erosion, microbial activity, plant uptake, weathering, leaching and new mineral formation (Paton et al. 1995; Pierzynski et al. 2005). Soil mineralogy and characteristics such as size of grains, pores and pore thoats, pH, organic content and competing ion effects can influence the effectiveness of immobilisation and encapsulation techniques (White et al. 2012).

The concentration of silica in a soil solution depends largely on solubility and the relative rates of dissolution and adsorption of silica compounds in soils (Ler 1979; Sommer et al. 2006). The solubility of mineral and amorphous forms of silica in soil generally remains low between pH 2.5 and 8.5 (Chen 1989; Sommer et al. 2006). Buffering of pH may be required in highly acidic soils (i.e. in soils where pH < 4) to avoid polymerisation of soluble silicates prior to immobilisation or encapsulation of contaminants (Mitchell et al. 2000a, b).

Silica treatments perform better in slightly acidic soils due to the greater potential for exchange between mobile metals and silica treatments in acidic environments (Mbhele 2007). However, silica treatments are also effective in neutral to slightly alkaline soils (Arocha et al. 1996; Fytas et al. 1999; Abdel-Hamid et al. 2012). Treatment performance may be reduced in highly alkaline environments if metals form polymeric ions or metal hydroxides which can block the pores of the silica structure, thereby reducing retention capacity and the potential for immobilisation or encapsulation (Algarra et al. 2004; Mbhele 2007). Soil organic acids (e.g. oxalic, citric, malic and acetic acid) in the rhizosphere can also liberate metals due to chelating effects of the organic acids on metals (Debela et al. 2010). Also, organic carbon can constrain reactions rates dramatically by preventing crystal growth on surfaces (Lang and Kaupenjohann 2003). Silica treatments are more effective in sandy soils when compared to silty soils (Arocha et al. 1996; Vandiviere and Evangelou 1998; Mbhele 2007).

Microorganisms can play a pivotal role in the dissolution of silica in natural soil systems. Bacteria and fungi actively decompose plant litter which release silica or instigate active mineral dissolution (Hoffland et al. 2002; Smits et al. 2005; Sommer et al. 2006). The mechanisms of mineral dissolution were described by Ehrlich (1996) and involve the production of metabolic products such as organic acids which act as acidulants or ligands and furnish protons that assist in the degradation of Si-O and Al-O bonds through protonation and catalysis. Some acids also act as ligands which pull cations from silica and further facilitate the degradation of chemical bonds (Ehrlich 1996). Alternatively, the cell membranes of some microorganisms may function as catalysts for silica mineral precipitation (also known as biomineralisation), which should increase immobilisation efficiency (Lierman et al. 2000; Kawano and Tomita 2001; Inagaki et al. 2003; Sommer et al. 2006).

This review highlights some of the environmental factors which should be considered prior to applying silica treatments to contaminated soil, and a thorough site assessment should precede the conversion of methods and results from controlled experimental environments to the in situ application of silica treatments under natural field conditions.

5.6: Management of contaminants using silica treatments

5.6.1: Immobilisation of metals using silica treatments

Following mining and smelting activities and their use in agricultural, manufacturing and industrial applications, metals have become widely distributed across the globe (Järup 2003, Poland et al. 2003). Adverse impacts of metal exposure are well reported (e.g. Järup 2003, Taylor et al. 2013). Silica treatments are one technique with demonstrated potential for the management of metal contaminants (Mitchell et al. 2000a, b; Mbhele 2007).

In 2001, the Mine Waste Technology Program, the United States Environment Protection Agency (US EPA) and the Office of Research and Development (US EPA, 2004) investigated the feasibility

of a silica treatment at preventing sulphate oxidation and immobilising Al, Fe, As and Zn. The field trial used a highly acidic waste material excavated from the Gilt Edge Mine, South Dakota (pH 2.75) (US EPA 2004).

The silica treatment was applied as a spray solution and monitored over a two year period (US EPA 2004). Details of the treatment composition applied were not provided. The treatment reduced Al and Fe concentrations in leachate by 88.1% and 94.8%, respectively, but failed to reduce As and Zn to below the South Dakota water discharge limits (US EPA 2004). The silica treatment's inability to immobilise As and Zn was attributed to insufficient dosage levels and the study recommended an increase in the treatment dosage from 0.6 wt% to 3.0 wt% in future studies (US EPA 2004).

The same silica treatment was applied to contaminated soil obtained from Gold Field Mine, South Africa in a laboratory-based study (Mbhele 2007). The soil was treated with the silica treatment at a 1:1 ratio, mixed manually and soil and leachate samples were obtained over a 10 day period (Mbhele 2007). The study indicated that the treatment was effective at immobilising metals in acidic (pH 2) and basic (pH 9) soils, with immobilisation occurring within two days (Mbhele 2007). Immobilisation of metals by silica was less effective in clay soils in comparison with sandy soils (Mbhele 2007). Treatment with silica reduced leachable concentrations of Cr, Co, Cu, Zn and Pb by 78, 73, 74, 68 and 45% in sandy soils (pH 2) and by 55, 43, 40, 16 and 39% in sandy soils (pH 9), respectively (Mbhele 2007). Whereas leachable concentrations of Cr, Co, Cu, Zn and Pb were reduced only by 49, 31, 9.3, 15 and 30% in clay soils (pH 2) and by 1.6, 7.9, 8.1, 0.3 and 22% in clay soils (pH 9), respectively (Mbhele 2007). No explanation for the effect of clay content on treatment performance was provided; however, it is possible that reduced treatment efficiency in clay soils may be due to the adsorption of metals onto the surface of negatively charged clay particles (Alpaslan and Yukselen 2002). Silica treatment performance was also found to be improved by the addition of an anionic surfactant (in dosages up to 0.5 wt% of the Si treatment solution) (Mbhele 2007).

Abdel Hamid et al. (2012) trialled a silica gel treatment on an alkaline (pH 7.74) Ni, Cd and Pb contaminated sandy soil from the East Rosetta Estuary in Egypt. The soil was treated with silica gel at 0.5 wt% and 1 wt% dosage levels and the soils were analysed for diethylene triamine pentaacetic acid (DTPA) extractable concentrations of metals after 28 days. The gel treatment reduced DTPA extractable Pb by 69.3-88.3%, Cd by 61.7-82.6% and Ni by 72.4-74.3% (Abdel-Hamid et al. 2012).

These case studies demonstrate that silica treatments can immobilise metal contaminants; however, a paucity of studies limits an understanding of the efficacy of this remediation technique under a range of environmental conditions.

5.6.2: Encapsulation of hydrocarbons using silica treatments

Hydrocarbon contamination typically occurs at petrochemical sites and storage areas, waste disposal sites, refineries and fuel spill sites (Masih and Taneja 2006). Many hydrocarbons are persistent organic contaminants which are toxic, carcinogenic and can bioaccumulate in the environment (Masih and Taneja 2006).

Arocha et al. (1996) investigated the feasibility of silica treatments as a technique for encapsulating hydrocarbons under laboratory conditions. A silty loam (pH 7.9), spiked with the aromatic hydrocarbon toluene (2 g soil mixed with 4 μg/L liquid toluene) and mixed with shredded tire particles (10% w/w), was silica treated (Arocha et al. 1996). The tire particles were added to act as an adsorbent and ensure that desorption would not occur during the subsequent addition of acetic acid or a surfactant, used to furnish an acidic medium for silica precipitation (Arocha et al. 1996). The surfactant used in this study consisted of citric acid (4%), dodecyl benzene sulphonic acid (5%), ethanol (4%) and water (91%) (Arocha et al. 1996). Following the application of acetic acid or the surfactant, silica treatments solutions containing SiO_2, Na_2O and H_2O (pH 11.3) were applied (30 wt% or 60 wt%) as a solution treatment (Arocha et al. 1996).

In total, 81% of toluene in soil was retained by treatment with shredded tire particles and the silica treatment (Arocha et al. 1996). Of the 81% of toluene retained, 50% was retained by the silica treatment and 31% was adsorbed onto the shredded tire particles (Arocha et al. 1996). Permeation of toluene throughout the soil material was significantly reduced after treatment (Arocha et al. 1996). A single application of the silica treatment reduced toluene by 50% and two applications decreased toluene to less than 25% (Arocha et al. 1996). Soil treated with acetic acid formed larger silica agglomerations than soil pre-treated with a surfactant (Arocha et al. 1996).

Hydrocarbon encapsulation by silica treatments was undertaken by Mbhele (2007). Hydrocarbon and metal contaminated sandy soils and soils with high clay content were pH buffered to 2.0, 8.2 and 13.1 and treated at a 1:1 ratio. Encapsulation of hydrocarbons in all soils was evident within two days of treatment application, but was more effective in acidic, sandy soils and when a surfactant was applied prior to the application of a silica treatment (Mbhele 2007). McDowell (1994) reported similar results and found that silica treatments reduced mean Total Petroleum Hydrocarbons (TPH) by approximately 99.8% and 95% in sandy and clay soils, respectively.

5.6.3: Management of acid mine drainage using silica treatments

Oxidation of pyrite in waste material from mining is the main source of Acid Mine Drainage (AMD). In low pH environments (pH $\leq$ 3), Fe^{2+} released from pyrite can becomes oxidised rapidly by *T. ferrooxidans* to form Fe^{3+} which amplifies the oxidation of pyrite and instigates AMD (Vandiviere and Evangelou 1998; Zang and Evangelou 1998; Mitchell and Wheaton 1999). A common approach to

the management of AMD relies on the application of alkaline materials such as limestone to neutralise the products of AMD; however, this technique has a limited lifespan (Fytas et al. 1999; Evangelou 2001) due to passivation of the limestone surface by reaction products such as jarosite. An alternative approach to the management of AMD was provided by Vandiviere and Evangelou (1998) who demonstrated the potential of silica treatments at inhibiting AMD in a column based study.

Two types of pyritic waste were used as the soil models for this study. The first was a pyritic waste (pyrite content of 80%), obtained from a Canadian metal refinery (Vandiviere and Evangelou 1998). The soil was stored under water-saturated conditions to create a reducing environment and mixed with sand at a 1:20 ratio, giving 4 wt% pyrite. The second type of pyritic waste was highly weathered coal spoil material with 21.4 wt% pyrite and was obtained from a site in Kentucky (USA). The spoil was mixed with sand at a ratio of 1:10, giving a final pyrite content of 19 wt% (Vandiviere and Evangelou 1998).

The prepared soil was used in a column study consisting of three groups of treated and leached columns (Vandiviere and Evangelou 1998). The first group included soil from the Canadian mine tailings with sufficient limestone to neutralise 113.5% of potential acidity in the pyrite material. The second and third groups included enough limestone to neutralise 9% of the potential acidity in the pyrite material (one group used soil from the Canadian mine tailings and the other was based on the soil obtained from Kentucky) (Vandiviere and Evangelou 1998). The lower amount of limestone used in the second and third groups were chosen to allow for distinctions between the effects of limestone from the effect of the chemical treatments. Each of these three column groups consisted of a control, a phosphate treatment, a silica treatment (containing Na_2SiO_3 and NaOAc), and a limestone treatment (all treatments were duplicated) (Vandiviere and Evangelou 1998). The columns were either leached with a coating treatment or deionised water and then moved to a field nearby to simulate on-site treatment under natural environmental conditions (Vandiviere and Evangelou 1998). The columns were sampled and monitored over 28 months.

After 28 months of sampling and monitoring, all treatments significantly reduced pyrite oxidation when compared to the control columns (Vandiviere and Evangelou 1998). The pH in the control columns were also significantly lower (pH ≤ 2) than the treated columns (pH 7), reflecting higher rates of pyrite oxidation in the control columns (Vandiviere and Evangelou 1998). Of the treatments investigated, silica treatments demonstrated the most potential and the limestone treatments were least effective (Vandiviere and Evangelou 1998). The limestone treatments failed to inhibit Fe release and pyrite oxidation over the 28 month study period (Vandiviere and Evangelou 1998). The phosphate coatings were reasonably effective at inhibiting AMD in the Canadian mine tailings, but less effective for the Kentucky spoil material (Vandiviere and Evangelou 1998). Alternatively, the silica or silica-

limestone coating treatments performed most effectively in both the Canadian mine tailings soil material and Kentucky spoil (Vandiviere and Evangelou 1998). In the Kentucky spoil material columns treated with silica and limestone, Fe concentrations were ~ 579 times lower than the control columns (Vandiviere and Evangelou 1998). The silica coatings effectively managed pyrite oxidation in the Canadian mine tailings over 18 months (Vandiviere and Evangelou 1998).

A similar study was conducted by Evangelou (2001) in chromatographic leaching columns loaded with 0.1 g of pyrite and 0.9 g of >0.1 mm sand. The columns were leached with a silica treatment composed of H_2O_2 (0.106 M), NaCl (0.01 M) and Na_2SiO_3 (0.001 M) (Evangelou 2001). The silica coating was found to inhibit 90% of pyrite oxidation due to the formation of an iron-oxyhydroxide silica coating (Evangelou 2001). The coating formed by oxidation of pyrite by H_2O_2 when leached with the silica treatment solution. Ferric iron (a product of pyrite oxidation) was then hydrolyzed to form an iron-oxyhydroxide precipitate on pyritic surfaces (Evangelou 2001). The pH buffer in the treatment successfully sustained a pH of 6 which is favorable for the formation of $Fe(OH)_3$. Subsequently, the SiO_4 in the coating solution reacted with OH to generate a silica polymer on the Fe-oxyhydroxide surface (Evangelou 2001). Once the surface became covered with the silica polymer, additional condensation of silica produced a layered silica film which constituted an iron-oxyhydroxide silica coating (Evangelou 2001).

Fytas et al. (1999) trialled silica treatments on fresh, non-oxidised mine tailings from Bouchard Hébert Mine, Canada. The pyritic tailings contained 41 wt% Fe, 0.42 wt% Mg and 32 wt% S, and x-ray diffraction confirmed the presence of pyrite, muscovite, quartz and siderite (Fytas et al. 1999). The silica treatments were applied as solutions (Table 5.2). Leachate samples were obtained over 80 days following treatment application, and they were measured for pH and analysed for iron and sulphate (Fytas et al. 1999).

Table 5.2: Summary of treatments trialled by Fytas et al. (1999). M=moles, Y/N=Yes/No

Treatment ID	Tailings (g)	Sodium silicate (M)	Sodium acetate (M)	Hydrogen peroxide (M)	Calcium carbonate (g)	Calcium sulphate (Y/N)	Solution volume (L)
Control	200	0	0	0	0	N	0
A	500	0.02	0.1	0.4375	0	Y	2
B	166.66	0.1	0.01	0	0	Y	1
C	200	0.1 and 0.05	0.01	0	0	N	1
D	371.85	0.11	0	0.01	20.05	N	2
E	371.85	0.11	0	0	20.05	N	2
F	200	0.11	0	0	7	N	0.5
G	200	0.125	0	0	7	N	0.5
H	200	0.14	0	0	7	N	0.5

The study demonstrated that silica treatments can establish a ferric hydroxide-silica coating on pyrite particles, thereby controlling oxidation and preventing the release of Fe and S (Fytas et al. 1999). Of the treatments trialled, the treatments most effective at suppressing Fe and S were treatments D and E (Table 5.2). Fe and S concentrations in leachates obtained from treatments D and E were well below those obtained from the control columns (Fytas et al. 1999). The performance of silica treatments improved with increasing concentrations of silica in the treatment solution (Fytas et al. 1999). The final pH of the leachate samples obtained from treatments D and E were between 6 and 7, whereas the pH of leachate obtained from the control was ~ 3 (Fytas et al. 1999).

These studies demonstrate the effective use of silica treatments for the prevention of AMD; however, longer-term studies aimed at assessing the durability and chemical stability of silica treatments under a range of environmental conditions would be beneficial for the development of this treatment technique.

5.7: Conclusion

Contaminated land is a global problem (Järup 2003), and there is a need for fast, cost-effective and versatile approaches to remediation. There are several benefits associated with silica treatments. Firstly silica treatments are suitable for a wide range of organic and inorganic contaminants (Arocha et al. 1996; Billings and Burns 1997; Fytas et al. 1999; Li et al. 2012). The treatments are also fast, with encapsulation occurring within two days of treatment (Mbhele 2007). Finally, the treatments can be applied on-site or in situ, which is less disruptive to the environment, reduces the costs associated

with excavation and transportation of contaminated material, and reduces the need for landfilling (Martin and Ruby 2004; Filler et al. 2006).

Despite the demonstrated potential of silica treatments, the shortage of published studies describing the performance of treatments under a range of environmental conditions limits our current understanding of this remedial technique. Consequently there are aspects of silica treatments which require further investigation. Of critical importance is the need for long-term studies which demonstrate the stability of products immobilised or encapsulated by silica treatments. Studies reporting on the direct relationship between environmental conditions such as soil condition, temperature, pH, oxidation-reduction potential, microbial behavior and treatment performance would also be beneficial. Potential environmental risks associated with silica treatments should also be investigated.

Due to the remaining uncertainty associated with silica treatments they should only be applied in situ after a thorough site assessment and consideration of factors such as soil characteristics, climate and technology limitations. This review demonstrates that silica treatments are a promising technique for contaminated land management, but further research is required before this technique can be considered a proven, safe and reliable remediation technique.

5.8: References

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Section 2: Addendum

The distinction between ORP and Eh

Oxidation-Reduction Potential (ORP) or redox is a potentiometric measurement of the potential of a medium to transfer electrons (American Public Health Assocaition 1992). ORP is sensed by an inert metal electrode and read relative to a reference electrode immersed in the same medium. Positive ORP results indicate an oxidising environment, whereas negative values represent a reducing environment. ORP data is particularly useful in water environments that contain high concentrations of redox-active species and strong oxidising or reducing agents such as chlorine or sulphite ion agents (YSI Environmental 2005). Similarly, Eh also quantifies the potential of a medium to transfer elections. However, the reference electrodes and voltage offsets are different. Eh is defined as a voltage reading vs. the Standard Hydrogen Electrode (SHE), whereas ORP is a more relative measurement (American Public Health Association 1992). Obtaining data using SHE is difficult in the field, thus only ORP data was collected during this study. Although voltages obtained as ORP readings can converted into Eh values (YSI Environmental 2005), it is important to recognise they refer to different measurements and are not interchangeable terms.

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Section 3: Research Objectives

Chapter 6: Research focus and objectives

The Antarctic Treaty is the principal legislative force in Antarctica (Fryirs et al. 2013, 2015). Annex III to the Protocol on Environmental Protection to the Antarctic Treaty (Waste Disposal and Management) establishes the requirement for all past and present work sites to be restored unless the site is considered to be a monument of historical value or unless disturbance is likely to result in greater adverse environmental impacts (SCAR 1993; Snape et al. 2001; Fryirs et al. 2013).

The volume of contaminated soil, sediment and waste in Antarctica is estimated to be between 1 and 10 million m^3 (Snape et al. 2001). The majority of this material is situated on ice-free areas which account for 0.3% of the land area of the continent. These areas are where wildlife, research and tourism activities are most concentrated (Pickard 1986; Snape et al. 2001; Tin et al. 2009). Many of the terrestrial and marine organisms that inhabit Antarctica are adapted to the unique, isolated and cold Antarctic environment (Bargagli 2008). Environmental contaminants can be persistent in the Antarctic environment (Gore et al. 1999; Stark S.C. et al. 2003; Fryirs et al. 2015), and exposure to contamination can generate significant stress on the adapted, sensitive and rare species that inhabit Antarctica (Hill et al. 2009; Tin et al. 2009; Poulsen et al. 2012; Mooney et al. 2013; Payne et al. 2014; Marcus-Zamora et al. 2015).

Undertaking remediation in Antarctica is confounded by environmental and logistical constraints (Poland et al. 2003), and a recent study indicates that the financial cost of remediation is in Antarctica is typically ten times greater than in temperate, industrialised regions (Tin et al. 2009). Additional complications arise at sites such as Wilkes, where competing interests such as the preservation of cultural heritage and remediation of contaminated land co-exist, at sites concealed by ice, and at sites where conventional approaches to remediation such as dig-and-haul are impractical, unaffordable or unfeasible (Tin et al. 2009). At such sites, there is need to adapt existing, or develop new approaches capable of safely, effectively and efficiently managing contaminated land.

The successful application of orthophosphate and silica treatments to contaminated sites in temperate environments (Arocha et al. 1996; Mbhele 2007; Abdel Hamid et al. 2012; Tang and Yang 2012; Debela et al. 2013) indicates these technologies may be applicable to contaminated sites in remote, cold regions. As such, the overriding objective of this thesis is to assess the potential of these technologies for the management of metal contaminated soil and soil co-contaminated with metals and petroleum hydrocarbons at Wilkes. Wilkes was selected as the case study for this research primarily due to the presence of extensive legacy waste, metal contaminated soil and soil co-contaminated with metals and petroleum hydrocarbons, making it suitable for trials assessing the efficacy of orthophosphate and silica treatments under cold conditions (Snape et al. 1998; Babicka 2000; Stark J.S. et al. 2003, 2006; Fryirs et al. 2013, 2015). The unique history, location and cultural

heritage status of Wilkes also provided a suitable context for a discussion surrounding the co-management of remediation and cultural heritage preservation in Antarctica (Stark S.C. et al. 2003, Chapter 8).

The primary research objectives addressed in this thesis are:

1) To delineate the ice-covered landfill at Wilkes using a non-invasive geophysical method,

2) To investigate the effectiveness of orthophosphate and silica treatments for immobilising metal contaminants in Antarctic landfill materials,

3) To develop an understanding of the effects of applying treatments homogenously at contaminated sites, where zones of low-level metal contamination exist,

4) To observe the products which form when metals react with orthophosphate, silica and orthophosphate-silica mix treatments under cold conditions; and

5) To assess the remediation potential of silica treatments on soil co-contaminated with metals and petroleum hydrocarbons, under cold conditions.

Although the majority of research included in this thesis is specific to Wilkes, the reported research outcomes extend beyond Wilkes, and it is intended that this research will be applicable to similarly contaminated sites in Antarctica and other remote, cold regions.

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Section 4: Wilkes

Chapter 7: Introduction to Wilkes Station, East Antarctica

7.1: Historical overview

Wilkes is an abandoned research station situated on Clark Peninsula, in the Windmill Island group, East Antarctica that was constructed by the United States of America (USA) as part of Operation Deep Freeze 2 during the International Geophysical Year (1957-1958). Wilkes was designed primarily as a temporary, strategic base for scientific research and exploration and was constructed in 16 days (Fryirs et al. 2013). Scientific research undertaken at Wilkes during its occupation covered various disciplines including ionospheric physics, cosmic rays, geomagnetism, seismology, glaciology, meteorology, biology and the physiology of humans working in Antarctica (Snape et al. 1998; Fryirs et al. 2013).

During the construction of Wilkes, more than 11,000 tonnes of fuel, building supplies and scientific equipment were transported on-site (Fryirs et al. 2013). Station records report that excess supplies remained in their original landing positions and later became buried by snow (Clark and Wishart 1989; Fryirs et al. 2013). The precise volume of these materials remains unknown (Fryirs et al. 2013).

After the completion of the International Geophysical Year, administrative and operational control of Wilkes was transferred to Australia (Fryirs et al. 2013; Chapter 8). In 1961, exclusive control of of Wilkes was transferred to the Australian National Antarctic Research Expeditions (ANARE) (Chapter 8). Australia occupied the station for 10 years before abandoning the station in 1969 due to frequent burial by snow and ice and fire hazards associated with fuel seepages (Snape et al. 1998; Fryirs et al. 2013; Chapter 8). All equipment, buildings, supplies, fuel and a landfill were left in situ and despite a number of small-scale clean-up efforts, the majority of this material remains on Clark Peninsula. The abandonment of Wilkes coincided with the opening of the original 'Old Casey' Station on Bailey Peninsula, approximately 2 km south of Wilkes. 'Old Casey' was also abandoned in 1989 after the construction of the larger and more energy efficient 'New' Casey Station, also situated on Bailey Peninsula a further 1 km to the south. Old Casey has subsequently been removed and associated landfill remediated (Deprez et al. 1999), leaving Wilkes as the largest environmental liability in the area.

7.2: Environmental setting

Wilkes is located immediately west of Antarctic Specially Protected Area 136 (ASPA 136) which was established for the protection of moss and lichen, and contains an Adélie penguin (*Pygoscelis adeliae*) rookery (Fryirs et al. 2013).

Windmill Islands hosts the most extensive vegetation in continental Antarctica, with ~27 species of macrolichens and four species of bryophytes in the region (Smith 1988; Wasley et al. 2012). Wilson's

storm petrels (*Oceanites oceanicus*), snow petrels (*Pagodroma nivea*), southern giant petrels (*Macronectes giganteus*), cape petrels (*Daption capense*), southern fulmars (*Fulmarus glacialoides)*, Antarctic petrels (*Thalassoica antarctica)*, south polar skuas (*Stercorarius maccormicki*) and emperor penguins (*Aptenodytes forsteri*) are also well established in the region (Orton 1963; Woehler et al. 1991, 1994; Melick and Bremmers 1995; Melick and Seppelt 1997). The coastal waters surrounding Wilkes support a large diversity of marine fauna including weddell seals (*Leptonychotes weddellii)*, crabeater seals (*Lobodon carcinophaga*), ross seals (*Ommatophoca rossii*), leopard seals (*Hydrurga leptonyx*) and elephant seals (*Mirounga leonina*) (Murray and Luders 1990).

The region surrounding Wilkes is a polymetamorphic basement consisting of granulite facies magmatic pelites, psammites and granite gneisses of the Windmill Metamorphic Series (Blight and Oliver 1977; Paul et al. 1995; Snape et al. 1998). The dominant lithologies are potassic granites with subordinate manganiferous semipelites, pelites and mafic layers which are intercalcated at 10-100 m scales (Snape et al. 1998). Snape et al. (1998) also reported that magmatic fluid infiltration in the basement has occurred, which may account for some mineralisation or enrichment of soluble elements which could influence background concentrations of trace metals.

Melick and Seppelt (1994) describe the climate of the Windmill Islands as frigid-Antarctic. Extremes of temperature for the region range from 9.2 °C to -41 °C. Annual precipitation is approximately 175 mm per year rainfall equivalent, which falls predominately as snow. Approximately 96 days of gale force wind conditions (i.e. >63 km/h) occur each year and the predominant wind direction is from the east, east-north-east or south (Melick and Seppelt 1994; Miller et al. 1996; BOM 2015).

7.3: Environmental contamination

The first official assessment of environmental contaminants at Wilkes was conducted by Australian Army Engineers during summer seasons between 1987 and 1994 (Snape et al. 1998; Fryirs et al. 2013). During this time, several small-scale clean-up operations were undertaken that resulted in the removal of an unknown amount of legacy waste. Although the precise amount of material removed remains unknown, Snape et al. (1998) and Fryirs et al. (2013) suggest that at least 10 m^3 of caustic soda, 110,000 L of diesel fuel and 4.5 m^3 of ferrosilicon were removed. The venting of 300 gas cylinders and destruction of 12 kg of explosives was also achieved during the Australian Army clean-up operations at Wilkes (Snape et al. 1998; Fryirs et al. 2013).

Several studies reporting on localised contamination with metal and petroleum hydrocarbons have been undertaken since the initial site assessment and clean-up operations conducted by the Australian Army Engineers (Snape et al. 1998; Snape and Riddle 1998; Babicka 2000; Stark et al. 2003a, 2006; Fryirs et al. 2013, 2015). The presence of remaining macro-contaminants and legacy waste from human activities including batteries, food remains, scrap metal, gas cylinders, copper wire, piping,

hazardous substances and mechanical components is also described in the literature specific to Wilkes (Snape et al. 1998; Deprez et al. 1999; Fryirs et al. 2013 and Figures S7.1-14). The majority of waste items from the station precinct are concentrated in a landfill located east-south-east of the station (Figure 8.1). The topography of Wilkes encompasses low-lying depressions on the southern side of the station precinct which host the fuel storage area and landfill (Fryirs et al. 2013). During summer these areas become enveloped by streams which disperse contaminants into nearby marine areas (Fryirs et al. 2013). Several studies report elevated metal concentrations in sediment collected from several hundred metres into Newcomb Bay, situated south of Wilkes landfill (Figure 8.1) (Stark et al. 2003a, 2006; Townsend and Snape 2008; Townsend et al. 2009; Fryirs et al. 2013).

A site assessment by Fryirs et al. (2013) used waste categories listed in Annex III, Article 2 of the Madrid Protocol (1991) to identify and classify legacy waste items at Wilkes. Data obtained from historical records of station operations and past clean-up reports were used in conjunction with site assessments by Snape et al. (1998) and Babicka (2000) to classify and map the distribution of legacy waste and potential heritage items at Wilkes (Fryirs et al. 2013). Fryirs et al. (2013) identified 536 sites with one or more legacy waste items. Approximately 1,020 partially full fuel drums were identified, and petroleum hydrocarbon contaminated waste and sediment was observed at 38% of the sites (Fryirs et al. 2013). Solid, non-combustible waste including scrap metal, copper wire, copper pipes, vented gas cylinders and steel mechanical parts represented the most dominant waste category (Fryirs et al. 2013. These items were observed at 25% of surveyed sites (Fryirs et al. 2013). Harmful waste or potentially hazardous items including electrical batteries, fuel bladders, food remains, treated timber and containers containing persistent compounds were observed at 28% of sites (Fryirs et al. 2013). Hazardous substances including caustic soda, photographic chemicals, acid bottles, tins of solvent, explosives and asbestos were reported at 9% of the sites, but represent a significant environmental contamination and health concern (Fryirs et al. 2013). Legacy waste items with potential heritage value were found at approximately 10% of sites surveyed (Fryirs et al. 2013).

Completing a detailed area-by-area assessment of Wilkes is a large and complicated task as legacy waste is scattered over an area of 1.0 km × 1.5 km (Fryirs et al. 2013). Recent estimates also indicate that more than 70% of legacy waste material at Wilkes is buried under snow and ice (Fryirs et al. 2013). These factors complicate visual assessments of the amount and distribution of legacy waste substantially. Thus, the opportunistic sampling regime adopted in this research provides a broad distribution of data useful for the identification of hotspots and areas of environmental concern, but does not provide a representative indication of contamination across the site.

A recent and systematic assessment was undertaken by Fryirs et al. (2015). This survey applied the Australian and New Zealand Environment and Conservation Council (ANZECC) sediment and water

guidelines and background concentration levels (BCL) to assess metal and petroleum hydrocarbon contamination at Wilkes (Fryirs et al. 2015). Sixty seven sediment and 93 water samples were collected for analyses of metals and metalloids. The mean concentrations of Cr, Mn, Fe, Ni, Cu, Zn, As, Ag, Sb, Sn, Hg and Pb in sediment samples was 170, 660, 17, 49, 130, 200, 14, 3.5, 75, 170, 5 and 10 mg/kg, respectively (Fryirs et al. 2015). Seventy two percent of sediment samples were contaminated with at least one metal or metalloid, while 19% were contaminated with four or more metals or metalloids (Fryirs et al. 2015). The mean concentrations of Cr, Mn, Fe, Ni, Cu, Zn, As, Ag, Sb, Sn, Hg and Pb in the 93 water samples collected were 41, 2.9, 12, 2.7, 12, 360, 31, 1.8, 23, 17, 3.8, 3.9 and 150 μg/L, respectively (Fryirs et al. 2015). At least one metal or metalloid in concentrations exceeding the ANZECC trigger guidelines occurred in 96% of the water samples obtained (ANZECC 2000; Fryirs et al. 2015).

Total petroleum hydrocarbons in sediment (n=27) and water (n=18) samples collected from areas visibly contaminated were generally below quantification limits (Fryirs et al. 2015). Ten sediment samples returned concentrations of C_9-C_{18} hydrocarbons (winterised, or "dewaxed", diesel range organics) above NEPC (ASC) 1999 guidelines (Fryirs et al. 2015). Five samples contained C_9-C_{28} hydrocarbons (diesel range organics) above guidelines, and one sample contained concentrations of C_{29}-C_{36} hydrocarbons lubricating oil) above guidelines (Fryirs et al. 2015). Fifteen of the 18 water samples collected returned concentrations of petroleum hydrocarbons below quantification limits for dissolved hydrocarbons (Fryirs et al. 2015). Fryirs et al. (2015) attributed the low concentrations of petroleum hydrocarbons at visibly contaminated sites to i) the small volume of water samples obtained, resulting in high quantitation limits, ii) visible contamination and odour being the result of an organic compound other than petroleum hydrocarbons, and iii) evaporation, dispersal or biotic degradation of petroleum hydrocarbons in the environment (Fryirs et al. 2015).

The high concentrations of dissolved metals in water samples obtained from Wilkes indicate that contaminants are mobilised from sediment sources during snow and ice melt (Fryirs et al. 2015). They also suggest that contaminated sediments and legacy waste at Wilkes provide ongoing sources of contaminated runoff across Clark Peninsula (Fryirs et al. 2015). At nearby Thala Valley landfill (Figure 8.1), metal concentrations in both surface and subsurface waters were found to increase by up to 1000 times as melt water passed through the waste materials (Snape et al. 2001; Stark et al. 2008). Similar processes occur at Wilkes landfill where runoff discharges into Newcomb Bay and has resulted in the detection of high concentrations of metals (13-40 mg/kg > BCL) several hundreds of metres into the bay (Stark et al. 2003a, 2005; Townsend and Snape 2008; Fryirs et al. 2015). Other metals including Cu, Zn and Cd have also dispersed into the surrounding marine environment, affecting soft-sediment benthos (Stark et al. 2003b). These impacted areas are characterised by fewer benthic taxa, lower species diversity and lower species richness (Stark et al. 2003a).

Fryirs et al. (2013, 2015) demonstrated that environmental contamination at Wilkes represents a serious environmental problem and they identified areas of particular concern. Due to the expansive and complex distribution of contamination at Wilkes, it is likely a staged or zoned approach to remediation would be most practical. If such an approach was implemented, it is probable that the initial clean-up efforts would be concentrated at the landfill and fuel farm where contamination presents the most immediate threat to the environment.

The volume of contaminated legacy waste within the Wilkes landfill area was estimated at 10,000 m^3 (Snape and Riddle 1998). More recently, Freidman et al. (2015) estimated the volume of waste within the landfill to 17,000 m^3. The most recent estimate is 25 times greater volume of material than what was originally estimated to be stored within the nearby Thala Valley landfill which was excavated between 1996 and 2004 (Hafsteinsdóttir 2012; Freidman et al. 2014; Statham 2014). Excavating the material from Wilkes landfill for off-site treatment or storage would require filling and transporting approximately 1,000 half-height shipping containers (6.0 x 2.5 m) from Antarctica to Australia (Statham 2014). This represents a large logistical operation and financial expense that relies on currently non-existent earth moving equipment and shipping infrastructure (Snape and Riddle 1998; Statham 2014).

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7.5: Supplementary

Figure S7.1: Remnant buildings at Wilkes (Fryirs et al. 2013).

Figure S7.2: Remnant buildings and legacy waste at Wilkes (Fryirs et al. 2013).

Figures S7.3 and 4: Fuel drums and discarded machinery (Fryirs et al. 2013).

Figures S7.5 and 6: Food scraps, jars and fuel spill from drum (Fryirs et al. 2013).

Figures S7.7 and 8: Fuel drums, gas cylinders, treated timber and plastic (fuel bladder) (Fryirs et al. 2013).

Figures S7.9 and 10: Fuel drums and legacy waste (Fryirs et al. 2013).

Figures S7.11 and 12: Legacy waste and discarded machinery (Fryirs et al. 2013).

Figure S7. 13: Exposed landfill material at Wilkes landfill (D Camenzuli 2014).

Figure S7.14: Gas cylinders at Wilkes (L Mason 2014).

7.5.1: References

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Chapter 8: Managing legacy waste in the presence of cultural heritage at Wilkes Station, East Antarctica

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Citation: Camenzuli D., Fryirs K.A., Gore D.B. and Freidman B.L. 2015. Managing legacy waste in the presence of cultural heritage at Wilkes Station, East Antarctica. *Polar Record 51*, 151-159.

Submitted: 19 June 2013; *Accepted for publication:* 15 October 2013; *Published online*: 16 December 2013

Abstract

The Antarctic Treaty has been the principal governing force in Antarctica since 1961. The Protocol on Environmental Protection to the Antarctic Treaty (Madrid Protocol) requires that all past and present work and wastedisposal sites are cleaned up unless doing so would cause greater environmental damage or the site is considered to be a monument of significant historical importance. Despite this requirement, legacy waste issues remain unresolved in parts of Antarctica. Clean-up operations in Antarctica are complicated by a combination of restricted access, extreme weather, financial limitations and logistical constraints. Further complications arise at sites such as Wilkes Station, where the requirement for clean-up coexists with the desire to preserve potentially valuable heritage items. Several buildings and artefacts with potential heritage value remain at Wilkes Station. However, Wilkes Station is not officially designated as a historic site or monument under the Antarctic Treaty, nor is it a national or world heritage place under Australian domestic legislation. Consequently the buildings and relics at Wilkes Station are afforded little protection under the existing relevant domestic and international legislative frameworks. This paper uses Wilkes Station as a case study of the complexities associated with conducting clean-up operations at contaminated sites with informal heritage value in Antarctica. The legislative and environmental considerations surrounding clean-up operations at Wilkes Station are also investigated. Furthermore, we argue the importance of a multi-disciplinary approach to operations which facilitate the clean-up of legacy waste and preservation of the potential heritage values at Wilkes. Finally, we recognise that the complexities discussed in this paper have wider applicability and we investigate the relevance of these issues to other Antarctic contaminated sites with formal or informal heritage value.

8.1: Introduction

Environmental contamination associated with legacy waste from human activities remains unresolved in many locations in Antarctica, despite the widespread perception that it is a pristine wilderness (Snape et al. 2001a; Poland et al. 2003). Legacy waste in Antarctica includes all forms of historical waste associated with human activities remaining on-site, and is typically concentrated around abandoned research stations. Many of the remaining abandoned stations in Antarctica were in operation prior to the ratification of the Protocol on Environmental Protection to the Antarctic Treaty (Madrid Protocol 1991). Prior to the ratification of the Madrid Protocol, waste generated on station was typically stored in on-site landfills or was disposed onto sea ice (Kennicutt et al. 1995; Stark et al. 2006; Haward and Griffiths 2011; Fryirs et al. 2013). In several instances, remnant waste associated with abandoned stations presents a significant threat to the Antarctic environment (Kennicutt et al. 1995; Snape et al. 2001a; Stark et al. 2006; Fryirs et al. 2013).

The Madrid Protocol provides clear guidelines for the protection of the Antarctic environment. Annex III (Waste disposal and waste management) establishes the requirement for all past and present work sites to be cleaned up by the generators and users of sites unless the site is considered to be a monument of historical value, or unless disturbance would result in greater adverse environmental impacts (Snape et al. 2001a; Poland et al. 2003; Evans 2007). Annex V (Management of protected areas) provides guidance for the designation and protection of historic sites and monuments (HSMs) approved for listing by the Antarctic Treaty Consultative Meeting (ATCM). This listing prohibits damage to HSMs and provides strict conditions for their preservation. Annex V also requires treaty parties to identify HSMs in a systematic framework and include them in the series of Antarctic Specially Protected Areas (ASPAs). However, no timeframes for this requirement are specified (Evans 2007). Australia has not yet completed this requirement, nor has it sought HSM listing for any potential heritage sites by the ATCM. Currently there are 80 listed HSMs in Antarctica (Roura 2011). Additional guidance on the handling of pre-1958 historic remains with unknown locations is provided in resolution 5 (2001) of the Antarctic Treaty (ATCM 2001).

The Madrid Protocol's requirements for managing past and present work sites are seemingly clear. However, managing legacy waste remains an arduous task in many parts of Antarctica. Extreme weather, restrictions to access and financial constraints can form major obstacles to clean-up operations (Snape et al. 2001a; Blanchette et al. 2002; Poland et al. 2003). Further obstacles may arise at sites such as Wilkes Station (hereafter Wilkes), where the need for clean-up co-exists with the desire to preserve items with potential historical or cultural heritage value remaining on-site (Evans 2007, 2011).

For the purpose of this paper, we consider an item with historical heritage value to be items that provide visual, symbolic or functional historical evidence of the past (Scazzosi 2004). Items with cultural heritage values are those which have the ability to interact with a memory or are considered to hold a recognised tangible or intangible value of cultural identity or diversity (Vecco 2010). Items with 'potential heritage value' are those which may hold a cultural or historical heritage value which is not yet recognised under existing relevant legislative frameworks.

Wilkes and other abandoned research sites raise significant questions about the management and clean-up of legacy waste, the heritage value of abandoned Antarctic research sites, and the protocols relevant to their protection. Accurate environmental impact assessments, classi- fications of the amount and distribution of on-site waste, and cultural heritage surveys can provide information vital for development of strategic approaches to clean-up and preservation programmes. However, the ambiguity of what constitutes a historical item, particularly when distinguishing relic from rubbish can make such assessments contentious (Blanchette et al. 2004; Evans 2007, 2011).

Due to the paucity of studies describing a multidisciplinary approach to clean-up operations in Antarctica, this paper discusses some of the complexities associated with the management of legacy waste at sites with informal heritage value. The legislative frameworks governing the clean-up of legacy waste and protection of heritage items in Antarctica are reviewed and we investigate any potential legislative and environmental considerations surrounding clean-up operations at Wilkes. Finally, we argue the importance of a holistic approach to remediation which facilitates the clean-up of legacy waste and preservation of potential heritage value at Wilkes.

The case study of Wilkes is used in this paper to place in context the complexities associated with cleanup operations in Antarctica and to provide a platform for a discussion of the potential for co-managing legacy waste and heritage values. The issues raised in this paper extend beyond Wilkes, and the complexities discussed at Wilkes extend to other sites in Antarctica

8.1.1: Co-managing legacy waste and heritage in Antarctica

Environmental management practices in Antarctica typically involve on-site assessments of the ecological, engineering, historical, cultural and aesthetic aspects of a site (Lazer 2006; Evans 2011; Fryirs et al. 2013). These aspects frequently collide and assessments seldom involve an integration of research from both scientific and heritage-based disciplinary approaches. This can generate complications which can delay clean-up operations, the formal heritage listing of a site, or protection of items with potential heritage value (Evans 2007).

Recommendations relating to the management of heritage items have been a part of the Antarctic Treaty system since the first ATCM meeting in 1961 (Evans 2007, 2011). Items with formal heritage or potential heritage value in Antarctica exist in the form of artefacts, relics, monuments and other

vestiges of human behaviour including former sites of human activities (Blanchette et al. 2004; Evans 2007, 2011). At some sites with informal heritage value, the desire to preserve items with potential heritage value conflicts with the Madrid Protocol requirement to clean-up all past and present work sites. While items with informal heritage value remaining at contaminated sites may provide a wealth of historical and cultural information worthy of preservation, contaminants such as asbestos, lead and hydrocarbons present serious environmental health concerns and necessitate remedial action (Blanchette et al. 2004).

Concerns surrounding the increased risk of damage to items with potential heritage value associated with clean-up operations have been discussed in several recent publications specific to Antarctic sites (Blanchette et al. 2002, 2004; Evans 2007, 2011; Roura 2011). These publications provide evidence of the competing priorities surrounding the management of legacy waste in Antarctica at sites with formal or informal heritage value and suggest that there is a need for a transition towards multi-disciplinary approaches to clean-up operations in Antarctica.

8.2: Environmental setting

8.2.1: Location and historical overview

Wilkes is located on Clark Peninsula, East Antarctica (Figure 8.1) and was established by the United States of America (USA) as part of Operation Deep Freeze 2 during the International Geophysical Year (IGY) (1957-1958). The IGY culminated in a formal hand-over ceremony in which administrative and operational control of Wilkes was transferred to Australia. In 1961, Wilkes came under the exclusive control of the Australian National Antarctic Research Expedition (ANARE) (AAD 2002). Australia occupied Wilkes until 1969 when it was abandoned due to frequent burial by snow (Deprez et al. 1999).

Logistical constraints prevented the complete removal of buildings and equipment at Wilkes and the majority of buildings, equipment and waste material remains onsite (Fryirs et al. 2013). Prior to the Madrid Protocol (1991), the acceptable standards for waste management were considerably less strict than current standards, and the abandonment of research stations was not uncommon (Haward and Griffiths 2011; Roura 2011).

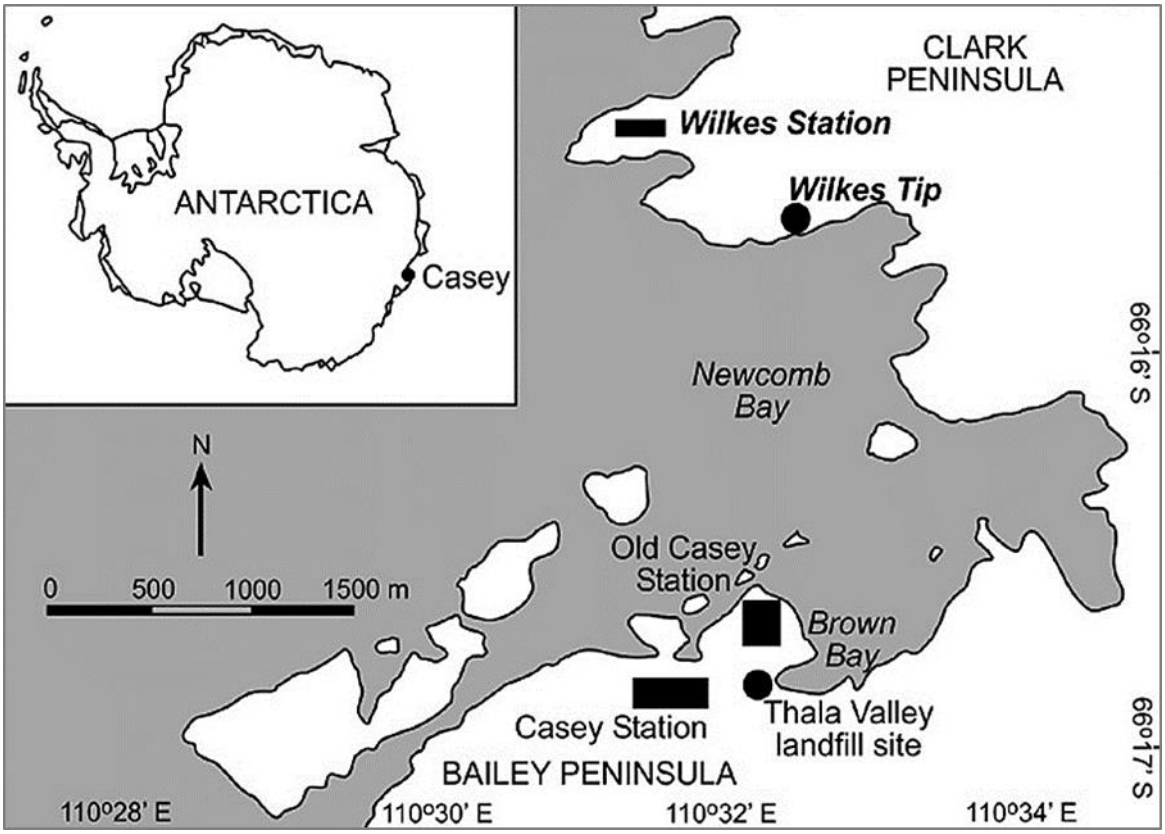

Figure 8.1: Regional map of Wilkes Station showing the location of the landfill adjacent to Newcomb Bay (Fryirs et al. 2013).

8.2.2: Vegetation and wildlife

The Windmill Islands (including the Clark Peninsula) support some of the most extensive and well-developed vegetation in Antarctica (Smith 1998; Wasley et al. 2012). Vegetation includes at least 27 macrolichens and 4 bryophytes (consisting of 3 moss species and 1 liverwort) (Wasley et al. 2012). Adjacent to Wilkes is ASPA 136 which was established for the protection and study of mosses and lichens and contains an Adélie penguin Pygoscelis adeliae colony (Fryirs et al. 2013). Wilson's storm petrels Oceanities oceanicus and snow petrels Pagodroma nivea are also well established within the area. The coastal waters surrounding Wilkes host a large diversity of marine flora and fauna (Orton 1963; Melick and Seppelt 1997).

8.2.3: Environmental contamination at Wilkes

Localised metal and petroleum hydrocarbon contamination at Wilkes from legacy waste has been well documented (Snape et al. 1998; Snape and Riddle 1998; Babicka 2000; Stark et al. 2003, 2006; Fryirs et al. 2013).

A recent site assessment by Fryirs et al. (2013) used waste categories listed in Annex III, Article 2 of the Madrid Protocol (1991) to identify and classify on-site legacy waste items. Batteries, food remains, scrap metal, gas cylinders, copper wire, piping, hazardous substances, mechanical components and approximately 1000 fuel drums were reported in the assessment (Fryirs et al. 2013). The majority of

this legacy waste is concentrated in a landfill with an estimated volume of 20,000 m^3, located east-southeast of the station precinct (Figure 8.1) (Snape et al. 1998; Fryirs et al. 2013).

Several studies report on metal-contaminated groundwater associated with the landfill discharging into Newcomb Bay and elevated metal concentrations have been reported in sediments collected from sites adjacent to the landfill (Snape and Riddle 1998; Stark et al. 2003, 2006; Townsend and Snape 2008; Townsend et al. 2009; Fryirs et al. 2013). The threat to the local marine environment posed by hydrocarbon contamination is evidenced by large fuel slicks sighted across Newcomb Bay during a large melt episode in 1992 (Fryirs et al. 2013).

There has been no systematic large-scale clean-up of legacy waste at Wilkes; however, small-scale cleanup operations have been undertaken during the 1980s and 1990s (Fryirs et al. 2013). These operations involved the removal of hazardous materials, decanting fuel drums and venting gas cylinders (Fryirs et al. 2013). As the generators and users of the site, both Australia and the USA hold responsibility for the management of legacy waste at Wilkes. Australia is the current custodian of Wilkes, has occupied the station for the longest period and has generated the majority of legacy waste at Wilkes and consequently must have the greatest responsibility for the management of legacy waste at Wilkes.

8.2.4: Heritage status of Wilkes

Wilkes is one of the most well preserved research stations constructed during the IGY (Evans 2007). Remnant infrastructure consists of barrack buildings, semi-cylindrical store buildings, work stations and scientific laboratories (Clark and Wishart 1989; 1999). Forty of the forty-five buildings at Wilkes remain. However, almost all are deteriorating, contain asbestos or are buried under snow and ice (Thearle 1990; Fryirs et al. 2013). Several graves of former Wilkes expedition members also remain within the station precinct. The Australian Government has not sought HSM listing for Wilkes under the ATCM, despite the completion of an on-site cultural heritage assessment which reports several buildings and items with potential heritage value at Wilkes (Clark and Wishart 1989). The Australian Government has not publicly justified why HSM listing has not been sought for Wilkes.

Historical sites or monuments are defined in the Antarctic Treaty as follows:

1. A particular event of importance in the history of science or exploration of Antarctica occurred at the place.

2. A particular association with a person who played an important role in the history of science or exploration in Antarctica.

3. A particular association with a notable feat of endurance or achievement.

4. The site is representative of, or forms part of, some wide-ranging activity that has been important in the development and knowledge of Antarctica.

5. Particular technical, historical, cultural or architectural value in its materials, design or method of construction.

6. The potential, through study, to reveal information or has the potential to educate people about significant human activities in Antarctica.

7. Has symbolic or commemorative value for people of many nations (Madrid Protocol 1991).

Wilkes is representative of human activities in Antarctica during the IGY and was the launch site for the famous 3,000 km Vostok traverse in 1962 (Haward and Griffiths 2011). Therefore, if the above criteria are applied to Wilkes, HSM listing may be justifiable on the basis that it is representative of activities that took place during the IGY, has potential to provide knowledge about Antarctica and educate people about the significance of human activities in Antarctica. Wilkes also holds symbolic value to the Australians and Americans who resided at Wilkes. Establishing HSM listing of Wilkes by the ATCM would require a detailed assessment as to how Wilkes satisfies these criteria and establishes why the potential heritage values at Wilkes should be preserved. This is beyond the scope of this paper and would require a detailed on-site cultural and historical heritage assessment.

Wilkes is listed as an indicative place on the Register of National Estate of the Australian Heritage Commission but is not registered as a national or world heritage site under the Environment Protection and Biodiversity Conservation Act (EPBC 1999) (Fryirs et al. 2013). Therefore, Wilkes has no formal heritage value and is afforded limited protection under the Antarctic Treaty system or the relevant domestic legislative frameworks (Evans 2007).

8.3: Discussion

The complexities surrounding clean-up operations at Wilkes provide a platform for a discussion of the potential for co-managing legacy waste and heritage values at contaminated sites in Antarctica. Here we discuss the legislative frameworks and environmental considerations governing the clean-up of legacy waste and protection of potential heritage items in Antarctica. We argue for the importance of a holistic approach to operations at Wilkes which facilitate the clean-up of legacy waste and preservation of the potential heritage values. Finally, we discuss the relevance of the issues described at Wilkes to other contaminated sites in Antarctica.

8.3.1: Legislative frameworks and environmental considerations surrounding clean-up operations at Wilkes

All human activities in Antarctica are governed by international agreement between nations under the Antarctic Treaty system; however, the domestic legislation of Treaty members addressed through

ATCM meetings can be applied to Antarctica (Snape et al. 2001a; Bastmeijer 2003). There are several legislative aspects to consider in respect to Wilkes.

Australian domestic legislation can be applied to Antarctic sites under Australia's administrative control. Thus, Australian legislation can be applied to the management of Australian heritage in Antarctica. The EPBC Act (1999) provides a legal framework for the protection of sites and items of heritage significance and could be applied to the preservation of heritage at Wilkes. The Act prohibits actions likely to have an impact on national or world heritage values at declared national or world heritage places without approval from the Constitutional Corporation, Commonwealth Agency or Federal Minister. However, Wilkes is not recognised as a national or world heritage place under the EPBC Act and is therefore provided no protection under this legislative framework.

The Antarctic Treaty provides protection for items or sites with heritage value if listed as a HSM on the ATCM list. Wilkes is not so listed; therefore, the items with potential heritage value remaining on-site are not protected. However, resolution 5 (ATCM 2001) provides guidelines for the handling of pre-1958 historic remains whose locations are unknown. It stipulates that artefacts should not be removed from Antarctica and if artefacts are discovered during construction activities all activities must be discontinued until the artefacts have been appropriately recorded and evaluated. If any uncertainty surrounds the age of an artefact it is to be managed as a pre-1958 artefact. An artefact is considered to be any item which meets the following criteria:

1. Has a particular association with a person who played an importance role in the history of science of exploration of Antarctica.

2. Has a particular association with a notable feat of endurance achievement.

3. Are representative of some wide ranging activity that has been important in the development of knowledge of Antarctica.

4. Has particular technical or architectural value in its materials, design or construction.

5. Has the potential through study to reveal information or educate people about significant human activities in Antarctica.

6. Items which have symbolic or commemorative value for people of many nations.

While guidance on the handling of pre-1958 artefacts is provided in resolution 5 (ATCM 2001), no clear legislative consequences of non-compliance with its requirements are stipulated.

A further legislative consideration surrounds Australia's clean-up obligations as a signed Antarctic Treaty party member. The Madrid Protocol requires comprehensive protection of the environment

by all nations operating in Antarctica. As a signatory to the Antarctic Treaty, custodian of Wilkes and a producer of legacy waste at Wilkes, Australia is responsible for its waste management. While the treaty has effect under international law, it does not make the Australian Government liable for penalties or prosecution (Harris and Meadows 1992). Therefore, despite Australia having responsibility for waste management at Wilkes, it is unclear whether a contravention in Australia's obligations for clean-up will have enforceable legal consequences under existing domestic or international legal frameworks (Harris and Meadows 1992).

A further unlikely, but potential consequence of not undertaking clean-up operations at Wilkes may be disputes with other treaty nations as a result of Australia's inactivity to complete the requirements of the Madrid Protocol. In this unlikely instance, and in the absence of a peaceful agreement between nations, an outcome would be determined by the International Court of Justice, as per article XI of the Antarctic Treaty (The Antarctic Treaty 1959; Antarctic Treaty Environment Protection Act 1980). As Wilkes is not HSM listed under the treaty, nor is it recognised as a national or world heritage place under the EPBC Act; the potential heritage values at Wilkes are not protected heritage items under the relevant legislative frameworks (Evans 2007).

The environmental considerations relevant to legacy waste and clean-up operations at Wilkes surround concerns of the risk of contaminant migration, impacts to biodiversity and the risk of instigating further adverse environmental impacts during clean-up operations (Snape et al. 2001a; Stark et al. 2003).

Wilkes is situated adjacent to ASPA No. 136; therefore, contaminant migration from Wilkes may present a threat to cryptogamic species and penguin colonies (Fryirs et al. 2013). Clark and Wishart (1999) sighted Adélie penguins in the landfill during their cultural heritage survey of Wilkes in 1988-1989. The threat to biodiversity posed by legacy waste and contaminant migration at Wilkes represents an important environmental consideration and warrants effective waste management.

The Wilkes landfill or tip site presents similar environmental hazards to those reported at Thala Valley land- fill nearby (Fig. 1) (Snape and Riddle 1998). The effectiveness of clean-up operations at Thala Valley demonstrates that prompt and effective remediation at Wilkes is achievable. Prior to the completion of successful cleanup operations, the concentration of metal contaminants in runoff obtained from the Thala Valley was shown to increase when melt-streams travelled across the landfill into Brown Bay (Deprez et al. 1999; Snape et al. 2001a). Since the geographical setting of Wilkes landfill is similar to that of Thala Valley, clean-up operations at Wilkes should aim to prevent the migration of metal-contaminated runoff into Newcomb Bay.

Reducing the potential for the mobilisation and migration of contaminants during excavation and clean-up operations is an important engineering concern which must be managed to prevent further

adverse environmental impacts associated with clean-up operations. Snape and Riddle (1998) report strategies applicable to Wilkes which could be used to reduce the environmental impacts associated with excavation and clean-up operations.

8.3.2: Co-managing clean-up operations at Wilkes and preservation of heritage

The complexities surrounding the management of legacy waste and the informal heritage values at Wilkes provide a platform to discuss the potential for multi-disciplinary approaches to waste management in Antarctica.

A principal objective of clean-up operations at Wilkes would be to reduce the environmental impacts of legacy waste in accordance with the framework provided in the Madrid Protocol. Preventing further adverse environmental impacts associated with clean-up operations is a vital component of this objective. Despite its non recognition as a protected site resolution 5 (ATCM 2001) of the Antarctic Treaty requires the protection of pre- 1958 artefacts remaining on-site. Therefore, there is a need to co-manage the requirements to clean-up legacy waste at Wilkes, while preserving pre-1958 artefacts and on-site items with potential heritage value. This can only be achieved by a multi-disciplinary approach to the management of the environment and heritage.

The development of a multi-disciplinary approach to managing legacy waste and heritage at Wilkes first requires an integrated environmental, engineering and heritage assessment. An appropriate assessment would review the relevant legislative frameworks and sitespecific priorities such as contaminant types, distribution, mobility and their potential for environmental harm as well as describe the heritage values on site and the importance of their preservation. Similar to the cultural heritage survey by Clark and Wishart (1999) and site assessment by Fryirs et al. (2013), a current characterisation, documentation and location of legacy waste and heritage value at Wilkes would aid in the development of a holistic approach to environmental management. Such an assessment should describe the location and heritage value of individual items, distinguish relic from rubbish and identify potential environmental impacts of legacy items. The relationship of individual items to the site and the value associated with their preservation onsite should also be assessed (Roura 2011). A similar framework to resolution 5 (ATCM 2001) could be used to distinguish the differences between rubbish, cultural remains or heritage items (Roura 2011). In the absence of supporting legislation for sites with informal heritage value, this assessment could provide a framework for the protection of potential heritage items in Antarctica and could be pivotal to the development of a holistic approach to clean-up operations.

Evans (2011) argues that complete removal of rubbish can sanitise and falsify the historical picture. Similarly, other conservation approaches raise concern about the potential for lost cultural and historical information as a result of removal of legacy items remaining on-site (Evans 2007). Pearson

(2004) recognises that not all legacy material surrounding historical sites contributes to our understanding of history but argues that excavation and uncontrolled clean-up operations threaten the potential for the preservation of evidence. For instance, the removal of ice by picks and shovels from Scott's Hut, Cape Evans during 1960-1961 was found to damage artefacts (Pearson 2004). In order to prevent damage to items with potential heritage value, an awareness and respect for history must be incorporated into clean-up strategies.

Reducing the environmental risks associated with legacy waste at Wilkes is likely to require a large scale clean-up operation with excavation. Wilkes is a large, complicated contaminated site; however, contamination at Wilkes is not homogenously distributed (I. Snape, personal communication, 21 April 2013). Therefore, it is possible for a staged approach to clean-up operations to be undertaken. A staged approach should identify priority areas which present the greatest threat to the environment and initial clean-up operations should be concentrated in these high risk areas. This approach would reduce the risk of damage to potential heritage items substantially.

Site assessments by Snape et al. (1998), Snape and Riddle (1998) and Fryirs et al. (2013) demonstrate the environmental hazards associated with the Wilkes landfill. Therefore, initial clean-up operations could be concentrated at this site following a detailed multi-disciplinary site assessment. Fryirs et al. (2013) estimate that 13% of the landfill material holds heritage value; thus caution must be applied during excavation of the landfill to prevent damage to potential heritage items and pre-1958 artefacts. A strategy which priorities clean-up at the landfill will also allow the preservation of remnant buildings in the station precinct.

Excavation at the landfill site will require the removal of hazardous items such as zinc-coated iron drums, unidentifiable chemicals, food supplies and contaminated landfill material adjacent to Newcomb Bay (Snape et al. 2001a). During this process it is likely that items with potential heritage value may need to be removed temporarily or permanently. Any items which must be removed to facilitate clean-up operations should be appropriately documented and managed according to the relevant legislative requirements (for example resolution 5 (ATCM 2001)).

Locating heritage items in the landfill often concealed by ice is difficult. Hence any excavation or clean-up operations at Wilkes should be undertaken by a multidisciplinary team of remediation professionals and cultural and historical heritage experts (Evans 2007, 2011). Where waste materials with heritage value are identified as a threat to the environment (items such as chemically treated building materials), they should be properly assessed, removed and preserved ex situ (Splettstoesser and Rossnes 2002). In such circumstances other avenues for the preservation of culture and history (for example museums) could be considered. This approach was adopted during clean-up operations

at Cape Hallett Station when waste materials with heritage value were removed and displayed at the Canterbury Museum in Christchurch, New Zealand (Roura 2011).

Various remediation techniques applicable to metal and hydrocarbon-contaminated sites in cold environments exist; however, in situ techniques are preferable as they prevent unnecessary excavation, disruption to the environment and contaminant migration (Martin and Ruby 2004). In situ techniques not requiring excavation are also less likely to damage relics and artefacts remaining onsite (Martin and Ruby 2004).

Managing legacy waste and metal and hydrocarbon contamination at Wilkes will require the remediation of both contaminated groundwater and soil material. Groundwater contaminated by landfill material could be managed using pump and treat systems or permeable reactive barriers (PRBs) (Martin and Ruby 2004). Pump and treat systems use extraction wells, often with submersible pumps to extract contaminated groundwater and control the movement of contaminated groundwater, reduce contaminant migration and reduce the dissolved concentrations of contaminants. Once groundwater is extracted it is purified by filtration, precipitation and ion exchange media which remove the contaminants (Higgins and Olsen 2009). PRBs are subsurface barrier systems that consist of reactive materials and are installed in situ, down gradient of a contaminated groundwater plume (Gore 2009). When contaminated groundwater flows through a PRB, the barrier materials react with contaminants to immobilise them. Barriers can be customised according to site-specific requirements and a wide range of effective barrier designs has been described (for example Snape et al. 2001b; Henderson and Demond 2007; Fu and Wang 2011; Gibson et al. 2011). These techniques can provide a long term, logistically feasible and low-maintenance management solution for contaminated groundwater without disturbing heritage items. PRBs installed at Wilkes should be designed to treat metal and hydrocarbon contaminants (Snape et al. 2001a) which could be achieved using absorptive media coupled with natural biodegradation of the hydrocarbons (Mumford et al. in press). These strategies might need to be in place for decades in order to treat long-lived hydrocarbons (Gore et al. 1999).

Managing metal-contaminated soil could be also achieved by chemical fixation, encapsulation, electrokinetic remediation, bioremediation or vitrification technologies (see Martin and Ruby 2004; US EPA 2006; White et al. 2012). Hydrocarbon contaminated soil at Wilkes could be managed using natural attenuation by microbial activity; this has been successfully on trial at sub-Antarctic Macquarie Island (Rayner et al. 2007).

These technologies could all be adapted for in situ usage at Wilkes to achieve controlled clean-up of legacy waste and reduce the need for large-scale excavation, thereby limiting the associated risk to heritage items as described by Blanchette et al. (2002, 2004). In situ clean-up following a

comprehensive site assessment and development of multi-disciplinary approach to clean-up, could facilitate a holistic approach to the co-management of legacy waste and heritage at Wilkes.

8.3.3: Relevance of Wilkes to other Antarctic sites with formal or informal heritage value

Legacy waste and contamination exist at various Antarctic sites with formal or informal heritage (Poland et al. 2003; Tin et al. 2009). Remnant huts, buildings and artefacts from early expeditions offer an abundance of information which warrants preservation; however, at many of these sites, similarly to Wilkes, contaminants remaining on-site (for example asbestos, metals and hydrocarbons) present an environmental health risk (Blanchette et al. 2004).

Blanchette et al. (2004) reported elevated mean concentrations of soil-lead at Cape Royds Hut (1621 mg/kg) and Discovery Hut (1222 mg/kg). High concentrations of zinc, cadmium and lead have prompted clean-up operations at Atlas Cove Station on Heard Island (Stark S.C et al. 2003). Similarly, metal contamination has been reported in the region surrounding the French Port-Martin Base (Management Plan (MP) ASPA No. 166 2006). Port-Martin Base is situated within ASPA No. 166 and is required to be listed as a HSM as per the requirements of annex V, of the Antarctic Treaty (ATCM 2006). This complicates clean-up operations at this site significantly. The abandoned Port Lockroy Base on Goudier Island (UK; designated in 1995), East Base on Stonington Island (USA; designated in 1987) and Aguirre Cerda Base on Deception Island (Chile; designated in 2001) have also attracted significant environmental concern (Roura 2011). Evidently, the issues discussed in this paper are not exclusive to Wilkes.

Blanchette et al. (2004) discuss other complexities associated with managing contamination at early huts. Sites reflective of the 'heroic era' of Antarctic exploration such as Robert Scott's Discovery Hut, Douglas Mawson's Hut and Ernest Shackleton's Hut are attractive to tourists and hold recognised heritage value (Hughes 1992; Blanchette et al. 2004). Visitation at these sites generates additional complications for the preservation of heritage items in the presence of contamination. The risk of structural damage to wooden heritage buildings or compromised integrity of historic items from visitors or clean-up operations is a serious concern at these sites and is difficult to monitor (Blanchette et al. 2002).

Logistical constraints present a challenge for both clean-up operations and the conservation of historical sites in Antarctica. Poland et al. (2003) report on the challenges that isolation and climate impose on transport requirements, safety and equipment transfer surrounding remediation operations. Conservators of heritage sites must overcome similar logistical challenges associated with the delivery of required materials to remote locations. In instances where both site-remediation activities and heritage works are required, collaborations which facilitate consultation surrounding the coexisting

needs of remediation and maintenance of historical integrity are favourable. Such collaborations also have the potential to reduce the risks to the environment or potentially valuable heritage items.

The complexity of managing legacy waste and contamination in the presence of heritage remains an arduous task at many sites. However, these sites represent a great opportunity for collaboration between scientists, engineers and cultural and historical experts. Collaboration between these disciplines can aid in the development of holistic solutions to environmental and heritage management. In this paper we argued for the need for a holistic approach to land management at Wilkes; however, the existence of similar problems at sites such as Port-Martin Base indicates that any solutions developed and implemented at Wilkes will have wider relevance to similar sites. The solutions developed at Wilkes and other contaminated sites in Antarctica may also be relevant to the Arctic where disputes between human expansion, mineral exploration and protection of heritage persist (Roura 2011).

8.4: Conclusion

The Madrid Protocol requires that all past and present work sites in Antarctica are cleaned up by the generators and users of waste at such sites. The presence of items with formal or informal heritage value at sites such as Wilkes warrants a transition towards a multidisciplinary approach to the clean-up of legacy waste and management of heritage. While clean-up of legacy waste and the preservation of heritage value may occasionally represent conflicting interests, they should not be seen as mutually exclusive. In this commentary we have argued that effective clean-up can be achieved without compromising the integrity of heritage items if a multi-disciplinary approach to assessment and clean-up operations is adopted.

Wilkes does not formally hold a heritage value under the relevant domestic and international legislative frameworks and Australia has not taken formal action to ensure the protection of items with potential heritage value at Wilkes. However, caution and respect for historical items should be executed if clean-up operations are undertaken, as per the requirements of resolution 5 (ATCM 2001). We argue that in situ remediation facilitated by a multidisciplinary team of scientific and heritage experts may represent the best means of satisfying clean-up requirements at Wilkes without instigating unnecessary damage to items with potential heritage value. We also argue the importance of a holistic assessment of legacy waste and cultural heritage at Wilkes to distinguish relic from rubbish and characterise the potential for environmental harm posed by legacy waste, prior to the commencement of clean-up operations.

Finally, we acknowledge that the issues presented in this paper are not exclusive to Wilkes or to Antarctica, and anticipate that the issues presented here are of wider relevance in a global discussion of the need for co-management of legacy waste and heritage.

8.5: Acknowledgements

We thank Eric Portenga and the anonymous reviewer for their helpful feedback on the original manuscript. This work was supported by Australian Antarctic Science (grant number 4029).

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Chapter 9: Locating an ice-covered Antarctic landfill using ground magnetometry

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Citation: Freidman B.L., Camenzuli D. and Lackie M. 2014. Locating an ice-covered Antarctic landfill using ground magnetometry. *Antarctic Science 26*, 361-368.

Submitted: 12 August 2013; *Accepted for publication*: 10 November 2013; *Published*: 13 February 2014

Abstract

At former Antarctic research stations, legacy waste often remains in situ and concealed by ice. Consequently, the location, characteristics and potential environmental impact associated with legacy waste remains poorly documented. This study applies ground magnetometry to map the spatial extent of the landfill at the abandoned Wilkes Station. Magnetic anomalies indicate that the landfill extends north-west to south-east and is close to, and perhaps prograding into, the ocean. The landfill is characterised by large magnetic variations of .1500 nT with asymmetrical magnetic anomalies which suggest variable orientations of material and random dumping. Magnetic susceptibilities .0.02 SI units beyond the landfill area reveal elevated magnetic properties of the basement geology. However, a contrast in anomaly shape reliably distinguishes large anomalies generated by landfill material. Surface and subsurface melt streams (observed at the shoreline) flowing from the survey area suggest elevated potential for metal contamination of the nearshore and marine environment. The survey demonstrates a cost-effective and non-invasive method for gathering information to guide the clean-up of landfills beneath ice.

Keywords: Magnetic Anomaly; Proton Magnetometer; Steel Drums; Susceptibility; Wilkes.

9.1: Introduction

The assessment and clean-up of contaminated land can be time consuming and expensive, particularly in polar environments such as Antarctica (Snape et al. 2001a; Poland et al. 2003). Therefore, preliminary site investigations should be undertaken to facilitate effective clean-up over concurrent field seasons (Gibson et al. 1996; Stark et al. 2006). This typically requires an assessment of the type, forms, distribution and extent of contamination at a site. These assessments may be hindered by remoteness, financial and logistical constraints, extreme weather and a shortage of governing guidelines and legislation (Snape et al. 2001b; Poland et al. 2003; Snape et al. 2003). Furthermore, old waste disposal sites are often poorly documented and, where snow and ice has buried material, their location and boundaries are often obscured (Stark et al. 2006). Thus establishing definitive timeframes for clean-up are often hampered by limited knowledge of precise locations of waste.

Annex III to the Protocol on Environmental Protection to the Antarctic Treaty (1991), known as the Madrid Protocol, prohibits the discharge of waste onto ice-free areas and soils in Antarctica (SCAR 1993; Webster et al. 2003; Bargagli 2008). Waste storage, disposal and removal, as well as recycling and source reduction, are important operational considerations under Article 1(3) of Annex III (SCAR 1993). Prior to the Madrid Protocol, less stringent controls on the use, storage and disposal of waste, coupled with a limited awareness of the risks posed to the environment by inappropriate disposal of waste, resulted in contamination near research stations by fuel residues, solid wastes and leachates (Snape et al. 2001a; Webster et al. 2003; Bargagli 2008). Waste from most Antarctic stations was typically dumped in landfills close to the station, disposed of onto sea ice and allowed to drift out to sea or burnt in open air (Poland et al. 2003; Stark et al. 2006; Bargagli 2008; Fryirs et al. 2013).

The Madrid Protocol (1991) established the obligation for assessment and clean-up of abandoned work and waste disposal sites (Stark et al. 2006; Bargagli 2008). Amongst others, clean-up operations have been conducted at the Thala Valley landfill at the Old Casey Station (Deprez et al. 1999; Snape et al. 2001a, 2001b; Stark et al. 2006), Atlas Cove Station on Heard Island (Stark et al. 2003), Vanda Station and Cape Hallet Station in Victoria Land (Waterhouse 1997; Roura 2011) and along the eastern shoreline of Winter Quarters Bay near the McMurdo Station (Manheim 1992; Massey 1992; Claridge et al. 1995; Crockett and White 2003; Bargagli 2008). Clean-up operations at McMurdo Station focussed on the removal of exposed and surface waste material, leaving buried landfill material in situ (Manheim 1992; Stark et al. 2006). Australian Defence Force clean-up operations in 1991-92, 1992-93 and 1993-94 (Fryirs et al. 2013) focussed on rendering safe any explosives and gas bottles, leaving significant volumes of buried landfill material at the abandoned Wilkes Station.

Decades of snow and ice accumulation at Wilkes have resulted in the concealment of legacy waste, with the precise location of the landfill remaining largely unknown. Fryirs et al. (2013) estimated the

landfill area at c. 100 x 250 m, comprising approximately 20 000 m^3 of material. During a short summer melt period, metal and petroleum hydrocarbon contaminated groundwater has been reported flowing from the landfill into the neighbouring marine environment (Snape et al. 1998; Townsend and Snape 2008; Fryirs et al. 2013). The high variability of snow deposition and summer thaw at Wilkes makes it economically risky to plan major efforts on the expansive waste dump because shipping capacity, specialised plant and equipment, and personnel must all be engaged well in advance of field operations which may be rendered impractical or impossible by snow and ice conditions (Roura 2011). Article 8(3) of Annex III to the Madrid Protocol requires Treaty Parties to prepare an inventory of locations of past activities before information is lost (SCAR 1993; Deprez et al. 1999). Ground magnetometry provides a rapid, non-invasive method for identifying landfill boundaries, recovering lost information and aiding the development of clean-up strategies.

Previous geophysical investigation at the Wilkes landfill consists of reconnaissance ground penetrating radar (GPR) surveying, coupled with geographical information system database development (Babicka 2000). Ground magnetometry has been widely applied in temperate regions for subsurface detection of steel drums, tanks, unexploded ordnance and pipes (Tyagi et al. 1983; Barrows and Rocchio 1990; Roberts et al. 1990; Marchetti et al. 1998; Godio 2000; Prezzi et al. 2005). However, use of this technology has been limited to geological and archaeological investigations in polar regions (Chaparro et al. 2007; Hodgetts et al. 2011). This study applies the magnetic method to characterise the spatial extent, distribution and depth of ferrous materials in the Wilkes landfill. Potential anomalies associated with magnetic minerals in the bedrock and glacial sediment were accounted for using rock magnetic susceptibility. A magnetometer survey for this purpose was conducted across two days during the 2012-13 field season.

9.2: Study area

Wilkes is an abandoned research station established in the International Geophysical Year (IGY) 1957-58 and operated by the USA from 1957-59 and by Australia between 1961 and 1969. Wilkes is situated on Clark Peninsula, approximately 3 km north of Old Casey Station and was decommissioned in 1969 due to ongoing snow and ice accumulation (Figure 9.1) (Snape et al. 1998). Due to logistical constraints, the removal of buildings, equipment and waste was not undertaken (Fryirs et al. 2013). Consequently, around 40 buildings, mechanical equipment, a fuel farm and a landfill remain in situ (Snape et al. 1998; Fryirs et al. 2013). The landfill is 800 m south-east of the station precinct and is comprised of mechanical and domestic items including drums, food containers, batteries, mechanical spares and gas cylinders (Figure 9.2) (Fryirs et al. 2013). Some of these materials breach the ice surface during major melt years, such as in 2002-03 (Figure 9.2). Mean daily temperature is 38 ºC and -20 ºC in the summer and winter months, respectively (Deprez et al. 1999).

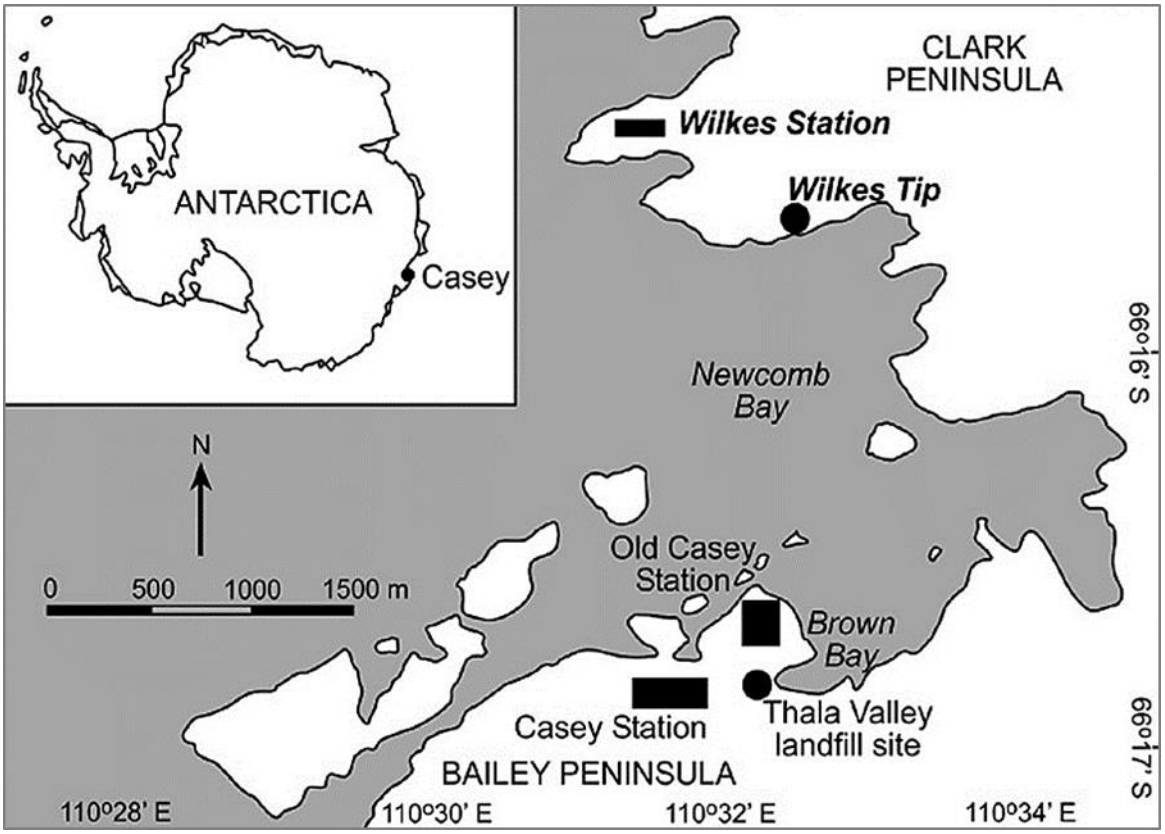

Figure 9.1: Regional Map of Wilkes (Fryirs et al. 2013).

Figure 9.2: Waste material exposed during a large melt at Wilkes during 2002-03. (Photos courtesy of Bill Burch).

The Wilkes basement is polymetamorphic with granulites, magmatic pelites, psammites and granite gneisses of the Windmill Metamorphic Series (Blight and Oliver 1977; Paul et al. 1995). The Windmill Metamorphic Series was formed in the Mesoproterozoic era between 1600-1000 million years ago (Paul et al. 1995).

Surficial sediments are several metres thick in low-lying depressions and are largely unconsolidated coarse sands and gravel (Snape et al. 1998). However, larger clasts and regional variability is common. The porous material undergoes many freeze-thaw cycles annually, creating melt streams on the ice surface and at the ice-sediment/rock interface which result in contaminated water flow (Snape et al. 1998). Contaminated subsurface water movement also occurs via small channels at the base of the sediment active layer (Snape et al. 2001a). Subsurface channelling can also be associated with dykes or sills that produce detectable magnetic anomalies against the surrounding basement geology (Blight and Oliver 1977). A large hydrocarbon sheen observed on the seawater across Newcomb Bay during a major melt period in 1992 is evidence of offsite contaminant transport (Potter, personal communication 1992 in Fryirs et al. 2013).

An excavation of the landfill was undertaken during November 2012. This excavation revealed an ice thickness of 1.7 m overlying landfill material and frozen sediments. The Wilkes landfill is unlined and has no leachate collection system to isolate waste from the environment (Roura 2011).

9.3: Materials and methods

9.3.1: Magnetometry

The magnetic survey was performed using a GeoMetrics Inc. G-856 Proton Precession Magnetometer. This instrument was selected as it is not impeded by high electrical ground conductivities commonly associated with saline groundwater or high levels of contamination.

The sensor was mounted vertically on a lightweight non-magnetic pole 2.5 m above the ground to distance it from metal detritus at the surface. As part of quality assurance and quality control procedures, several magnetic readings were taken at the beginning and end of each day to ensure the magnetometer was operating consistently. All readings were obtained with the sensor orientated north-south for greater pole-to-pole anomalies (Breiner 1999). Total field strength was reported in nanotesla (nT) with an average positional error of approximatrly 1 nT. Diurnal variation was corrected at one minute intervals using the Casey Station EDA 3-component flux-gate magnetometer (Geoscience Australia 2011). Belt buckles, watches, handheld transceivers and other metal items were removed while surveying to prevent interference with sensor operation.

Magnetic susceptibility measurements were carried out using a portable magROCK Susceptibility Meter (750 Hz), Alpha Geoscience Pty Ltd (range 1 x 10-5 - 10 SI units). Field measurements were acquired from three surrounding ridgelines and from the excavation pit to ensure mineralogical variability was accounted for in the measurements (Figure 9.3). The meter was zeroed in air after each reading. These readings provided a background susceptibility and contrast with subsurface landfill

properties that ensure accurate depth to material (based on present ice thickness) could be delineated (Breiner 1999).

Magnetic data were uploaded to GeoMetrics MagMap2000, a post-acquisition processing and analytical tool. Using MagMap2000, magnetic data were spatially adjusted from dGPS site measurements and diurnal corrections were made using base station flux-gate magnetometer readings. Magnetic and spatial information data were then exported to Golden Software's Surfer 9 mapping programme for display. Where landfill material was detected, modelling of magnetic anomalies and susceptibilities was conducted using Model Vision Software V.12.00.07 (Tensor Research).

9.3.2: Survey set-up

A 350 x 150m survey grid was constructed, guided by previous GPR surveying (Figure 9.3) (Babicka 2000). The survey was conducted along north-south parallel lines with 36 profiles forming the grid. Each profile was spaced 10 m apart. Total field magnetic readings were acquired every 2 m to ensure multiple readings were obtained for any anomaly encountered. Where landfill material was subsequently observed to protrude further south, survey lines were extended beyond 150m to capture material in these areas (Figure 9.3). Spatial information was recorded using a Trimble dGPS Pathfinder ProXHTM Rover with decimetre accuracy in real-time. The limited battery life of the Trimble ProXHTM base station dGPS, situated at an accurately-known fixed location at Wilkes Station, resulted in only start and end points of each line being recorded. Interpolation and mapping of lines was conducted using ESRI ArcGIS 10.1 Software.

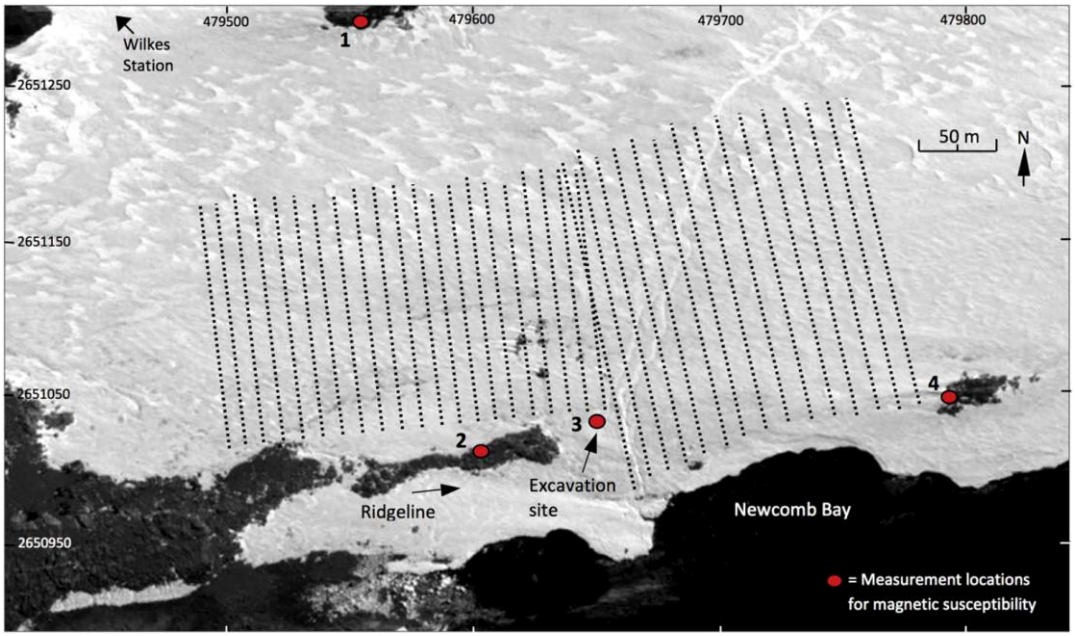

Figure 9.3: Magnetometer survey profiles at the Wilkes landfill (Google Earth 2013/MagPick).

9.4: Results

Wilkes landfill possesses sufficient magnetic properties to be distinguishable as an anomalous feature within the survey area (Figure 9.4). While Figure 9.4 indicates a positive anomaly (observed as a surface fuel drum) in the west of the survey area (200-400 nT), the cluster of high amplitude anomalies in the centre of the survey area suggests the main waste deposit extends 160 m south-east to the northern boundary of Newcomb Bay (Figure 9.3). From the anomalies generated, it is estimated that the main waste deposit covers 6,250 m^2 and comprises 17,000 m^3. The estimate of the size of the waste deposit is taken simply from the volume of the polygons (strike length 30 m) used to model the magnetic data (Model Vision V.12).

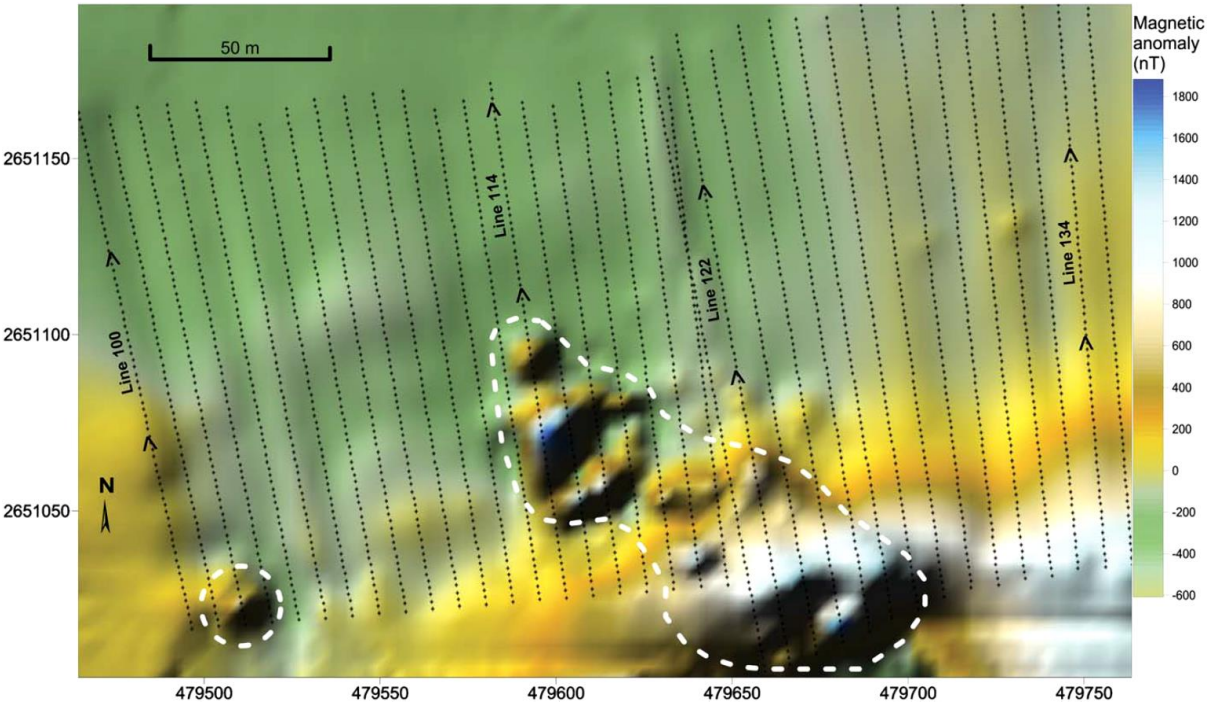

Figure 9.4: Wilkes landfill delineation from magnetometer measurements (MagMap2000/Surfer 9).

An increase in magnetic intensity from north to south indicates that the surrounding geology had a significant influence on the data generated (Figure 9.4). Geomagnetic properties in the north of the survey area (-200 nT, 0.001 SI units) progressively strengthen to the south (.1000 nT, 0.012 SI units), producing similar magnetic readings to landfill material and reducing image clarity in the south of the survey area (Table 9.I, Figure 9.4). Despite geomagnetic distortion, anomalies of .1500 nT amongst bedrock readings of 1000 nT clearly defined the boundaries between natural structures and waste material (Figure 9.4).

Table 9.1: Magnetic susceptibilities of the surrounding geology at Wilkes landfill.
Measurement ID on Figure 3.

Measurement ID	Measurement location	Magnetic susceptibility (SI)	Mean magnetic susceptibility (SI)
1	U49, 479559 E, 2651288 N	0.00174 0.00055 0.00071	0.001
2	U49, 479604 E, 2651011 N	0.00936 0.01214 0.01394	0.012
3	U49, 479652 E, 2651032 N	0.07431 0.07644 0.08001	0.07-0.08
4	U49, 479793 E, 2651044 N	0.03586 0.01568 0.01236	0.021

The sharpness of magnetic anomalies suggests the variable depth of material in the northern section of the landfill (Figure 9.4). A high amplitude anomaly between 1700-1800 nT and modelled susceptibilities between 0.26-0.4 SI units are indicative of greater amounts of ferrous objects (Figure 9.5a). Adjacent to this peak, lower amplitude anomalies (400-500 nT) and magnetic susceptibilities (0.07-0.25 SI units) indicate waste material at greater depths (Figure 9.5a). While modelled susceptibilities vary along profile 114 (Figure 9.5a), anomaly wavelength remains similar suggesting waste material composition is continuous. Polygon shape by strike length modelling in this section estimates material volume at 3900 m^3.

Modelling of profile 122 provided information on the characteristics in the central and southern zones of the landfill (Figure 9.5b). In the centre of the outlined landfill site, lower amplitude anomalies are present averaging 500-800 nT (0.07-0.08 SI units) with peak amplitude at 1100 nT (Table 9.I, Figures 9.4 and 9.5b). Profile 122 illustrates that the anomalies of interest are superimposed on a much broader anomaly which we attribute to the magnetic properties of the bedrock. Small, scattered anomalies suggest the presence of small ferrous fragments amongst a sediment matrix. This waste distribution is supported by an excavation during November 2012 (Figure 9.3). The southern section of the landfill is characterised by larger anomalies attributable to surface melt exposing waste material (Figures 9.2 and 9.5b). Anomaly maxima in this section was 1500 nT with an average of around 800-900 nT (Figures 9.4 and 9.5b). A 3 x 4 m section of exposed landfill material is partially responsible for anomaly amplitude exceeding values in the centre of the landfill (Figure 9.2). The high and fluctuating

magnetic susceptibilities (0.2-0.4 SI units) again confirm the presence of large amounts of ferrous material below the bedrock ridgeline. Polygon shape by strike length modelling in this section estimates material volume at 4,700 m^3.

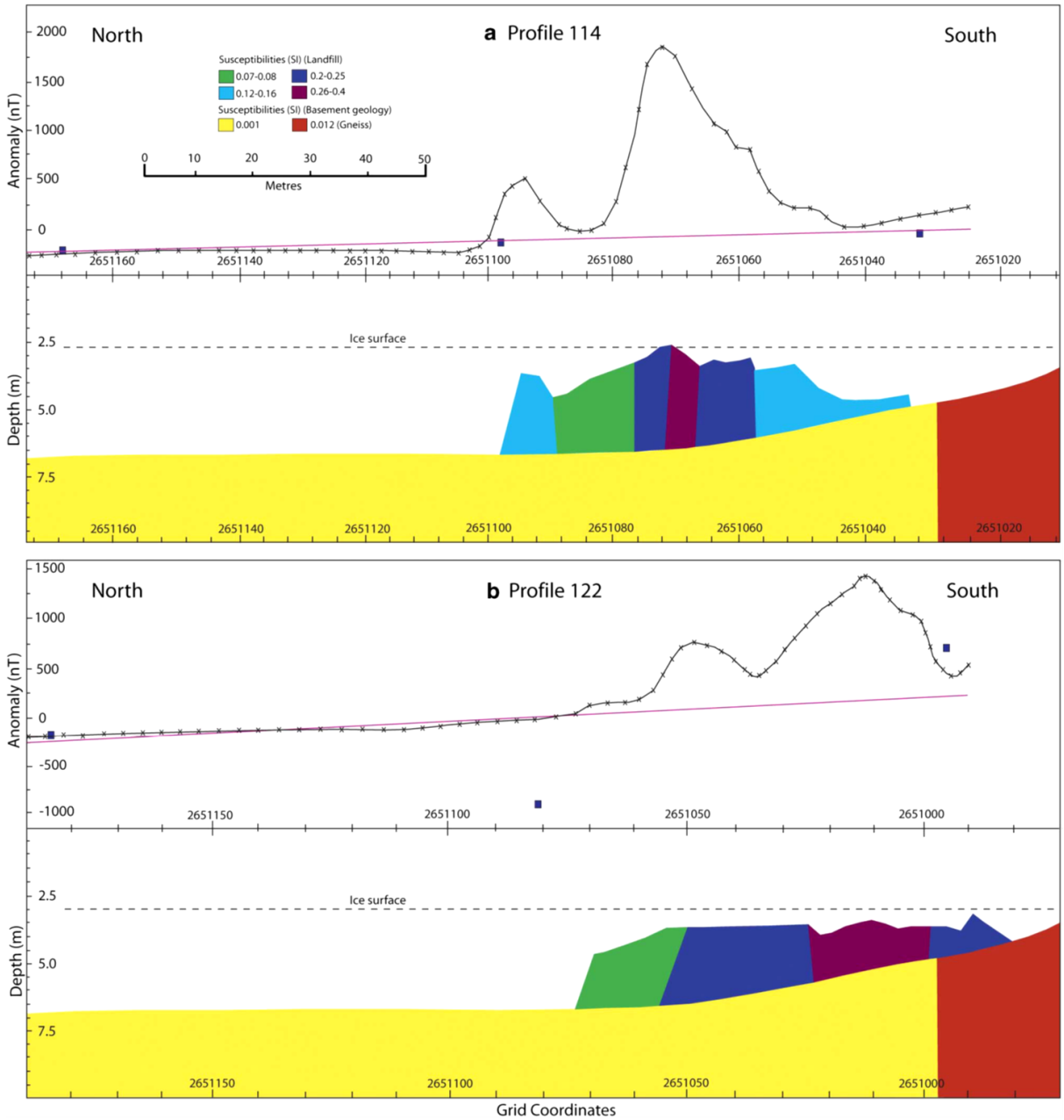

Figure 9.5: Models of the magnetic data for profile 114 and profile 122 (Model Vision). Blocks represent different magnetic susceptibilities and show the waste material sitting on the geological basement.

These high magnetic values are also attributable to a ridgeline susceptibility of 0.021 SI units (acquired east of profile 134), indicative of 0.6% magnetite in the surrounding geology (Breiner 1999) (Table 9.1, Figure 9.4). This is responsible for the elevated readings (.1000 nT) beyond the landfill boundary in the south-east corner of the survey area (Figure 9.4). In the absence of anomalies associated with

randomly distributed metallic objects and the presence of broad, smooth wavelengths (Figure 9.4), we infer that this region is free of large waste material. However, the complex interaction between buried ferrous objects and geology may mask smaller waste items in this zone. Therefore, this area neighbouring the landfill site requires further investigation before being declared devoid of waste material. While surveying to the ice edge was prohibited for safety reasons, gas cylinders observed on the shoreline of Newcomb Bay suggest that the landfill may also extend beyond the survey limit in that direction.

9.5: Discussion

Approximately 7,000 fuel drums remain in situ at Wilkes, 500 of which are almost permanently buried by ice (Snape et al. 1998; Fryirs et al. 2013). The location and removal of these drums is paramount to the environmental protection of Clark Peninsula (ATCM 2009; Fryirs et al. 2013). Metal drums exhibit strong magnetic anomalies and, when dumped randomly, will produce large-amplitude but highly variable anomalies (Barrows and Rocchio 1990; Gibson and George 2003). Prezzi et al. (2005) report that drums buried at 1 m depth produce anomalies of .1500 nT, while at 1.5 m anomalies decrease to 300 nT. Therefore, anomaly amplitudes generated in the north of Wilkes landfill suggest the highest concentration of buried steel drums across the landfill area. The short wavelength and depression between anomalies suggests that steel drums have been piled near the surface resulting in regular exposure during the summer months. However, this exposure and measured wavelengths are subject to annual variation, regulated by the intensity and path of summer melt flows. The unevenly configured fall-off rate and asymmetry of the main peak also reveals voids between materials and suggests that drums were empty when dumped or have since discharged fuel (Barrows and Rocchio 1990; Breiner 1999). Recognising that many of the drums may still contain fuel is critical if 'dig and haul' clean-up techniques are implemented at the site.

The broader wavelength anomalies produced further south suggest a response derived from the geology of the area. Historical observations indicate that many ferrous objects were dumped prior to 1961 and progressively melted or sank into the snow and soft sediments during the warm summer months (Burch personal communication 2013). Since Wilkes was the last IGY station to be established by the USA, leftover machinery, building materials and transport vehicles from previously constructed stations were unloaded on the shoreline of Newcomb Bay (Burch personal communication 2013). This explains the high amplitude and erratic anomalies generated south of the bedrock ridgeline, as well as the southern tip of the landfill positioned within metres of the shoreline (Figure 9.5b). Alternatively, sharp magnetic boundaries and more evenly spaced anomalies in the northern section (Figure 9.5a) suggest material organisation and surface stacking, perhaps immediately prior to the decommissioning of Wilkes Station. As landfill material has accumulated through varying operations above and below the ridgeline (Prezzi et al. 2005), there is a pattern of tipping histories and zonation

of waste at the Wilkes landfill. While historical communication provides some insight into waste zonation, it is not known whether this is significant for contaminated leachate generation and the off-site movement of contaminants.

Anomaly variation between the two survey dates provides insight into the influence of ice thickness on the magnetic values acquired. While survey profile 120 (23 December 2012) and profile 121 (21 January 2013) overlap in the central section, an increase from 900 nT (profile 120) to 1050 nT (profile 121) occurs at the point of intersection. While dGPS measurement accuracy between the two survey dates may contribute to this offset in magnetic intensity, a higher amplitude anomaly is probably associated with buried material being closer to the surface due to melting of the ice. This is supported by comparing the results of an excavation earlier in the 2012-13 field season where ice thickness was recorded at 1.7m with observations on 23 December 2012 where material fragments were observed at the surface. Thus, the summer melt is intertwined with the magnetic anomalies produced at the Wilkes landfill and annual variability in measurements should be expected both within and between field seasons. From engineering and management perspectives, this may positively or negatively impact clean-up timeframes. Depth perceptions are particularly important for clean-up operations when landfill sites are adjacent to marine ecosystems as surface disruption may mobilise potentially harmful contaminants.

The clean-up and removal of landfill material at Wilkes is required under the Protocol on Environmental Protection to the Antarctic Treaty (1991). As clean-up of the landfill will occur over multiple field seasons, ground magnetometry can be applied to prioritise locations for material removal. The bedrock ridgeline occurs at a higher elevation than the landfill (Figure 9.5a and b), providing a trapping mechanism for contaminants migrating in the soil profile from the north of the landfill. Furthermore, with material 1-2 m below the ice surface in the north (Figure 9.5a), disturbance could enhance and concentrate melt stream flow capacity and flush contaminants in the lower sections of the landfill. As this zone is located 150 m from Newcomb Bay, it may not pose an immediate threat to the marine environment.

In contrast, subsurface waste material detected south of the bedrock ridgeline probably poses a more urgent threat to the marine ecosystem. Subsurface imaging shows no topographical barriers to contaminant migration with large melt streams recorded across this region (Snape et al. 1998).
Clean-up of landfill material downhill of the ridgeline should be a priority in order to prevent greater adverse environmental impacts in accordance with Article 1(5) of Annex III (SCAR 1993). Subsequent clean-up in the north of the landfill may require the installation of a permeable reactive barrier in the south to ensure contaminants migrating off-site are captured and treated effectively (Snape et al. 2001b).

Although this survey provided detailed mapping of subsurface ferrous properties at Wilkes, magnetometry profiling may not be a universal technique for the complete characterisation of a landfill site (Gibson et al. 1996; Gibson and George 2003). With the lateral dispersal of water-borne contaminants occurring via both surface and subsurface melt streams at Wilkes (Snape et al. 1998), resistivity surveys during melt periods are crucial for detecting and tracking contaminant plumes. Understanding the interaction between waste material type and subsurface flow paths is essential in order to manage contaminant leaching during clean-up operations at landfills where geo-membrane liners were not installed, such as at Wilkes.

9.6: Conclusion

Ground magnetometry was well suited to the spatial characterisation of the landfill at Wilkes. Buried material and the boundaries of the landfill were clearly delineated from anomalies produced. Buried drums, which can contain dangerous pollutants, were identified with high amplitude anomalies of .1000 nT in the north of the landfill. Varying amplitudes were used to infer the presence of smaller metallic material amongst steel drums. These data provide a platform for developing and implementing future clean-up strategies at the Wilkes Station landfill.

9.7: References

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Section 5: Laboratory studies

Chapter 10: Immobilisation of metals in contaminated landfill material using orthophosphate and silica amendments: A pilot study

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Citation: Camenzuli D., Gore D.B. and Stark S.C. 2015. Immobilisation of metals in contaminated landfill material using orthophosphate and silica amendments: A pilot study. *International Journal of Environmental Pollution and Remediation 3*, 27-32.

Submitted: 29 August 2014; *Accepted for publication*: 13 March 2015; *Published*: 31 March 2015

Abstract

Immobilisation and encapsulation of contaminants using silica and orthophosphate based chemical treatments are emerging technologies applicable to the management of metal contaminated soil. While the efficacy of orthophosphate treatment is well documented, there is a paucity of research on the application of silica or coupled orthophosphate and silica chemical treatments to metal contaminated soil. This paper presents a pilot scale bench study on the use of silica and coupled orthophosphate-silica treatments for the immobilisation of metal contaminants in soil material obtained from the Thala Valley landfill, East Antarctica, which in places has petroleum hydrocarbons mixed with metalcontaminated sediment. The performance of the treatments trialed was assessed by the concentrations of copper, zinc, arsenic and lead released using the Toxicity Characteristic Leaching Procedure. The results of this pilot study demonstrate that the orthophosphate-silica treatment was the most effective and reduced leachable copper, zinc and lead by 95%, 96% and 99%, respectively, relative to the experimental controls. Further development of this technique will require additional research evaluating its long-term performance under a range of environmental conditions. Studies investigating potential adverse effects of silica and orthophosphate-silica treatments are also necessary, to demonstrate the environmental risk and efficacy of these remediation technologies.

Keywords: Contamination; Remediation; Silica; Orthophosphate; Landfill; Chemical Fixation.

10.1: Introduction

Human activities such as mining, smelting, manufacturing and agriculture have resulted in a broad distribution of metal contaminated sites across the globe (Järup 2003). The legacy and exposure effects of contaminants such as copper, cadmium and lead on the environment and human health are well documented (Järup 2003; Poland et al. 2003; Taylor et al. 2010, 2013), and the management of these contaminated sites remains an ongoing global problem. Efficient management of metal contaminated sites requires the development of cost-effective techniques that are applicable under a range of environmental conditions, and do not engender environmental harm. Technologies being developed to manage metal contaminated land more efficiently include phytoremediation, bioremediation and electrokinetic remediation; however, the efficacy of these techniques relies heavily on favorable environmental conditions (Martin and Ruby 2004). Silica and orthophosphate based treatments also demonstrate potential for a range of contaminated sites and environments (Mitchell et al. 2000a, b; White et al. 2012).

Orthophosphate immobilisation has been trialed successfully in laboratory experiments conducted under cold (2 °C) conditions and through multiple freeze-thaw cycles (Hafsteinsdóttir 2011, 2013; White et al. 2012). However, two concerns remain with orthophosphate 28 treatments. Firstly, over dosage with reagents may lead to orthophosphate contamination of the environment, with the attendant risks of ecosystem disturbance including eutrophication. Secondly, if organic contaminants such as petroleum hydrocarbons have been co-disposed with inorganic waste, organic coatings on contaminants may hinder or even prevent effective reaction with orthophosphate. In this situation, silica amendments offer an alternative approach to contaminant immobilisation. Silica treatment can work via direct reaction with contaminants and by microencapsulation, allowing the immobilisation of hydrocarbon-coated contaminants. Therefore, its use alone or coupled with orthophosphate, may be far more efficient than treatment with orthophosphate only. A slight excess of silica in the environment is not of great concern in most earth surface environments where silicate rocks and sediments abound, and there is little foreseeable risk of ecosystem disturbance with the dosages to be applied using this method.

While the potential of orthophosphate treatments for remediating metal contaminated soil is well documented (Zhu et al. 2004; Sonmez and Pierzynski 2005; White et al. 2012; Camenzuli et al. 2014), there is a paucity of studies reporting on the efficacy of silica treatments at metal contaminated sites (Camenzuli and Gore 2013). Furthermore, we are not aware of any published studies on the use of coupled orthophosphatesilica treatments for metal immobilisation. Therefore, the purpose of this pilot study is to investigate the potential of two silica treatments and one orthophosphate-silica treatment for immobilising Cu, Zn, As and Pb in contaminated soil. This study will provide a platform

for subsequent investigations of these treatments on a wider range of contaminated materials and contaminants, and under varying environmental conditions.

10.2: Materials and methods

10.2.1: Experimental design

The contaminated soil used in this study was sourced in January 2008 from a stockpile at the Thala Valley waste disposal site at Casey Station, East Antarctica (Stark et al. 2006). Concentrations of leachable Cu, Zn, As and Pb in the soil averaged 1.3 ± 1.0, 2.6 ± 1.8, <0.01 and 3.0 ± 3 .8 mg/L, respectively (Thums et al. 2010).

Three treatments and one untreated control (Table 10.1) were applied in-duplicate at room temperature to columns loaded with 1 kg of Thala Valley soil sieved to <2 mm using a stainless steel mesh. The columns used in this study adopted a design similar to that described by Vandiviere and Evangelou (1998). The silica treatments were applied by mixing calcium carbonate powder with soil, followed by the application of sodium metasilicate dissolved in Type I (ASTM 2011) reagent water (Milli-Q). The phosphate-silica treatment contained Triple Super Phosphate (TSP), calcined magnesia ('Qmag'), calcium carbonate applied as powder, followed by the application of a sodium metasilicate solution (Table 10.1). X-ray diffractometry showed Qmag to consist mainly of anhydrite ($CaSO_4$) and quartz (SiO_2), with minor calcium montomorillonite ($Ca_{0.2}(Al, Mg)_2Si_4O_{10}(OH).2H_2O$), bassanite ($CaSO_4.0.5H_2O$) and trace amounts of other silicates.

The experiment was performed at room temperature, with each column leached daily with 100 ml of Milli-Q water for 10 days. Leachate samples were collected and stored unacidified (to prevent formation of a silica gel) for later analysis, if required. Six months after application of the silica treatments, two soil samples were obtained from each column. These 16 samples, along with 21 samples of untreated soil collected at the start of the experiment, were extracted according to the Toxicity Characteristic Leaching Procedure (TCLP; US EPA Method 1311; US EPA 1992) and analysed at the Australian Antarctic Division for metals using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Four composite soil samples from the landfill were also analysed for total metals by hot nitric acid digestion and ICP-OES at Analytical Services Tasmania.

Table 10.1: Composition of silica and orthophosphate-silica treatments applied to Thala Valley landfill material.

Treatment ID	TSP (g)	Qmag (g)	Sodium metasilicate pentahydrate (g)	Calcium carbonate (g)	Solution volume (ml)
Control	0	0	0	0	210
Silica 1	0	0	70	40	210
Silica 2	0	0	100	40	300
Orthophosphate-silica	30	20	70	30	210

10.2.2: Analysis of leachable metals by Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP simulates contaminant leachability from soil under landfill conditions, and can be used to estimate contaminant mobility or classify contaminated soil for disposal (Scott et al. 2005, 2007). To simplify this procedure, we adopted a modified version of US EPA Method 1311, employing smaller quantities of soil and leachate.

TCLP extractions were performed on the <2.0 mm soil with analytical grade reagents and Type I deionised water. The pH of the soil averaged 8.2 ± 1.2 (n=12). Soil samples (2.5 g) were weighed into 50 ml polypropylene tubes (Sarstedt), mixed with 45 ml 0.10 M sodium acetate (pH 4.9) prepared from glacial acetic acid, 1 M NaOH and deionised water, and extracted for 18 h at 20 ± 1 °C on a rotary sample tumbler. Following filtration using 0.45 μm cellulose acetate syringe filters (Sartorius) (Peterson et al. 1990; Guo et al. 2007, 2008; Statham 2014), the extracts were acidified to pH <2 with concentrated HNO_3 and analysed with a Varian 720-ES ICP-OES using standard operating conditions for the analytes. Analytical duplicates returned relative standard deviations for all elements of <0.5%. Analyte recovery was measured using matrix spikes and was >94% for all elements.

10.3: Results and discussion

Total concentrations of Cu, Zn, As and Pb in the soil averaged 114 ± 88, 190 ± 100 and 3 ± 1 and 210 ± 170 mg/kg, respectively. The TCLP results (Table 10.2, Figure 10.1) demonstrate that the phosphate-silica treatment was the most effective at reducing the leachable concentrations of metals from the landfill material. The orthophosphate-silica treatment reduced Cu, Zn and Pb by 94%, 96% and 99%, respectively, relative to the experimental controls. The silica treatments also reduced Cu and Zn relative to the controls. Silica 2 treatment was the only treatment which did not reduce Pb relative to the controls (Figure 10.1). Arsenic concentrations were increased by all the treatments (Figure 10.1), which we attribute to competitive phosphate-arsenate (PO_4^{3-}-AsO_4^{3}) and silicate-arsenate interactions

in the soil (Peryea 1991; Luxton et al. 2006; Burton and Johnston 2012). The mobilizing effect of phosphate on As represents a major shortcoming of phosphate based remedial techniques (Peryea 1991; Munksgaard and Lottermoser 2013).

Table 10.2: TCLP results from experimental controls and treated landfill material (mg/L)

	Cu	Zn	As	Pb
Untreated				
Mean	0.72	2.69	0.01	1.35
Range	0.48-1.02	2.24-3.52	0.01-0.02	0.63-2.68
Standard Deviation	0.25	0.57	0.00	0.95
Silica 1				
Mean	0.55	1.65	0.02	0.63
Range	0.37-0.71	1.52-1.90	0.03-0.03	0.04-1.57
Standard Deviation	0.13	0.18	0.00	0.51
Silica 2				
Mean	0.61	1.57	0.02	1.97
Range	0.49-0.83	1.50-1.62	0.018-0.026	1.30-2.34
Standard Deviation	0.15	0.05	0.00	0.56
Orthophosphate-silica				
Mean	0.04	0.12	0.03	0.02
Range	0.04-0.07	0.10-0.21	0.031-0.042	0.02-0.02
Standard Deviation	0.01	0.04	0.01	0.00

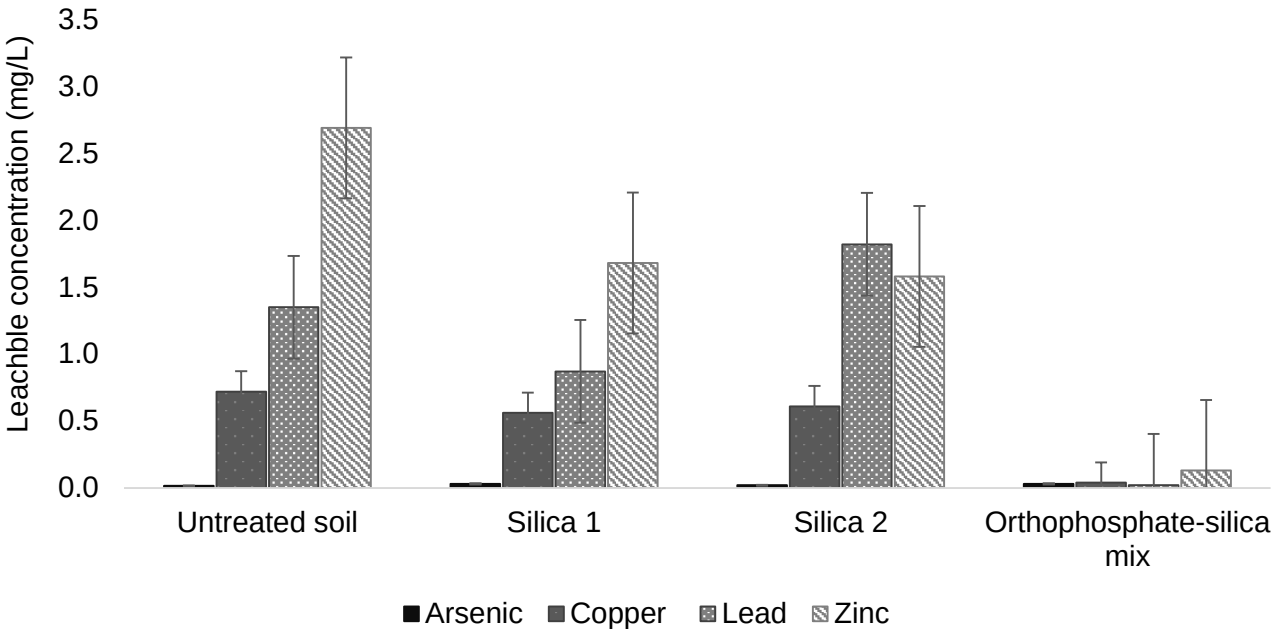

Figure 10.1: Mean TCLP results from treated and untreated landfill material (mg/L).
Standard deviation given by standard error bars.

These results demonstrate the potential of silica and phosphate-silica treatments as a technique for remediating metal contaminated land; however, a paucity of research offers only a limited understanding of this approach. Consequently, there are several aspects of this technique which warrant further investigation. Of critical importance are long-term studies which evaluate the performance of silica and phosphate-silica treatments under a range of environmental conditions, including the effects of soil pH, oxidation-reduction potential, soil character and temperature on treatment performance, and the stability of minerals and other compounds formed during treatment. A study which compares coupled orthophosphate-silica treatments with orthophosphate-only based treatments is essential to distinguish the remedial effects of orthophosphate from silica, and ideally would examine a wider range of analytes than that presented here. Any potential adverse environmental effects associated with these treatments should also be investigated.

10.4: Conclusion

This pilot study investigated the potential of silica treatments and a coupled orthophosphate-silica treatment as a remediation strategy for metal contaminated soil. Results for contaminant leachability six months after treatment indicate that the coupled orthophosphate-silica treatment was most effective for Cu, Zn and Pb, but mobilised As. However, due to the remaining uncertainty associated with this technique, further studies are required before *in situ* or on-site application to soil contaminated with metals and metalloids, particularly arsenic, is attempted. These should investigate the long-term effectiveness of the treatments under different environmental conditions. Coupled

orthophosphate-silica treatments may be a promising technique for metal contaminated sites if future research is able to validate its long-term safety and reliability.

10.5: Acknowledgements

The authors wish to thank the Australian Antarctic Division for financial support (AAS4029), and Geoff Stevens, Kathryn Mumford, Tom Statham and Benjamin Freidman for helpful discussions.

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Chapter 11: Treatment of soil contaminated with low levels of inorganics using orthophosphate and silica at sites with a heterogeneous distribution of contaminants

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In preparation for publication in Cold Regions Science and Technology.

Abstract

Orthophosphate and silica treatments are two technologies that are being developed for the management of inorganics at contaminated sites in cold regions. Previous studies have reported on the potential of these technologies in temperate regions; however, their suitability to cold regions and sites with a heterogeneous distribution of contaminants remains understudied. This study assessed the performance of four treatments (one orthophosphate, two silica and one coupled orthophosphate-silica) at immobilising Cr, Fe, Ni, Cu, Zn, As, Cd and Pb in heterogeneous soil contaminated with low-levels of inorganics. The results demonstrate that silica treatments were effective at reducing leachable concentrations of Fe, Ni, Cu, Zn, Cd and Pb, but did not reduce leachable concentrations of As. Orthophosphate and coupled orthophosphate-silica treatments reduced leachable concentrations of Fe, Cu, Zn, Cd and Pb, but were ineffective at reducing leachable concentrations of Cr, Ni and As. Leachable concentrations of P remained above environmentally safe levels in soils where treatments containing orthophosphate were applied, throughout the experiment. These results indicate that safe and effective field implementation of this technique at heterogeneous sites contaminated with low levels of inorganics may require a range of customised treatment dosages or coupling with complementary technologies capable of containing or treating excess P and mobilised contaminants.

Keywords: Remediation; Orthophosphate; Silica; Antarctica; Landfills; Metals.

11.1: Introduction

A consequence of the growing human presence in Antarctica is contaminated sites derived from active and abandoned research stations (Santos et al. 2005; Filler et al. 2006; Fryirs et al. 2013, 2015). Members of the Antarctic Treaty are committed to the protection of the Antarctic environment under The Protocol on Environmental Protection to the Antarctic Treaty (Poland et al. 2003; Fryirs et al. 2013). Annex III of the Madrid Protocol (Waste Disposal and Management) establishes the requirement for all past and present work sites to be cleaned up unless the site is considered to be a Monument or Historic Site by the Antarctic Treaty Consultative Meeting, or disturbance is likely to result in further adverse environmental impacts (Snape et al. 2001a; Poland et al. 2003; Bargagli 2008; Evans 2011; Fryirs et al. 2013). To satisfy the requirements of the Madrid Protocol, various innovative and environmentally sensitive technologies for managing contaminated sites are being adapted for use in Antarctica (Filler et al. 2006; Camenzuli et al. 2014). Technologies that can be used on-site or in situ are preferable in remote, cold regions as they are more practical in logistically constrained environments, less disruptive to the environment, prevent or minimise contaminant migration and reduce the need to transport contaminated material or generate additional landfills (Poland et al. 2003; Martin and Ruby 2004; Filler et al. 2006; White et al. 2012; Camenzuli et al. 2014). Two emerging technologies that are being developed for on-site or in situ treatment of soil contaminated with inorganics in Antarctica are orthophosphate (White et al. 2012; Hafsteinsdóttir et al. 2011, 2013, 2014, 2015) and silica (Camenzuli and Gore 2013; Camenzuli et al. 2015) treatments.

Orthophosphate and silica treatments have been successfully applied to metal contaminated sites in temperate regions (Mitchell et al. 2000a, 2000b; Prasad et al. 2008; Naja and Volesky 2009; Camenzuli et al. 2015; Hafsteinsdóttir et al. 2015). However, few studies have applied orthophosphate treatments under cold conditions (White et al. 2012; Hafsteinsdóttir et al. 2011, 2013, 2014, 2015), and no research on silica or coupled orthophosphate-silica treatments in cold regions has been undertaken (Camenzuli and Gore 2013; Camenzuli et al. 2015). The paucity of such research offers only limited understanding of the suitability of these technologies to cold, remote regions and provides insufficient data to support their safe application in Antarctica (Camenzuli and Gore 2013). This is particularly relevant to silica and coupled orthophosphate-silica treatments which have not been examined for their long-term environmental safety and reliability (Camenzuli and Gore 2013; Camenzuli et al. 2015).

Several research gaps surrounding the efficacy and safety of silica treatments have been identified (Camenzuli and Gore 2013), and represent substantial obstacles to the development and application of this technology. Unresolved research gaps surrounding silica treatments include uncertainty regarding the most appropriate treatment of soil contaminated with inorganics, petroleum hydrocarbons and co-contaminated materials; the type and stability of products formed during treatment, and a shortage of studies describing the relationships between the performance of silica

and environmental conditions including soil type, temperature, microbial activity and pH (Camenzuli and Gore 2013). The absence of published studies reporting on potential adverse environmental effects of the treatments also represents an important research gap (Camenzuli and Gore 2013).

A pilot trial which assessed the efficacy of silica and coupled orthophosphate-silica treatments for application at metal contaminated landfills using the Toxicity Characteristic Leaching Procedure (TCLP; US EPA Method 1311 1992) represents the first attempt at addressing these knowledge gaps (Camenzuli et al. 2015). The experiment demonstrated the potential for managing metal contaminated landfill materials using silica and coupled orthophosphate-silica treatments. However, the study was unable to provide a detailed understanding of the environmental safety and reliability of the technology. Understanding the safety of these technologies prior to in situ implementation is vital (Camenzuli and Gore 2013), particularly when considering application to Antarctic landfills which are complex environments, often characterised by a heterogeneous distribution of contaminants with slow degradation rates of biological materials and petroleum hydrocarbons (MacFarlane et al. 1983; Cambardella et al. 1994; Ding et al. 2001; White et al. 2012). In situations where orthophosphate, silica or coupled orthophosphate-silica treatments could be applied homogenously to landfills with an uneven distribution of contaminants, it is important to understand the impact of treatment overdose and under dose in areas contaminated with significantly lower or higher concentrations of metals. Ensuring the environmental safety of this technology in Antarctica under a range of conditions is also vital for compliance with the requirements of The Madrid Protocol (1998).

To advance our understanding of the safety of this technology, a batch experiment was undertaken using landfill material from Thala Valley adjacent to Casey Station, East Antarctica. Antarctic landfill material with low concentrations of inorganics was treated to investigate the environmental effects of applying chemical treatments in soil with low-level inorganic contaminants within landfills. Four chemical treatments were assessed in this experiment; one orthophosphate, two silica and one coupled orthophosphate-silica treatment. Treatments were assessed by measuring the total concentrations of metals and monitoring electrical conductivity (EC), oxidation-reduction potential (ORP) and pH in leachate samples collected over 185 days. The mobility of inorganics in soil before treatment, and 61 and 185 days after treatment was also assessed using TCLP extractions, as a measure of treatment performance. All results from treated materials were benchmarked against results obtained from untreated landfill material. The experiment was undertaken in a laboratory under cold conditions (2 °C) to simulate a typical East Antarctic summer climate and enable an evaluation of treatment performance under controlled conditions.

11.1.1: Remediation of metals using orthophosphate treatments

Orthophosphate fixation treatments react with and immobilise inorganics by precipitating sparingly soluble metal-phosphate minerals, for example chloropyromorphite (Ma et al. 1995; Hettiarachchi et al. 2000; Melamed et al. 2003; Basta and McGowen 2004; Cao et al. 2004; Chen et al. 2007; White et al. 2012; Hafsteinsdóttir et al. 2011; 2013, 2015). The processes responsible for the formation of insoluble metal-phosphate minerals are well understood and include adsorption, ion exchange, and dissolution and precipitation or co-precipitation reactions (Xu and Deventer, 2000; Nalaskowski et al. 2003; Pham et al. 2007; Prasad et al. 2008; White et al. 2012; Hafsteinsdóttir et al. 2011; 2013, 2015). The efficacy of orthophosphate fixation is reported, even in cold regions (White et al. 2012; Hafsteinsdóttir et al. 2011; 2013, 2014), and while this technique offers the advantages of cost-efficiency and capability for in situ application, two major disadvantages exist. Firstly, competitive orthophosphate-arsenate (PO_4^{3-}-AsO_4^{3-}) interactions can trigger the mobilisation of arsenic in soil and secondly, the risk of eutrophication associated with orthophosphate treatments is high (Peryea 1991; Luxton et al., 2006; Burton and Johnston 2012; Hafsteinsdóttir et al. 2014, 2015). These disadvantages represent serious environmental considerations which should be managed (Peryea 1991; Munksgaard and Lottermoser 2013), particularly in environmentally sensitive regions such as Antarctica (Mooney et al. 2013; Camenzuli et al. 2014; Payne et al. 2014).

11.1.2: Remediation of metals using silica treatments

Silica treatments react with and immobilise inorganics in soil via three mechanisms: i) the formation of hydroxides, ii) precipitation or co-precipitation of metal silicates or iii) production of silica gels which encapsulate metals or provide an active site for the adsorption of metals (Mitchell et al. 2000a, 2000b; Naja and Volesky 2009; Abdel-Hamid et al. 2012; White et al. 2012; Camenzuli and Gore 2013).

The formation of hydroxides, metal-silicate minerals and silica gels is driven primarily by hydration, precipitation or polymerisation reactions, respectively (Xu and Deventer 2000; Nalaskowski et al. 2003; Pham et al. 2007; Prasad et al. 2008). A range of calcium-silicate-hydrates, di- and tricalcium silicates, and calcium hydroxide crystals form during hydration reactions following treatment with silica (Acton 2013). The formation of metal silicate minerals via precipitation and co-precipitation reactions prompted by silica treatments is analogous to the processes that occur during orthophosphate fixation (Camenzuli and Gore 2013). Polymerisation of soluble silicates is more complicated (Pham et al. 2007). Silica gels form when the pH of a silica solution is lowered below pH 7, causing silicates to cross-link and form a gel (Pham et al. 2007; Camenzuli and Gore 2013). The structure of polymerised silicates provides active sites for adsorption or encapsulation of metal ions in solution and can range from fragile gels in dilute colloidal systems to strong polymer gels, depending on the stress-transfer between silica particles and the matrix (Poon et al. 1985; Shibayama 2006; Pham

et al. 2007; Camenzuli and Gore 2013). The high surface area and consequently high adsorptive capacity of the silica gels also provides a mechanism for the removal of any metals remaining in solution after passing through the gel (Poon et al. 1985). An additional advantage of silica treatments is that they can be applied to sites contaminated with inorganics, petroleum hydrocarbons or co-contaminated materials without increasing the risk of eutrophication.

11.2: Materials and methods

11.2.1: Experimental design

Soil was sub-sampled from material collected in January 2008 from a stockpile at Thala Valley landfill adjacent to Casey Station, East Antarctica (Stark et al. 2006). Thala Valley landfill operated between 1965 and 1986 and was a storage site for station domestic and building waste including food scraps and rusted cans, mattress springs, steel drums, discarded machinery and vehicle parts, white goods, batteries and photographic chemicals (Deprez et al. 1999; Snape et al. 2001b). Dissolution of metals by meltwater flowing through the surface and subsurface of the Thala Valley landfill was identified as the source of elevated concentrations of Cr, Fe, Ni, Cu, Zn, As, Cd and Pb in the waters and sediments of neighbouring Brown Bay (Deprez et al. 1999; Snape et al. 2001b; Stark et al. 2005). This prompted a 'dig-and-haul' clean-up of the site in 2003-04. After this initial clean-up, the remaining stockpile contained mostly low-level contaminated soil (Stark et al. 2006, Thums et al. 2010). Chemical assessment of the remaining stockpile material was undertaken in 2010 (Thums et al. 2010). Total analyte concentrations in five composite soil samples from the stockpile revealed mean concentrations of Cr, Fe, Ni, Cu, Zn, As, Cd and Pb of 13.5±3, 6000±2500, 8.5±1, 510±840, 220±36, 1.75±1, 0.85±0, 134±49 mg/kg, respectively (Thums et al. 2010). Leachable concentrations of Cr, Fe, Ni, Cu, Zn, As, Cd and Pb in the landfill material were found to averaged <0.01, <0.5, 0.02±0.01, 1.3±1.0, 2.6±1.8, <0.01 and 0.02±0.01 mg/L, respectively (Thums et al. 2010).

One orthophosphate, two silica and one coupled orthophosphate-silica treatments were applied in triplicate to PVC columns loaded with 1.0 kg of Thala Valley landfill material sieved to <2 mm using a stainless steel mesh (n=12) (Table 11.1). A further three columns loaded with 1.0 kg of untreated Thala Valley landfill material were used as experimental controls. Once treated, the columns were moved into an incubator (2 °C). The columns used in this experiment were constructed from polyvinyl chloride and adopted a design similar to those in Vandiviere and Evangelou (1998) (Figure S11.1).

The orthophosphate treatment in this experiment was adopted from Hafsteinsdóttir et al. (2014) and contained Triple Super Phosphate (TSP) and Qmag. This treatment was adopted because of its demonstrated ability to reduce metal mobility in Thala Valley landfill material (Hafsteinsdóttir et al. 2014). X-ray diffractometry revealed that Qmag consists mainly of anhydrite ($CaSO_4$) and quartz (SiO_2), with calcium montmorillonite ($Ca_{0.2}(Al, Mg)_2Si_4O_{10}(OH).2H_2O$), bassanite ($CaSO_4.0.5H_2O$)

and trace amounts of other silicates. Since TSP is a naturally impure product, X-ray fluorescence analysis of the reagents was undertaken prior to application to ensure that the concentrations of metals in the treatment reagents were at environmentally safe levels. The silica treatments used in this experiment were amended from Fytas et al. (1998) and Vandiviere and Evangelou (1998) and were applied by mixing calcium carbonate powder with soil, followed by the application of reagent grade sodium metasilicate dissolved in Type I reagent water (Milli-Q; ASTM 1999) (Figure S11.2). Orthophosphoric acid was applied after the sodium metasilicate solution to silica 2 treated soil to hasten polymerisation of soluble silicates (Mbhele 2007; Camenzuli and Gore 2013). The coupled orthophosphate-silica treatment contained TSP, Qmag and calcium carbonate (all applied as powders), followed by the application of reagent grade sodium metasilicate dissolved in Type I water.

Table 11.1: Composition of chemical mix treatments applied to Thala Valley landfill material.

Treatment ID	TSP (g)	Qmag (g)	Sodium metasilicate (g)	Calcium Carbonate (g)	Orthophosphoric acid (16% w/v) (mL)	Type I water (mL)
Untreated	0	0	0	0	0	210
Orthophosphate	30	20	0	0	0	210
Silica 1	0	0	70	40	0	210
Silica 2	0	0	70	40	70	300
Orthophosphate-silica	30	20	70	30	0	210

Samples were obtained by leaching each column with 100 mL of Type I water every 48 hours (equivalent to approximately 53% of the total pore volume) for the first 30 days of the experiment and 185 days after the treatments were applied. Samples were collected more frequently during the first 30 days of the experiment to determine the speed of immobilisation as previous studies indicate immobilisation is likely to occur within 30 days of treatment (Camenzuli and Gore 2013; Hafsteinsdóttir et al. 2015). Samples were collected 185 days after treatment to provide a longer term understanding of treatment performance.

ORP and pH were measured in leachate samples using calibrated electrodes (TPS general purpose combination redox and Mettler Toledo InLab Expert Pro combination probes, respectively) connected to a Mettler Toledo SevenEasy pH/mV meter. EC was measured using a TetraCon 325 probe connected to a WTW 1970i conductivity meter. Duplicate soil samples (20 g) were obtained from each column before treatment and 61 days (2 months) and 185 days (6 months) after treatment and analysed for leachable concentrations of metals using an amended version of the TCLP.

11.2.2: Analysis of total concentrations of phosphorus and metals in leachate

Analysis of leachate samples for P, Cr, Fe, Ni, Cu, Zn, As, Cd and Pb was undertaken with a Varian 720-ES ICP-OES using standard operating conditions for the analytes. Leachate samples obtained from orthophosphate and untreated systems were filtered using 0.45 μm cellulose acetate syringe filters (Sartorius) and acidified to pH <2 using concentrated analytical grade HNO_3 (Aristar, BDH) prior to analysis for total concentrations of elements. Leachate samples obtained from the silica or coupled orthophosphate-silica treated systems were filtered using 0.45 μm cellulose acetate syringe filters (Sartorius) but were not acidified to prevent the formation of silica gels, which would prevent analysis using ICP-OES. Analytical duplicates returned mean standard deviations for all elements of <5%. Analyte recovery was measured using matrix spikes and was >97 and <102% for all elements.

11.2.3: Analysis of leachable metals, arsenic and phosphorus in soil using the Toxicity Characteristic Leaching Procedure

The TCLP simulates contaminant leachability from soil under municipal landfill conditions, and can be used to estimate contaminant mobility (Stark et al. 2008). The method was scaled down to employ smaller quantities of soil and extractant solution. Extractions were performed on the dry <2.0 mm soil fraction with analytical grade reagents and in Type I water. The mean soil pH of 12 sub-samples, measured in an aqueous suspension with a soil: water ratio of 1:5 (g: mL), was 8.2±1.2. Duplicate soil samples (2.5 g) were weighed into 50 ml polypropylene tubes (Sarstedt) and mixed with 45 mL 0.10 M sodium acetate (pH 4.9) prepared from glacial acetic acid, 1 M NaOH and Type I water, and extracted for 18 h at 20±1 °C on a rotary sample tumbler. Following filtration through 0.45 μm cellulose acetate syringe filters (Sartorius) (Peterson et al. 1990; Guo et al. 2007, 2008; Statham 2014), the extracts were acidified to pH <2 with concentrated AR-grade HNO_3 and analysed with a Varian 720-ES ICP-OES using standard operating conditions for the analytes. Analytical duplicates returned relative standard deviations for all elements of <0.5%. Analyte recovery was measured using matrix spikes and was >97% and <105% for all elements.

11.3: Results

11.3.1: Electrical conductivity, oxidation-reduction potential and pH

EC increased in leachate immediately after treatment, but decreased steadily over 185 days. The EC of leachate collected from untreated soil was 7.80±0.14 mS/cm at its maxima, 24 hours into the experiment, and decreased to 0.73±0.04 mS/cm on day 185. The maximum EC of leachate obtained from soil treated with orthophosphate also occurred 24 hours after treatment (19.4±2.0 mS/cm) before decreasing to 0.31±0.03 mS/cm by day 185. The EC of leachate collected from soil treated with silica (silica 1, silica 2 and coupled orthophosphate-silica) were substantially higher and remained above the measurement range (>25 mS/cm) until day 16, 12 and 8 of the experiment, respectively.

On day 185, the EC of leachate collected from soil treated with silica 1, silica 2 and coupled orthophosphate-silica was 5.06±0.66, 5.77±0.51 and 7.35±0.61 mS/cm, respectively (Figure S11.3).

Small changes in ORP were detected in leachate collected from untreated soil. The maximum ORP was measured three hours after the experiment commenced (+160±0.4 mV) and declined to +140±2.4 mV on day 185. The ORP of leachate collected from soil treated with orthophosphate remained positive throughout the experiment, reaching its maximum (+250±13 mV) on day two before decreasing to +140±10 mV by day 185. Soil treated with silica maintained reducing conditions until the 30th day of the experiment, when the ORP in soil treated with silica 1, silica 2 and coupled orthophosphate-silica reached +4.1±5.7, +8.20±0.66 and +10.4±4.4 mV, respectively. On day 185, the ORP of these systems was +51.3±3.5, +50.0±3.0 and +69.0±1.7 mV, respectively (Figure S11.4).

The pH of soil before treatment was 8.22±0.1. After treatment, changes in pH occurred across all systems, but most significantly in the silica treated systems. The pH of untreated, orthophosphate, silica 1, silica 2 and coupled orthophosphate-silica treated soil was 8.35±0.1, 7.46±0.0, 10.55±0.1, 10.02±0.0 and 9.37±0.1, respectively. The pH of leachate collected from untreated soil gradually increased from 6.74±0.1 to 7.02±0.1 over 185 days. Treatment with orthophosphate produced acidic leachate (3.2±2.4 three hours after treatment), which stabilised at 6.8±0.0 by day 185. Silica treatments had the greatest effect on the pH of leachate samples, with the pH of leachate collected from silica 1, silica 2 and coupled orthophosphate-silica treated soil stabilising at 10.1±0.1, 10.1±0.0 and 9.7±0.6 on day 185, respectively (Figure S11.5).

11.3.2: Concentrations of metals, arsenic and phosphorus in leachate

After initially increasing, the concentration of inorganics in leachate decreased in all systems over 185 days (Figures S11.6-S11.11). Treatment with orthophosphate resulted in significantly lower concentrations of Cr, Fe, Ni, Cu, Zn, As, Cd and Pb in leachate samples (Figure S11.7). The orthophosphate-silica treatment was also effective at reducing concentrations of all inorganics, and was most the effective treatment for Fe, Zn, and Pb (Figure S11.8). Although treatment with silica 1 reduced the concentrations of all measured inorganics in leachate, it generally was least effective, except for Cd (Figure S11.9). Silica 2 was more effective than silica 1 but generally less effective than treatment with orthophosphate or coupled orthophosphate-silica (Figure S11.10).

The concentration of P in leachates decreased in all systems in the order of: orthophosphate (10,500-34 mg/L) > coupled orthophosphate-silica (7,125-108 mg/L) > silica 1 (96.03-2.9 mg/L) > silica 2 (5,394-340 mg/L) > untreated (0.21-0.07 mg/L). Although significant reductions in P were observed in all systems, concentrations of P remained above the US EPA (2000) and CCME (2004) guideline

of 0.01 mg/L in all leachates and above the ANZECC/ARMCANZ limit of 0.05 mg/L in leachates collected from systems where treatments containing orthophosphate were used (i.e. orthophosphate, coupled orthophosphate-silica and silica 2), even at the end of the experiment (Figure S11.11).

11.3.3: Concentrations of leachable metals in soil

Significant changes in the leachable concentrations of inorganics were observed after treatment with orthophosphate, silica or coupled orthophosphate-silica (Table 11.2). Treatment of Cu, Zn and Pb with coupled orthophosphate-silica or orthophosphate was most effective. However, leachable concentrations of Ni doubled and tripled after treatment with orthophosphate-silica and orthophosphate, respectively (Table 11.2). Treatment with silica 2 was highly effective for Fe, Ni, Cu, Zn and Pb, whereas treatment with silica 1 effectively reduced leachable concentrations of Fe, Ni, Cu, Zn and Pb but was ineffective for Cd relative to the experimental controls. Leachable concentrations of As increased after treatment with coupled orthophosphate-silica and silica 2 systems by 50%, whereas no change in leachable As was detected after treatment with silica 1 or orthophosphate. At the completion of the experiment, leachable concentrations of Fe, Cu, Zn and Pb were higher in the untreated experimental controls than in treated systems (Table 11.2).

Concentrations of P increased substantially in systems treated with orthophosphate, silica 2 or coupled orthophosphate-silica (which contained either TSP or orthophosphoric acid). The most significant increases occurred in soil treated with orthophosphate or coupled orthophosphate-silica, where concentrations of P increased from 0.14±0.02 to 76±19 mg/L and 0.18±0.03 to 82±16 mg/L, respectively (Table 11.2). The data is also presented as treatment effect ratios in Table S1.

Table 11.2: Mean TCLP results ± standard deviation (mg/L).

Day	P	Cr	Fe	Ni	Cu	Zn	As	Cd	Pb
				Untreated					
0	0.10 ±0.03	<0.01	0.36 ±0.08	0.02 ±0.00	0.93 ±0.35	4.6 ±0.66	<0.05	0.04 ±0.00	2.8 ±1.9
61	0.08 ±0.05	<0.01	0.75 ±0.11	0.02 ±0.00	1.6 ±0.75	8.1 ±12	<0.05	0.03 ±0.01	1.9 ±0.90
185	0.12 ±0.05	<0.01	0.57 ±0.13	<0.01	0.78 ±0.30	3.2 ±1.5	<0.05	0.02 ±0.00	1.6 ±0.85
				Orthophosphate					
Day	**P**	**Cr**	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
0	0.14 ±0.02	<0.01	0.58 ±0.14	<0.01	1.70 ±1.90	2.20 ±1.40	<0.05	0.21 ±0.32	6.80 ±9.50
61	74.00 ±4.30	<0.01	<0.01	0.02 ±0.00	0.25 ±0.03	1.40 ±0.30	<0.05	<0.01	0.02 ±0.00
185	76.00 ±19.00	<0.01	0.12 ±0.11	0.03 ±0.01	0.52 ±0.62	1.20 ±0.21	<0.05	<0.01	0.02 ±0.01
				Silica 1					
Day	**P**	**Cr**	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
0	0.13 ±0.05	<0.01	0.35 ±0.12	0.02 ±0.00	1.20 ±0.44	5.5 ±2.5	<0.05	0.04 ±0.00	2.40 ±0.70
61	0.12 ±0.03	<0.01	0.08 ±0.06	0.02 ±0.00	0.27 ±0.07	1.5 ±0.30	<0.05	0.02 ±0.00	0.35 ±0.13
185	0.15 ±0.03	<0.01	0.13 ±0.10	<0.01	0.29 ±0.09	1.5 ±0.50	<0.05	0.02 ±0.00	0.34 ±0.23
				Silica 2					
Day	**P**	**Cr**	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
0	0.12 ±0.05	<0.01	0.42 ±0.15	0.02 ±0.00	1.40 ±0.60	4.40 ±0.50	<0.05	0.03 ±0.00	17.00 ±24.00
61	63.00 ±8.20	<0.01	0.01 ±0.00	<0.01	0.68 ±0.82	0.86 ±0.22	<0.05	<0.01	0.04 ±0.02
185	46.00 ±3.20	<0.01	0.04 ±0.06	<0.01	0.15 ±0.18	0.46 ±0.38	<0.05	<0.01	0.02 ±0.02
				Coupled orthophosphate-silica					
Day	**P**	**Cr**	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
0	0.18 ±0.03	<0.01	0.32 ±0.18	<0.01	0.59 ±0.25	3.20 ±1.30	<0.05	<0.01	16.00 ±24.00
61	73.00 ±16	<0.01	0.04 ±0.00	0.03 ±0.00	0.04 ±0.01	0.26 ±0.17	<0.05	<0.01	<0.01
185	82.00 ±16.00	<0.01	0.06 ±0.02	0.02 ±0.00	0.03 ±0.03	0.21 ±0.10	<0.05	<0.01	<0.01

11.4: Discussion

11.4.1: Performance of treatments

Differences in the measured parameters were detected in all systems over 185 days, most prominently in the silica treated systems. The average EC and pH of the Thala Valley landfill material prior to treatment was 7.80±0.14 mS/cm and 8.2±1.2, respectively. Soils that produce leachates with EC>4

mS/cm and pH>7 are considered saline (Pierzynski et al. 2005; Hafsteinsdóttir et al. 2014), indicating the saline character of the landfill material before treatment. After 185 days, untreated and orthophosphate treated soil were no longer saline; however, soil treated wth silica or coupled orthophosphate-silica was highly saline, probably due to the addition of large amounts of reagent relative to the concentrations of electrolytes in the landfill material (Hafsteinsdóttir et al. 2014). This has important implications for remediation as metal availability increases with salinity due to competition for sorption sites by major cations, resulting in the solubilisation of some metals such as Ni (Du Laing et al. 2009; Li et al. 2010; Hafsteinsdóttir et al. 2014). The salinity of the landfill material may have also contributed to the initially high concentrations of metals in leachate, with desorbed metals becoming entrained by the water supplied to the systems as it permeated the soil (Hafsteinsdóttir et al. 2014). This effect was most prominent in the treated systems, shown by the distinct increase in EC and metal concentrations in leachate, which subsided over 185 days (Figures S11.6-S11.11).

Concentrations of dissolved metals are generally lower in reducing environments (María-Cervantes et al. 2011), whereas oxidising environments tend to solubilise metals; however, reducing conditions can also solubilise Mn and Fe and result in the release of adsorbed metals (Hermann and Neumann-Mahlkau 1985; Otero and Macías 2002; Du Laing et al. 2009; Conesa et al. 2011; Hafsteinsdóttir et al. 2014). The ORP of leachate from the untreated and orthophosphate treated systems maintained oxidising states throughout the experiment, whereas the ORP of leachate from systems treated with silica maintained reducing states until day 30 before transitioning into an oxidising state for the remaining 155 days of the experiment (Figure S11.4). The concentration of metals in leachate and leachable inorganics in soil did not increase in silica treated systems between days 30 and 185, despite ORP transitioning into an oxidising state (Table 11.2).

The acceptable pH range of drinking and ground waters is 6.5 to 8.5 (von Gunten 2003; US EPA 2009). Unlike silica treated systems, the pH of soil and leachates from untreated systems remained within the healthy range for groundwater throughout the experiment. The pH of soil and leachates from orthophosphate treated systems stabilised to within the healthy range for groundwater between days 30 and 185. The alkalinity observed in the silica treated systems was generated by the highly alkaline treatment solution (pH >13), and maintenance of this throughout the experiment indicates incomplete polymerisation of soluble silicates (Billings and Burns 1997; Pham et al. 2007). This was a consequence of insufficient addition of acid after the application of the alkaline silica treatment solution, preventing the silica treatment from reaching the optimum pH 7-9 for polymerisation (Billings and Burns 1997; Pham et al. 2007; Camenzuli and Gore 2013). Future experiments assessing the introduction of more acid after the silica treatment solution to reduce the pH of leachate and

enhance immobilisation efficiency by facilitating the sol-gel transition would be beneficial for the development of this technique (Billings and Burns 1997; Pham et al. 2007; Camenzuli and Gore 2013).

Metal concentrations in leachate initially increased in all treated systems after treatment (Figures S11.6-S11.11). In the orthophosphate treated systems, this is attributed largely to the acidifying effect of TSP treatment, which is beneficial for treatment as it mobilises metal cations, allowing metal-phosphate minerals to form (Hafsteinsdóttir et al. 2014, 2015). Alternatively, in the silica treated systems, metals are likely to have been mobilised following equilibration of the landfill material with high ionic strength silica treatment solutions. The high concentrations of Na^+ in the silica treatments, combined with cations solubilised from the saline landfill material, displaced sorbed metals from complexation sites on the soil particles by cation exchange, resulting in an initial increase in the concentrations of metals in leachate.

Leachable concentrations of Fe, Ni, Cu, Zn, Cd and Pb in soil were reduced significantly by treatment with silica 1 and 2, whereas treatment with orthophosphate or coupled orthophosphate-silica reduced leachable concentrations of Fe, Cu, Zn, Cd and Pb in soil. Similarly to the results of this experiment, Hafsteinsdóttir et al. (2014) found that treatment with orthophosphate increased concentrations of Cr and Ni (Hafsteinsdóttir et al. 2014) in leachate. Leachable concentrations of As did not increase in soil treated with orthophosphate, but rather in soil treated with silica 2 or coupled orthophosphate-silica. This may be the result of silicate-arsenate interactions in soil or the effect of pH and ORP on As speciation (Peryea 1991; Luxton et al. 2006; Burton and Johnston 2012; Hafsteinsdóttir et al. 2014; Camenzuli et al. 2015). Masscheleyn et al. (1991) found that As solubility increased by a factor of 13 alkaline pH conditions and in reducing environments of approximately -200 mV. The data presented in Figures S11.4 and 5 support this finding and possibly accounts for the observerable difference in As concentrations in orthophosphate treated systems relative to silica treated systems. However, a detailed study assessing Si-As interactions upon treatment is required to conclusively attribute the small increase in As concentration to Si-As interactions.

Observed increases in leachable Cr in soil treated with orthophosphate or coupled orthophosphate-silica is attributed to competitive effects between oxyanion species of Cr and PO_4^{3-} upon interaction with TSP (Peryea 1991; Seaman et al. 2001; Hafsteinsdóttir et al. 2014). Treatments containing orthophosphate in the form of TSP or orthophosphoric acid resulted in large concentrations of leachable P in soil and leachate, even at the end of the experimental period. Although excess P may be required to ensure complete reaction, this represents an important environmental concern associated with these treatments (Hafsteinsdóttir et al. 2014, 2015). Amending the silica 2 treatment by replacing orthophosphoric acid with another mineral acid may reduce the risk of eutrophication and increase the suitability of this treatment for contaminated sites in Antarctica.

11.4.2: Implications for remediation

Several adverse effects associated with chemical treatment of low-level contaminated materials exist. Firstly, the pH of soil and leachate is influenced by treatment, with orthophosphate treatments acidifying (Hafsteinsdóttir et al. 2014, 2015), and silica treatments alkalising soil and leachate. Extremely acidic or alkaline environments are problematic for soil structure, filtration and plant and microbial health (Smith and Doran 1996; Butterly et al. 2012). Microbial activity is affected by pH, with fungi, bacteria, protozoa and actinomycetes preferring pH 6-8 for survival and function (Smith and Doran 1996; Butterly et al. 2012; Courtney et al. 2014). EC, ORP and pH of the orthophosphate treated systems were stable by day 185, indicating that the long-term environmental effects of this treatment may be less significant than the potential harm presented by on-going leaching of metals into the environment, if excess P and mobilised contaminants are managed effectively (Hafsteinsdóttir et al. 2014). This is consistent with Hafsteinsdóttir et al. (2014) who found that EC and pH stabilised and leachable concentrations of Mn, Fe, Co, Cu, Zn, Cd and Pb decreased within one year of treatment, following an initial flush of metals from the contaminated soil in the first 24-48 h after treatment addition. As the silica treatments evaluated in this experiment produced highly alkaline environments, the composition of treatments must be amended before implementation in Antarctica can be considered safe.

To prevent eutrophication, dosages of treatments containing orthophosphate should be customised according to the concentrations of contaminants present (Hafsteinsdóttir et al. 2014). Where it is appropriate to apply treatments containing orthophosphate, precautions to prevent excess P entering the environment must be implemented (Hafsteinsdóttir et al. 2014; Camenzuli et al. 2015). To reduce potential adverse effects of treatment at complex heterogeneous contaminated sites, a site assessment with detailed zoning of contaminant type and concentration should be undertaken prior to treatment (Fryirs et al. 2015). Upon completion of contaminant zoning, several different dosages customised to contaminant concentration or a staged approach to remediation which incorporates technology coupling may also be required (Freidman et al. 2014). This may involve remediating critical areas first or implementing technology coupling prior to in situ application of chemical treatments (Freidman et al. 2014). For example, impermeable liners or permeable reactive barriers may be installed to contain excess reagent or mobilised contaminants, and prevent the migration of treatments into different zones of contamination (Snape et al. 2001b; Gore 2009; Mumford et al. 2013, 2014; Freidman et al. 2014; McWatters et al. 2014; Hafsteinsdóttir et al. 2014). Finally, to ensure the stability of the immobilised inorganics at sites where field implementation has been achieved, a long-term monitoring strategy for analytes, EC, ORP and pH should be maintained (Hafsteinsdóttir et al. 2014).

11.5: Conclusion

Significant reductions in the concentrations of measured analytes in leachate samples was observed between days 1 and 185 in all systems. The leachable concentrations of Fe, Cu, Zn, Cd and Pb in soil decreased after treatment, most significantly after treatment with the coupled orthophosphate-silica treatment. Reductions in the concentrations of leachable Ni increased were observed in all soils, except soil treated with orthophosphate or coupled orthophosphate-silica. Concentrations of leachable Fe increased in the untreated systems, whereas leachable concentrations of As only decreased in the untreated systems. To contain excess reagent or mobilised contaminants, technology coupling with complementary techniques such as impermeable liners or permeable reactive barriers is recommended during field-scale implementation.

This study also highlights the importance of detailed characterisation of contaminated sites and pilot scale experimentation of dosage suitability before in situ application. Safe and effective in situ remediation using this technique may also require heterogeneous contaminated sites to be treated as several, smaller contaminated sites with customised treatment dosages applied at different zones of contaminant concentration, or blending prior to treatment. Finally, this experiment provides preliminary information about potential effects associated with the assessed treatments. However, additional studies are required to optimise treatment performance and to investigate the form and stability of mineral products formed by treatment. These studies should facilitate a more robust assessment of the reliability and safety of this technology for the long-term management of inorganic contaminants in cold regions, including Antarctica.

11.6: References

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11.7: Supplementary

Figure S11.1: PVC columns used in experimental trial.

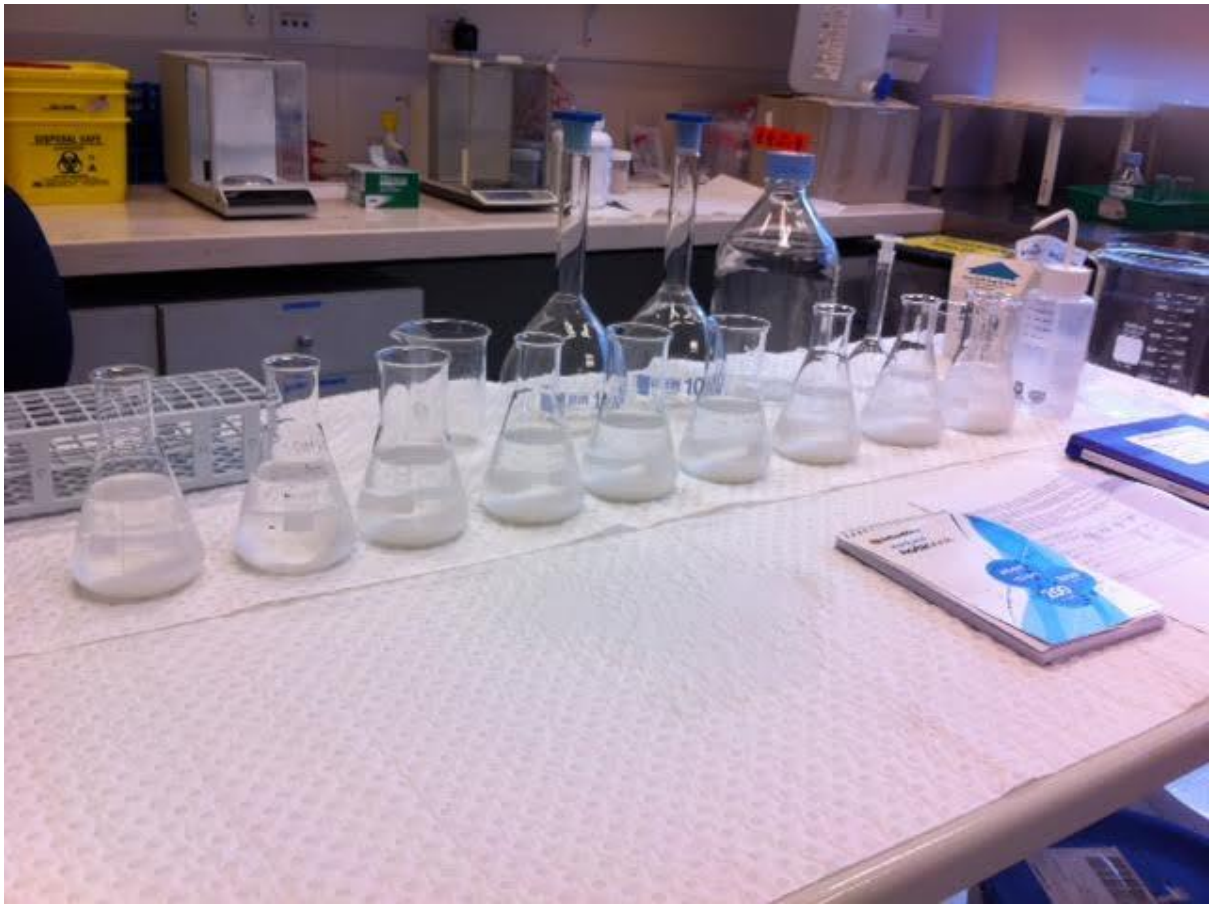

Figure S11.2: Silica treatments being prepared using sodium metasilicate.

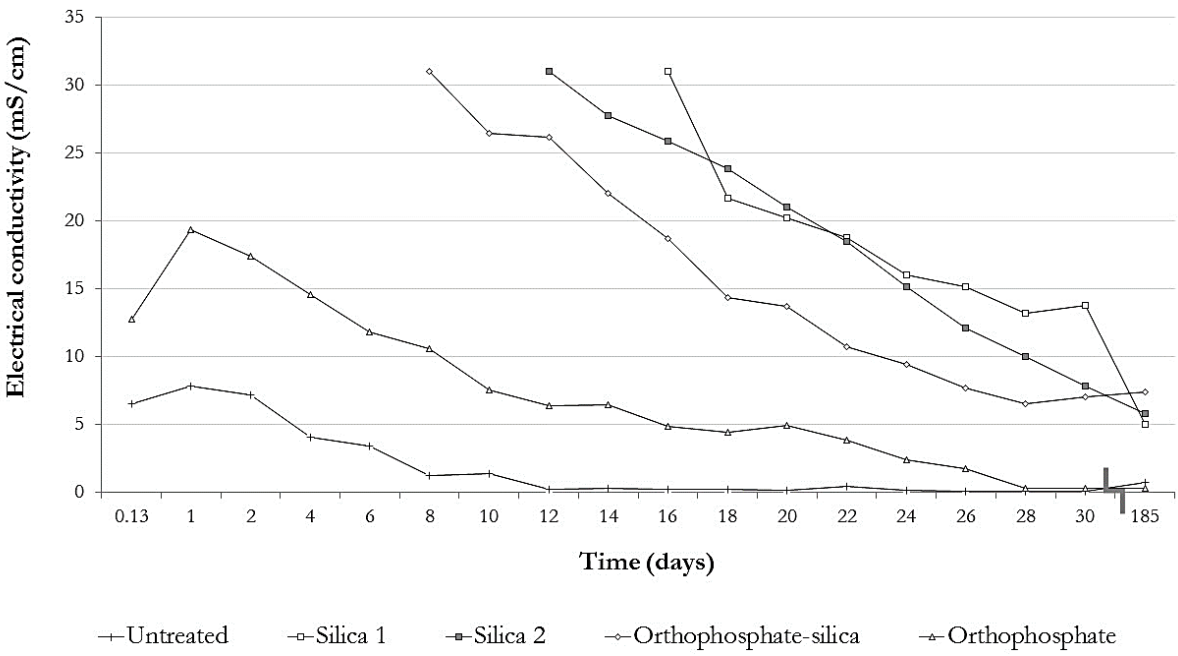

Figure S11.3: Electrical conductivity of leachate samples obtained over 185 days.

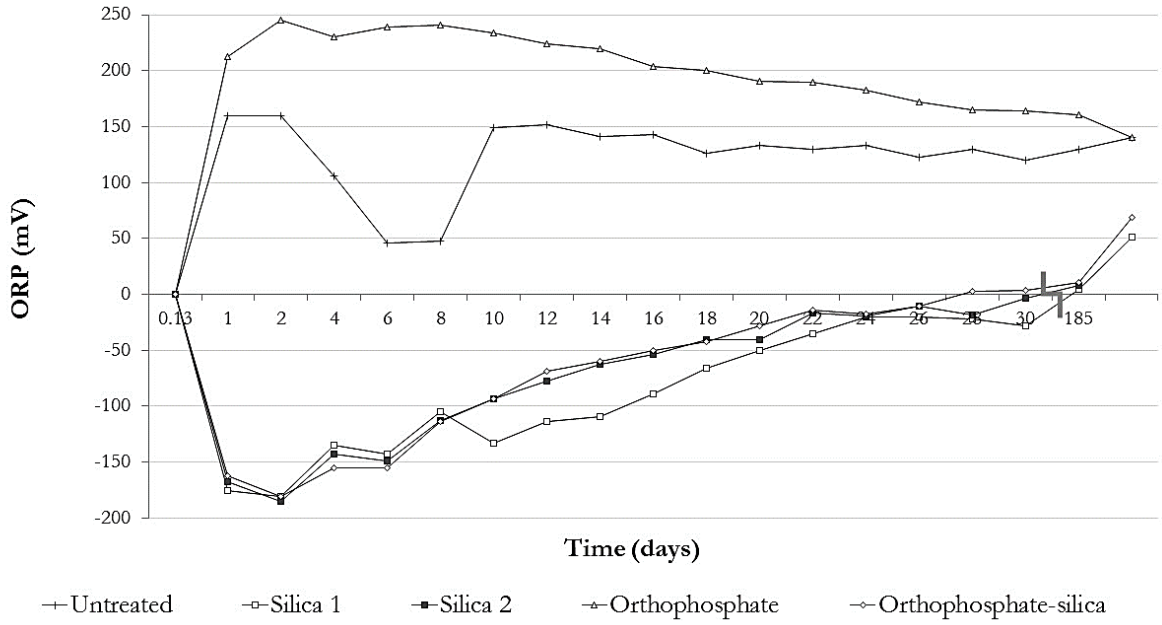

Figure S11.4: ORP measured in leachate samples obtained over 185 days.

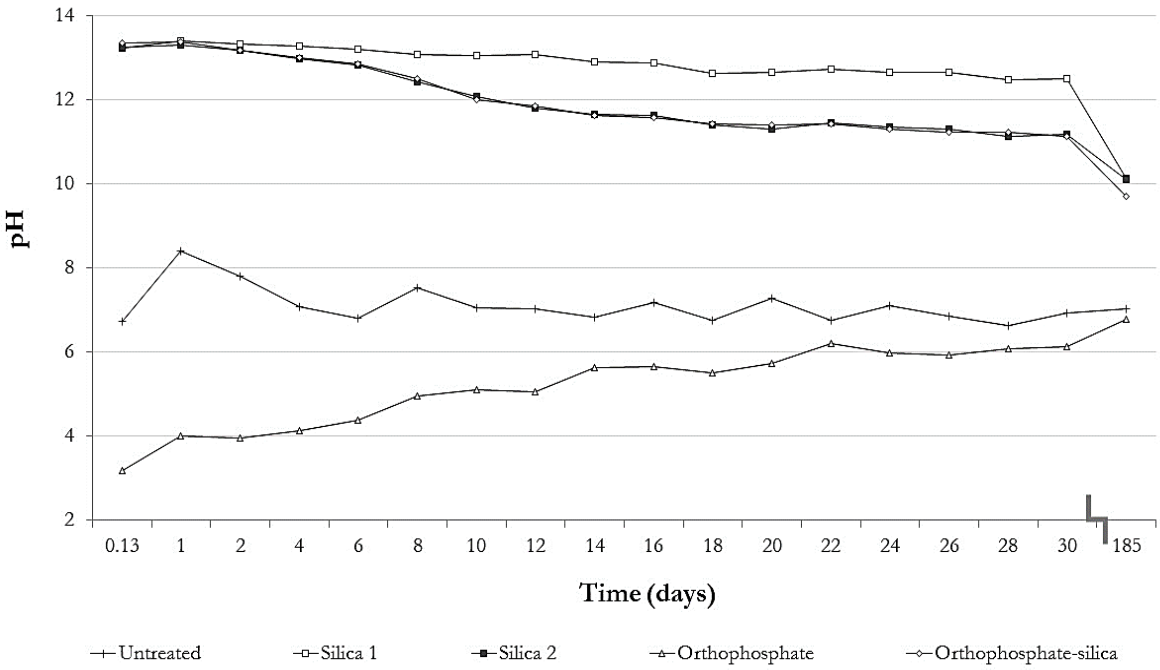

Figure S11.5: pH of leachate samples obtained over 185 days.

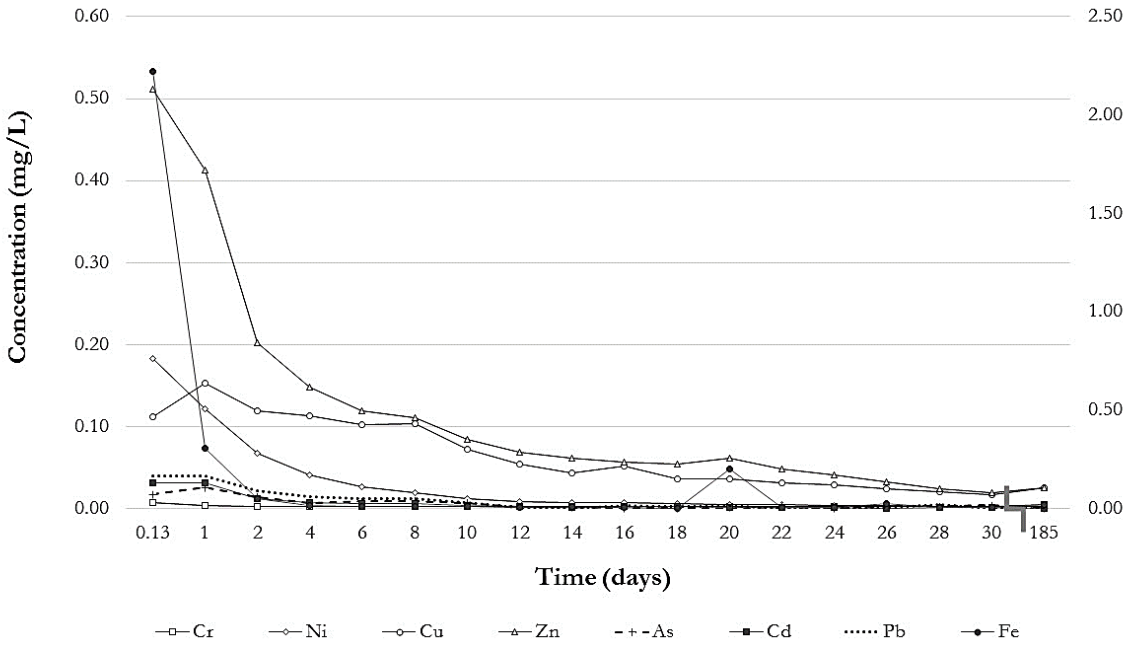

Figure S11.6: Concentration of inorganics in leachate collected from untreated soil orthophosphate. Concentration of Fe plotted on secondary axis.

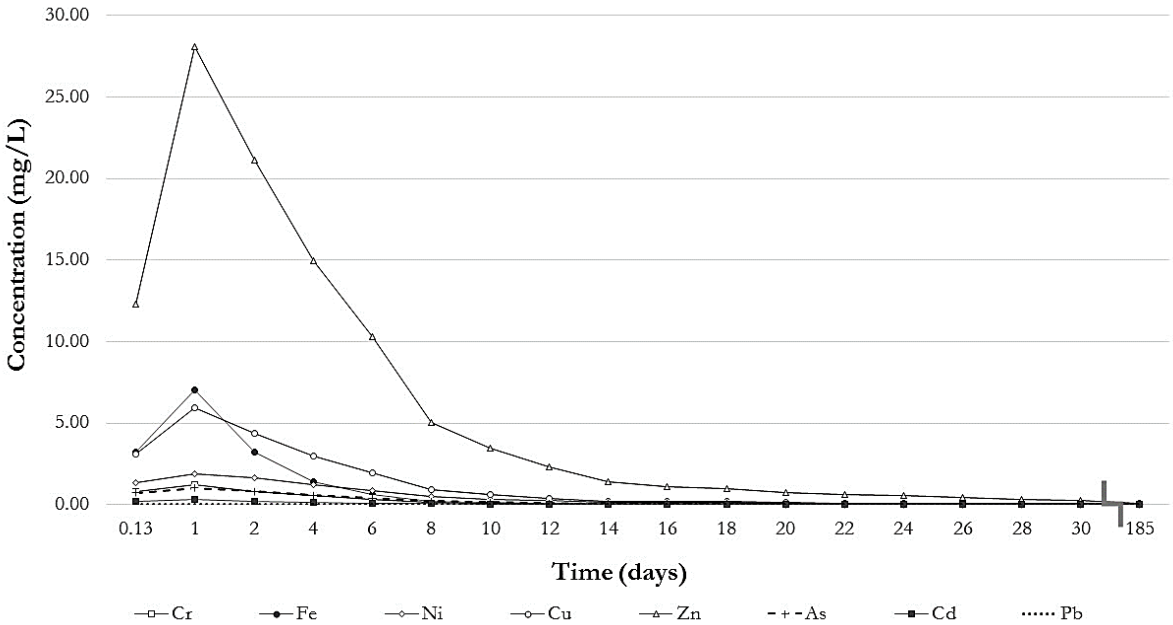

Figure S11.7: Concentration of inorganics in leachate collected from soil treated with orthophosphate.

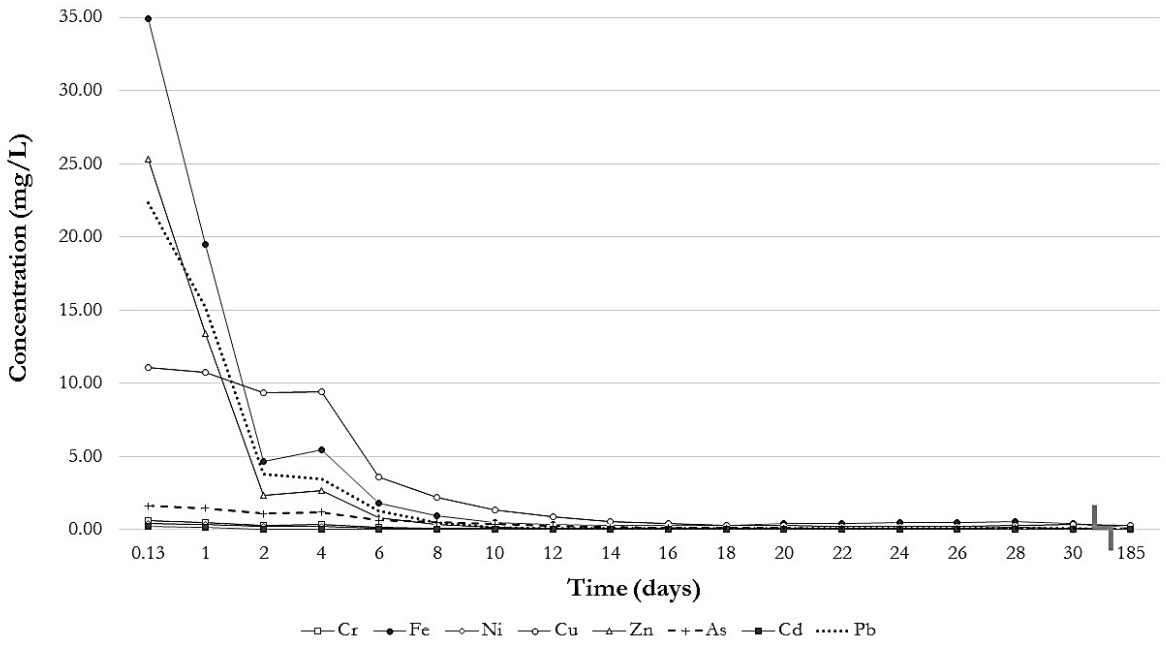

Figure S11.8: Concentration of inorganics in leachate collected from soil treated with coupled orthophosphate-silica.

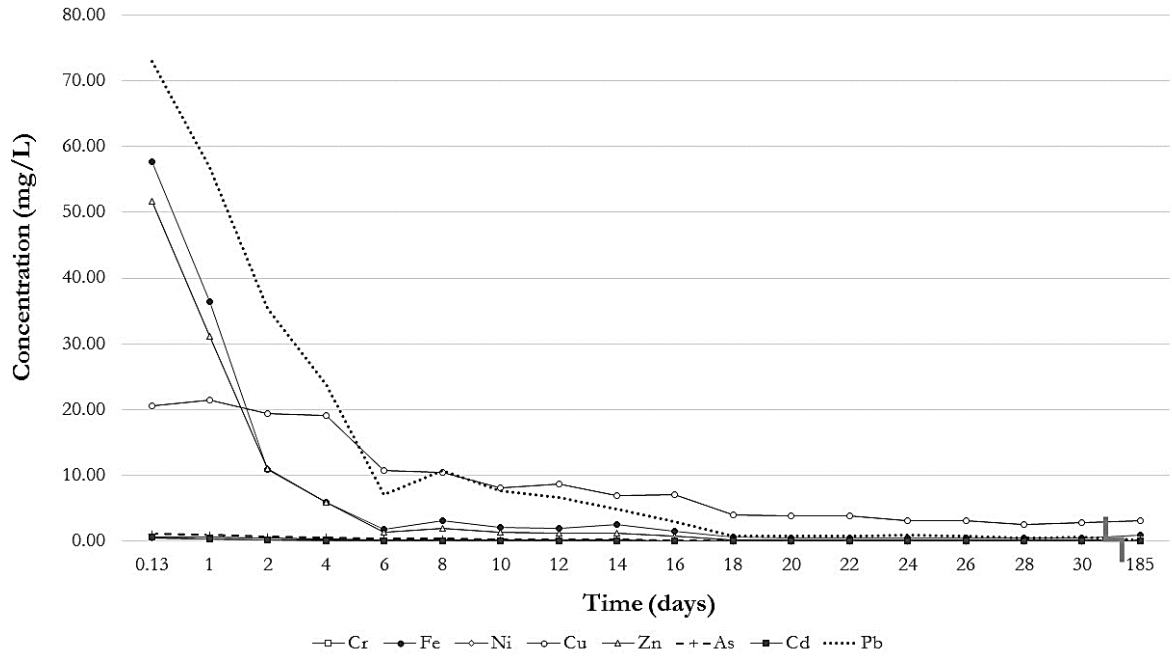

Figure S11.9: Concentration of inorganics in leachate collected from soil treated with silica 1.

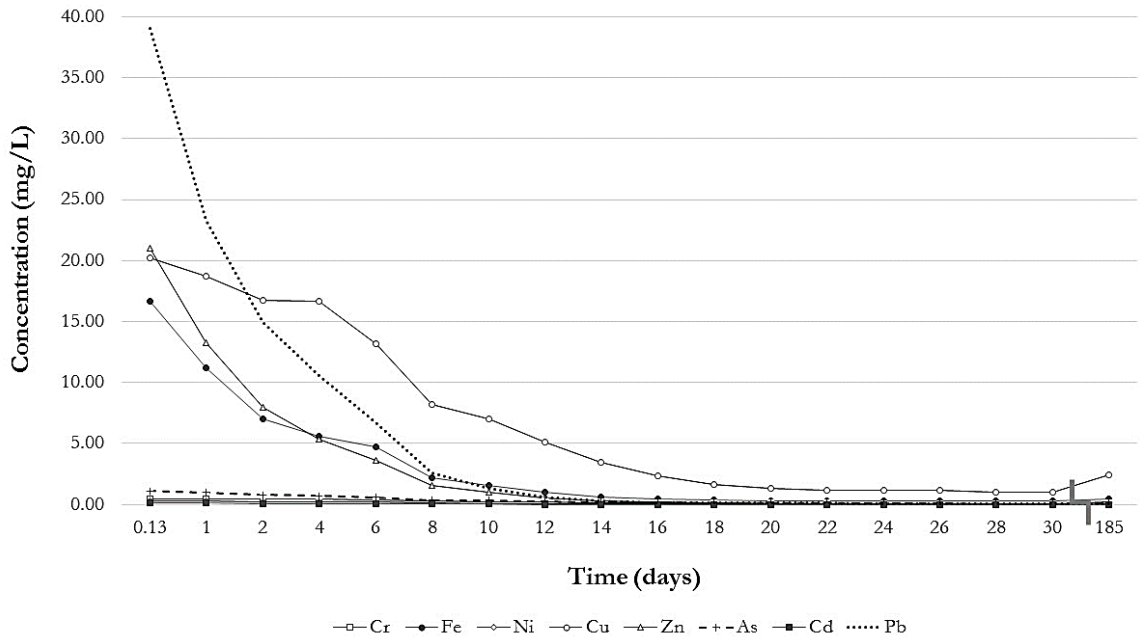

Figure S11.10: Concentration of inorganics in leachate collected from soil treated with silica 2.

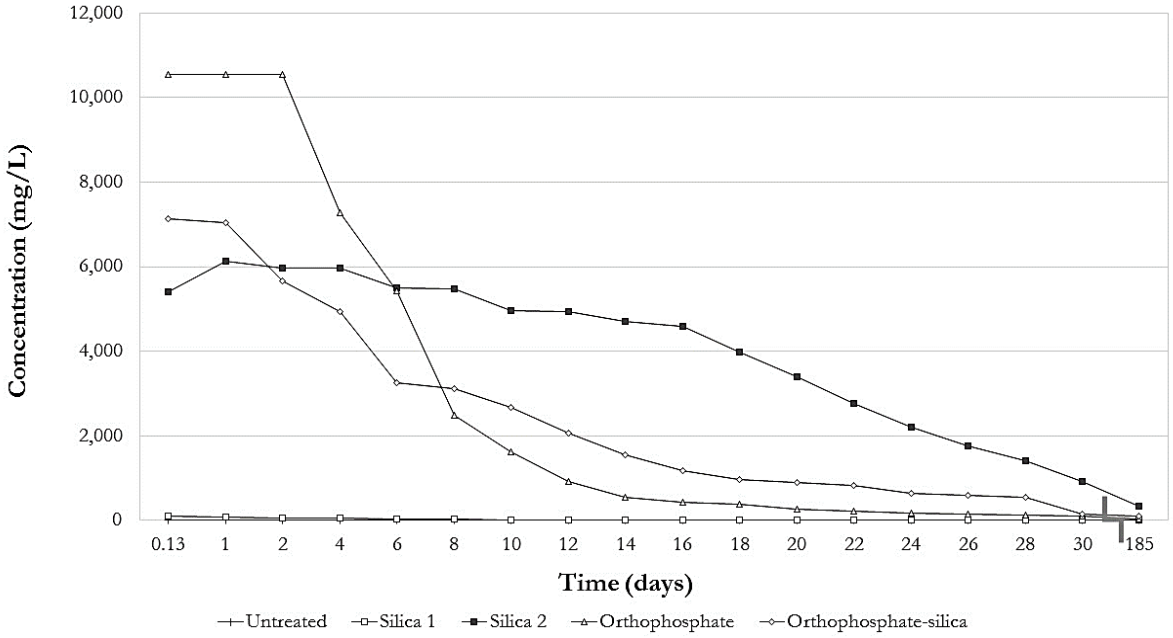

Figure S11.11: Concentration of P in leachate obtained over 185 days.

Table S11.1: Mass balance data presented as treatment effect ratios (calculated by leachable fraction of treated material/leachable fraction of untreated material). Values <1 indicate effective treatment. All treatments were effective for Fe, Cu, Zn and Pb.

Orthophosphate							
Day	**Cr**	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Pb**
0	1.0	1.6	0.5	1.8	0.5	1.0	2.4
61	1.0	0.0	1.0	0.2	0.2	1.0	0.0
185	1.0	0.2	3.0	0.7	0.4	1.0	0.0
Silica 1							
Day	**Cr**	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Pb**
0	1.0	1.0	0.5	1.3	1.2	1.0	0.9
61	1.0	0.1	1.0	0.2	0.2	1.0	0.2
185	1.0	0.2	3.0	0.6	0.5	1.0	0.2
Silica 2							
Day	**Cr**	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Pb**
0	1.0	1.2	1.0	1.5	1.0	1.0	6.0
61	1.0	0.0	0.5	0.4	0.1	1.0	0.0
185	1.0	0.0	1.0	0.1	0.1	1.0	0.0
Coupled orthophosphate-silica							
Day	**Cr**	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Pb**
0	1.0	0.9	0.5	0.6	0.7	1.0	6.0
61	1.0	0.1	1.5	0.0	0.0	1.0	0.0
185	1.0	0.1	2.0	0.0	0.0	1.0	0.0

Chapter 12: Characterising mineral products which form upon treatment of metals with orthophosphate, silica or coupled orthophosphate-silica treatments at 2 ºC

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Citation: Camenzuli D. 2015. Minerals Formed by Treatment of Heavy Metals with Orthophosphate, Silica or a coupled orthophosphate-silica Treatment under Cold Conditions. *International Journal of Environmental Science and Development 6*, 913-919.

Submitted: 30 September 2014; *Accepted for publication*: 2 March 2015; *Published*: 12 December 2015

Abstract

The application of orthophosphate and silica chemical treatments to contaminated land in cold regions remains understudied. The potential of coupled orthophosphate-silica treatments for the management of metal contaminated sites has not been examined. Investigation and characterisation of the mineral products which form during treatment, to ensure their suitability and stability for remediation and contaminant migration prevention is essential. This should be achieved prior to in situ implementation. This paper observes the mineral products formed by reaction between orthophosphate, silica and coupled orthophosphate-silica treatments and lead sulphate, copper oxide and zinc oxide systems over 114 days using X-ray diffractometry. Detectable changes to the mineral composition of analysed specimens occurred in all systems. Immobilisation was most effective for lead and least effective for zinc. This study demonstrates the potential of chemical treatments for the management of metal contaminated sites in cold regions. However, the results of this study demonstrate that treatments must be designed with consideration of factors such as environmental risk, the various stabilities of mineral products formed, temperature and the solubility of contaminant phases requiring treatment.

Keywords: Cold regions; Heavy metals; Immobilisation; Remediation; Stabilisation.

12.1: Introduction

Metal contaminated sites requiring treatment are widespread, even in remote, cold regions (Poland et al. 2003; Filler et al. 2006; Camenzuli et al. 2014). Managing contaminated land in cold regions is typically confounded by financial and logistical constraints, extreme weather and a lack of clear, governing legislation (Poland et al. 2003; Camenzuli et al. 2014). Cold regions are also characterised by low primary productivity, slow growth and degradation rates and are often more vulnerable to disturbance (Bargargli 2005; Filler et al. 2006; White et al. 2012). Excavation and subsequent removal of contaminated soil in cold regions is often not possible due to expense and large distances to secure landfills (White et al. 2012; Camenzuli et al. 2014). Furthermore, disturbance to contaminated material can result in the re-mobilization or re-suspension of contaminants. This is particularly relevant to permafrost, where thawing of previously frozen material may enhance metal contaminant solubility and the potential for contaminant migration (Deprez et al. 1999; Dyke 2001; Schindler and Lee 2010; White et al. 2012). Hence, technologies that can be applied on-site or in situ are often preferable when managing contaminated sites in remote, cold regions.

Chemical fixation technologies have been developed for on-site or in situ management of contaminated sites, and are widely used in temperate regions (Ma et al. 1993; Cao et al. 2008; Hafsteinsdóttir 2012; Camenzuli et al. 2014). Chemical fixation treatments immobilise metals and reduce the leachability and mobility of contaminants by converting metal ions into sparingly soluble, non-bioavailable minerals (Hafsteinsdóttir et al. 2011; White et al. 2012).

Several treatments have been developed and successfully applied to metal contaminated sites; for instance, orthophosphate, lime, bentonite, Portland cement and silicates (Basta and McGowen 2004; Guo et al. 2006; Shi et al. 2011; White et al. 2012; Camenzuli and Gore 2013). Studies reporting on successful immobilisation of metals using orthophosphate are abundant and the processes responsible for immobilisation are well described (Hafsteinsdóttir et al. 2015). Orthophosphate treatments achieve immobilisation by reacting with metal cations, including Mg^{2+}, Ca^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, and Pb^{2+}, to immobilise metals via precipitation or co-precipitation reactions in order to produce insoluble, metal-phosphate minerals (Hafsteinsdóttir et al. 2011; White et al. 2012; Camenzuli et al. 2014). However, there is a scarcity of research reporting on the successful application of silica treatments to metal contaminated sites (Camenzuli and Gore 2013). Silica treatments immobilise metals via one of three reactions: i) precipitation or co-precipitation reactions, ii) polymerisation of soluble silicates or iii) hydration-dehydration reactions (Mitchell et al. 2000a, b; Abdel-Hamid et al. 2012). Currently there are no published studies reporting on the application of silica or coupled orthophosphate-silica treatments to metal contaminated sites in cold regions, and consequently there is insufficient data to support their safe application in areas of freezing ground (Camenzuli and Gore 2013).

To assess the efficacy of silica treatments for the immobilisation of metals in cold regions, it is essential to first identify the metal-phosphate and metal-silicate products which form upon treatment and determine whether the formation of these mineral phases is rapid and stable enough to prevent contaminant migration (White et al. 2012). This study seeks to address this research gap by observing the products formed when orthophosphate, silica and a coupled orthophosphate-silica treatments react with metals in-vitro, in chemically simple systems, over 114 days at 2 °C, using X-ray diffractometry (XRD).

12.2: Methods

The experimental design of this study included two components. First, XRD was used to assess the purity of the treatment reagents and the other reactants used to form the three experimental systems; (i) lead sulphate ($PbSO_4$), (ii) copper oxide (CuO), (iii) zinc oxide (ZnO). These reagents were selected because of their presence in Antarctic landfills and use in prior studies, allowing comparisons (Hafsteinsdóttir et al. 2011; White et al. 2012). Reducing the number of reactants also meant that less abundant reaction products were more likely to be above detection limits, than if a larger number of phases were present in the specimens prepared and analysed.

In this experiment, the products formed by reactions between orthophosphate, silica and a coupled orthophosphate-silica treatment(s) and $PbSO_4$, CuO and ZnO were observed using XRD, under cold (2 °C) conditions. The composition and doses of treatments applied were based on previous studies (Fytas et al. 1999; Hafsteinsdóttir 2012; Camenzuli and Gore 2013; Camenzuli et al. 2015) Specimens were prepared by mixing duplicate 5 g portions of reagent grade $PbSO_4$, CuO and ZnO powders with orthophosphate, silica and a coupled orthophosphate-silica treatment(s) and loading the specimens onto stainless steel sample holders for analysis by XRD (n=24). The compositions of the four treatments applied are presented in Table 12.1.

Table 12.1: Composition of orthophosphate, silica and coupled orthophosphate-silica treatment

Treatment ID	Treatment composition	Total reagent
Orthophosphate	Triple super phosphate. Calcined magnesia.	1.88 g. 1.25 g.
Silica 1	Sodium metasilicate. Calcium carbonate.	1.88 g. 0.63 g.
Silica 2	Sodium metasilicate. Calcium carbonate. Orthophosphoric acid.	1.88 g. 0.63 g. 0.65 mL.
Orthophosphate-silica	Sodium metasilicate. Triple super phosphate. Calcined magnesia.	1.88 g. 1.88 g. 1.25 g.

Prior to the treatments being activated, the powder specimens were analysed on day 0 as experimental controls and to provide a benchmark for pre and post treatment comparisons (n=24). Once preliminary XRD analyses were completed, reactions were initiated by applying 1.88 g of sodium metasilicate dissolved in 3 mL of Type 1 deionised water to the silica treated specimens and 1 mL of Type I water to the orthophosphate and coupled orthophosphate-silica treated systems to prompt mineral formation. All reactions were conducted in air, as they would be in the field. Once treated, the loaded specimens were cooled to 2 °C in a Sanyo 253 incubator, and analysed 14, 77 and 114 days after treatment using XRD.

Diffractograms from 5 to 90° 2Θ were collected with a PANalytical X'Pert Pro MPD diffractometer, using 45 kV, 40 mA, CuKα radiation, X'Celerator detector, Bragg Brentano geometry, and a slew rate of 5° 2Θ per minute. Minerals were identified using PANalytical's Highscore Plus software v2.2.4, with ICDD PDF2 and PAN-ICSD databases.

12.3: Results

XRD analyses undertaken prior to treatment identified anglesite (lead sulphate) as the dominant mineral in all $PbSO_4$ systems. Semi-quantitative XRD analyses on day 0 indicated that the presence of anglesite and periclase (MgO) accounted for 80 wt% and 20 wt% of the minerals in $PbSO_4$ systems intended for treatment with orthophosphate or the coupled orthophosphate-silica treatment, respectively. Pre-treatment analyses of the systems intended for treatment with either silica 1 or silica 2 were characterised by 70 wt% anglesite and 30 wt% calcite (calcium carbonate).

Analyses of CuO systems on day 0, before orthophosphate or the coupled orthophosphate-silica treatments were activated were characterised as 70 wt% tenorite (copper oxide), with the remaining

30 wt% portion consisting of periclase and anhydrite (calcium sulphate). Trace levels of calcite were also detected on day 0 in the CuO systems intended for treatment with the coupled orthophosphate-silica. In CuO systems treated with silica 1 or silica 2, XRD analyses on day 0 identified the major peaks as tenorite and calcite. Semi-quantitative analyses indicated that tenorite and calcite accounted for 70 wt% and 30 wt% of the specimens, respectively.

Pre-treatment analyses of ZnO systems revealed that the mineral composition of specimens consisted of 70 wt% zincite (zinc oxide), and calcite and anhydrite accounted for 30 wt% in the orthophosphate systems. Pre-treatment analyses of ZnO specimens before treatment with silica 1 and 2 revealed the mineral composition as 70 wt% zincite and 30 wt% calcite. In the coupled orthophosphate-silica systems, semi-quantitative analyses on day 0 indicated that the samples consisted of approximately 70 wt% zincite with the remainder of the specimens being comprised of periclase and anhydrite minerals.

After treatment, distinct changes in the mineral composition of all analysed specimens were observed. Although several minerals formed within 14 days of treatment, the majority of minerals formed between days 14 and 114. A high level of consistency within the results of duplicate systems was achieved during pre and post treatment analyses in all systems. The most evident changes occurred in the $PbSO_4$ and CuO treated systems. Tables 12.2-12.5 summarise the predominant mineral products which formed over the 114 day study period and identifies their angular maximum intensity peak location.

The results from XRD analyses of $PbSO_4$, CuO and ZnO specimens treated with orthophosphate are in Table 12.2. Mineral formation as a result of treatment with orthophosphate was observed in $PbSO_4$ and CuO systems within 14 days of treatment and appear to have remained stable over the 114 day experimental period. Mineral formation in ZnO systems treated with orthophosphate was slower, but changes in the mineral composition of ZnO specimens were still detected by XRD before the end of the study period.

Table 12.2: Mineral products formed upon reactions with orthophosphate treatments and $PbSO_4$, CuO and ZnO (mineral name and 100% peak location in brakets).

Day	$PbSO_4$	CuO	ZnO
0	-Lead sulphate (anglesite) (29.71). -Magnesium oxide (periclase) (42.87).	-Copper oxide (tenorite) (35.50). -Magnesium oxide (periclase) (42.92). -Calcium sulphate (anhydrite) (25.50).	-Zinc oxide (zincite) (36.27). -Magnesium oxide (periclase) (42.88). -Calcium sulphate (anhydrite) (25.41).
14	-Lead sulphate (anglesite) (29.715). -Magnesium oxide (42.89). -Calcium phosphate hydroxide hydrate (brushite) (11.66). -Magnesium phosphate hydrogen hydrate (newberyite) (14.99).	-Copper oxide (tenorite) (35.50). -Magnesium oxide (periclase) (42.92). -Calcium sulphate (anhydrite) (25.46). -Calcium magnesium carbonate (calcite) (29.73). -Calcium iron silicate (30.94). -Silicon oxide (coesite) (29.08).	-Zinc oxide (zincite) (36.27). -Magnesium oxide (periclase) (42.88). -Calcium sulphate (anhydrite) (25.46).
77	-Lead sulphate (anglesite) (29.68). -Silicon oxide (coesite) (28.93). -Calcium phosphate hydroxide hydrate (brushite) (11.62). -Magnesium hydroxide (brucite) (18.60). -Magnesium phosphate hydrogen hydrate (newberyite) (14.72).	-Copper oxide (tenorite) (35.44). -Magnesium oxide (periclase) (42.91). -Calcium sulphate (anhydrite) (25.46). -Calcium magnesium carbonate (calcite) (29.73). -Calcium iron silicate (30.94). -Silicon oxide (coesite) (29.08).	-Zinc oxide (zincite) (36.26). -Magnesium oxide (periclase) (42.93). -Calcium sulphate (anhydrite) (25.468).
114	- Lead sulphate (anglesite) (29.68). -Silicon oxide (coesite) (29.18). -Calcium phosphate hydroxide hydrate (brushite) (11.60). -Magnesium hydroxide (brucite) (38.08). - Magnesium phosphate hydrogen hydrate (newberyite) (14.72). -Sodium calcium sulphate hydrate (bassanite) (31.76).	-Copper oxide (tenorite) (38.75). -Calcium sulphate (anhydrite) (25.50). -Calcium magnesium carbonate (calcite) (29.76). -Calcium iron silicate (30.94). -Silicon oxide (coesite) (29.08). -Calcium hydrogen phosphate hydrate (brushite) (11.65). -Magnesium phosphate hydrate (newberyite) (25.80).	-Zinc oxide (zincite) (36.36). -Magnesium oxide (periclase) (42.92). -Calcium sulphate (anhydrite) (25.50). -Calcium sulphate hydrate (bassanite) (29.76). -Magnesium phosphate hydrate (cattiite) (31.19).

In $PbSO_4$ systems, the predominant minerals formed upon reaction with orthophosphate included coesite, brushite, brucite, newberyite and bassanite. In CuO systems, anhydrite, calcium iron silicates,

coesite, brushite and newberyite formed. Although mineral formation in ZnO systems was slower and less pronounced than in $PbSO_4$ and CuO systems, bassanite and cattiite formed between days 77 and 114.

Mineral formation upon reaction between $PbSO_4$, CuO and ZnO systems with silica 1 treatment was more rapid and prominent in $PbSO_4$ systems than CuO and ZnO treated systems. Table 12.3 presents the results from XRD analyses and demonstrates that the predominant new minerals identified upon treatment with silica 1 in $PbSO_4$ systems were thenardite, cerrusite, coesite, gypsum, portlandite, brushite and leadhillite. Of further significance is the distinct decline in the intensity of anglesite peaks, with the complete disappearance of anglesite peaks at 22, 27, 36, 42, 44, 54, 68, 78, 83 and 86 °2Θ. Natron, cristobalite, tobermorite and mouetite formed in CuO systems treated with silica 1. Alternatively, no new mineral products were detected by XRD upon reaction between ZnO and the silica 1 treatment; however, the intensity of all zincite peaks detected by XRD declined significantly.

Table 12.3: Mineral products formed upon reactions with silica 1 and $PbSO_4$, CuO and ZnO (mineral name and 100% peak location in brakets).

Day	$PbSO_4$	CuO	ZnO
0	-Lead sulphate (anglesite) (29.73). -Calcium carbonate (calcite) (29.36).	-Copper oxide (tenorite) (35.47). -Calcium carbonate (calcite) (29.47).	-Zinc oxide (zincite) (36.25). -Calcium carbonate (calcite) (29.41).
14	- Lead sulphate (anglesite) (32.25). -Calcium carbonate (calcite) (29.47). -Sodium sulphate (thenardite) (29.706). - Silicon oxide (coesite) (29.26).	-Copper oxide (tenorite) (35.55). -Calcium carbonate (calcite) (29.50). -Sodium carbonate hydrate (natron) (32.32).	-Zinc oxide (zincite) (36.43). -Calcium carbonate (calcite) (29.41).
77	-Lead sulphate (anglesite) (32.25). -Calcium carbonate (calcite) (29.47). -Sodium sulphate (thenardite) (29.706). -Silicon oxide (coesite) (29.26). -Calcium sulphate hydrate (gypsum) (20.73). -Calcium hydroxide (portlandite) (34.10).	-Copper oxide (tenorite) (35.55). -Calcium carbonate (calcite) (29.39). -Sodium carbonate hydrate (natron) (16.50). -Silicon oxide (cristobalite) (22.26).	-Zinc oxide (zincite) (36.18). -Calcium carbonate (calcite) (29.41).
114	-Lead sulphate (anglesite) (32.10). -Lead carbonate (cerrusite) (24.92). -Calcium carbonate (calcite) (29.41). -Sodium sulphate (thenardite) (32.25). -Calcium sulphate hydrate (gypsum) (20.77). -Calcium hydroxide (portlandite) (34.10). -Calcium phosphate hydroxide hydrate (brushite) (11.60). -Lead sulphate carbonate hydroxide (leadhillite) (24.93).	-Copper oxide (tenorite) (35.56). -Calcium carbonate (calcite) (29.52). -Sodium carbonate hydrate (natron) (16.50). -Silicon oxide (cristobalite) (22.26). -Calcium silicate hydroxide (tobermorite) (29.47). -Calcium magnesium phosphate hydrate (mouetite) (26.59).	-Zinc oxide (zincite) (36.10). -Calcium carbonate (calcite) (29.37).

Substantial changes to the mineral composition of all specimens treated with silica 2 occurred within 14 days of treatment. By day 114, thenardite, gypsum, coesite, lead silicates and bearthite formed in

$PbSO_4$ treated systems. The intensity of anglesite peaks generally declined over time and all anglesite peaks detected before treatment between 73-90° disappeared by day 114. In CuO treated systems, carnegiete, bohmite and calcium magnesium silicate minerals formed. Interestingly, the ZnO systems treated with silica 2 demonstrated the largest growth of new minerals of any ZnO treated system. Unidentified zeolites, monohydrocalcite, chiral zincophosphate and hopeite all formed within 114 days in the ZnO silica 2 treated systems (Table 12.4).

Table 12.4: Mineral products formed upon reactions with silica 2 and $PbSO_4$, CuO and ZnO (mineral name and 100% peak location in brakets).

Day	$PbSO_4$	CuO	ZnO
0	-Lead sulphate (anglesite) (29.73). -Calcium carbonate (calcite) (29.47).	-Copper oxide (tenorite) (35.54). -Calcium carbonate (calcite) (29.40).	-Zinc oxide (zincite) (36.26). -Calcium carbonate (calcite) (29.40).
14	-Lead sulphate (anglesite) (29.68). -Silicon oxide (coesite) (29.41). -Zeolite (13.55). -Calcium silicate (32.79). -Calcium aluminum silicate hydroxide (clinozoisite) (30.88).	-Copper oxide (tenorite) (35.54). -Calcium carbonate (calcite) (29.47).	-Zinc oxide (zincite) (36.27). -Calcium carbonate (calcite) (29.45). -Sodium zinc phosphate hydrate (chiral zincophosphate) (11.37). -Calcium aluminum silicate (cristobalite) (22.16).
77	-Lead sulphate (anglesite) (29.37) -Sodium sulphate (thenardite) (32.14). -Calcium sulphate (gypsum) (20.73). -Silicon oxide (coesite) (29.35). -Sodium aluminum silicate (albite) (27.85).	-Copper oxide (tenorite) (35.54). -Calcium carbonate (calcite) (29.37). -Aluminum oxide hydroxide (bohmite) (14.49). -Sodium aluminum oxide silicate (carnegiete) (20.81). -Calcium iron silicate (ferrobustamite) (30.37).	-Zinc oxide (zincite) (36.09). -Calcium carbonate (calcite) (29.37). -Silicon dioxide (zeolite) (11.26). -Sodium zinc phosphate hydrate (chiral zincophosphate) (11.37). -Sodium aluminum silicate hydrate (24.61).
114	-Lead sulphate (anglesite) (29.71). -Sodium sulphate (thenardite) (32.25). -Calcium sulphate (gypsum) (20.74). -Silicon oxide (coesite) (29.35). -Lead silicate (30.85). -Calcium aluminum phosphate hydroxide (bearthite) (29.21).	-Copper oxide (tenorite) (35.25). -Calcium carbonate (calcite) (29.37). -Sodium aluminum oxide silicate (carnegiete) (20.82). -Aluminum oxide hydroxide (bohmite) (14.49). -Calcium magnesium silicate (30.40).	-Zinc oxide (zincite) (36.09). -Calcium carbonate (calcite) (29.18). -Silicon dioxide (zeolite) (11.26). -Calcium carbonate hydrate (monohydrocalcite) (20.52). -Sodium zinc phosphate hydrate (chiral zincophosphate) (11.37). -Sodium zinc phosphate hydrate (hopeite) (9.58).

Table 12.5 includes the results from $PbSO_4$, CuO and ZnO systems treated with the coupled orthophosphate-silica treatment. XRD analyses detected the formation of thenardite, coesite, brushite, hydroxylapatite and spurrite in the $PbSO_4$ systems treated with the coupled orthophosphate-silica treatment. Further, anglesite peaks at 22, 24, 26, 28, 29, 37 and 78° disappeared in $PbSO_4$ systems by day 114. In CuO systems, thenardite, and natrolite formed, while zeolite and anhydrite formed in ZnO systems treated with the coupled orthophosphate-silica treatment.

Table 12.5: Mineral products formed upon reactions with coupled orthophosphate-silica and $PbSO_4$, CuO and ZnO (mineral name and 100% peak location in brakets).

Day	$PbSO_4$	CuO	ZnO
0	-Lead sulphate (anglesite) (29.93). -Magnesium oxide (periclase) (42.92).	-Copper oxide (tenorite) (35.54). -Magnesium oxide (periclase) (42.94). -Calcium sulphate (anhydrite) (25.46). -Calcium magnesium carbonate (calcite) (29.73).	-Zinc oxide (zincite) (36.26). -Magnesium oxide (periclase) (42.89). -Calcium sulphate (anhydrite) (25.44).
14	-Lead sulphate (anglesite) (29.71). -Magnesium oxide (42.86). -Sodium sulphate (thenardite) (32.09). -Calcium lead phosphate hydroxide (hydroxylapatite) (30.72).	-Copper oxide (tenorite) (35.49). -Magnesium oxide (periclase) (42.94). -Calcium sulphate (anhydrite) (25.50).	-Zinc oxide (zincite) (36.27). -Magnesium oxide (periclase) (42.91). -Calcium sulphate (anhydrite) (25.49).
77	- Lead sulphate (anglesite) (29.68). -Sodium sulphate (thenardite) (32.09). -Silicon oxide (coesite) (28.93). -Calcium phosphate hydroxide hydrate (brushite) (11.60). - Calcium lead phosphate hydroxide (hydroxylapatite) (30.66). -Calcium carbonate silicate (spurrite) (33.14).	-Copper oxide (tenorite) (38.74). -Sodium sulphate (thenardite) (32.25). -Magnesium oxide (periclase) (42.89). -Zeolite (6.12). Silicon oxide (20.41).	-Zinc oxide (zincite) (36.27). -Magnesium oxide (periclase) (42.89). -Calcium sulphate (anhydrite) (25.44). -Sodium sulphate (thenardite) (32.25).
114	-Lead sulphate (anglesite) (29.68). -Sodium sulphate (thenardite) (32.10). -Calcium phosphate hydroxide hydrate (brushite) (11.60). - Calcium lead phosphate hydroxide (hydroxylapatite) (30.60). -Calcium carbonate silicate (spurrite) (33.14).	- Copper oxide (tenorite) (35.54). -Sodium sulphate (thenardite) (32.55). -Zeolite (6.16). -Sodium aluminum silicate hydrate (natrolite) (31.77).	- Zinc oxide (zincite) (36.27). -Magnesium oxide (periclase) (42.94). -Calcium sulphate (anhydrite) (25.54). -Sodium sulphate (thenardite) (32.19).

12.4: Discussion

The primary objectives of this research were i) to characterise the mineral products formed upon treatment of $PbSO_4$, CuO and ZnO with orthophosphate, silica or a coupled orthophosphate-silica treatment(s), and ii) to determine whether the mineral products formed upon treatment are suitably rapid and stable for the prevention of contaminant migration.

The results obtained from $PbSO_4$, CuO and ZnO systems treated with orthophosphate display a high level of consistency with results from laboratory trials (Hafsteinsdóttir et al. 2011; White et al. 2012; Hafsteinsdóttir et al. 2013), which investigated the efficacy of orthophosphate treatments at immobilising metal contaminants under cold conditions and examined the effects of freeze-thaw cycling on mineral stability. The orthophosphate treatment applied in this study had a detectable impact on all systems, but was most effective at reducing the intensity of anglesite XRD reflections in the $PbSO_4$ systems. Although no new Pb-orthophosphate minerals were quantified by XRD, all of the treatment reagents were either consumed or formed new products over the 114 day study period. This is evident by the presence of phosphate being detected by XRD only in the mineral forms of brushite and newberyite. The XRD detection limit (up to 2 wt%) may also explain why Pb-orthophosphate minerals were not detected after treatment.. Orthophosphate was also effective for CuO, with new mineral products being formed within 14 days of treatment and remaining stable over the 114 day study.

Treatment of ZnO with orthophosphate resulted in the precipitation of new mineral products including bassanite and cattiite between days 77 and 114 (Table 12.2). However, the primary contaminant phases anglesite, tenorite and zincite were still detectable by XRD in ZnO systems treated with orthophosphate at the end of the study period. This is attributed to the lower solubility of ZnO relative to $PbSO_4$ and CuO. Although less effective for ZnO, the clear reduction in the intensity of anglesite, tenorite and zincite peaks and formation of new, stable minerals including anhydrite, coesite, cattiite, bassanite, brushite and brucite after treatment with orthophosphate illustrates the potential of this treatment for metal contaminated sites in cold regions (Hafsteinsdóttir et al. 2011; Hafsteinsdóttir 2012; White et al. 2012; Camenzuli et al. 2014). However, there are two significant disadvantages surrounding this treatment strategy. Firstly, orthophosphate treatments have been found to mobilise metals and metalloids including arsenic (Peryea 1991), and secondly, over-dosage can lead to eutrophication. These represent important environmental risk considerations which must be addressed prior to on-site or in situ application of this treatment.

Hydroxides, calcium silicates and metal silicate minerals precipitated upon reaction between metals with silica, indicating that the pH declined to a level suitable for immobilisation (Mitchell et al. 2000a, b; Camenzuli and Gore 2013). This is consistent with the results of this study. XRD analyses identified hydroxides, calcium silicates and metal silicates in both silica 1 and 2 treated systems. Of the silica

treated systems, silica 2 was more effective at immobilising metals in all systems. Although several stable minerals also formed upon treatment with silica 1 (Table 12.3), a larger range of stable mineral products formed upon treatment with silica 2 (Table 12.4). This is most evident in ZnO treated systems, where reactions between ZnO and silica 2 treatment produced more stable minerals than any other treatment (Table 12.4). The increased immobilisation potential and efficiency of silica 2 demonstrated the effect of supplying orthophosphoric acid to the treated material directly after the application of a silica solution. Orthophosphoric acid improved immobilisation efficacy in two ways. Firstly, it facilitated direct reactions between phosphorus and metals which prompts the formation of new phosphate minerals, similar to the orthophosphate treatment. Secondly, the application of orthophosphoric acid decreases the pH of the treated material which enhanced the gelation reactions responsible for the polymerisation of soluble silicates, thereby initiating faster and more complete formation of insoluble silicate and calcium minerals (Camenzuli and Gore 2013). A further advantage of applying orthophosphoric acid directly after a silica treatment is the increased probability of producing a pH neutral post-treatment soil material.

The coupled orthophosphate-silica also was effective at immobilising metals, and unsurprisingly several minerals that precipitated in the orthophosphate and silica treated systems (including thenardite, coesite, natrolite, brushite and anhydrite) were detected in the specimens treated with the coupled orthophosphate-silica treatment.

The formation of measureable quantities of new mineral species, changes to the mineral composition of analysed specimens and reductions in the intensity of contaminant peaks was observed in all systems, over the 114 day study period. The results in this study are consistent with recent literature reviews (Camenzuli and Gore 2013; Hafsteinsdóttir et al. 2015) and experimental studies (Hafsteinsdóttir et al. 2011; Abdel-Hamid et al. 2012; White etl. 2012; Camenzuli et al. 2015). Although contaminant species remained present in all systems at the end of the study period, by day 114 the intensity of anglesite peaks in $PbSO_4$ systems were reduced to below detection limits in all treated systems, and CuO systems appeared to have reached equilibrium by the end of the study period. Immobilisation of ZnO was slower and less complete; however, the silica 2 and coupled orthophosphate-silica treatments demonstrate strong potential for ZnO immobilisation in cold regions.

Several factors can account for the variation in treatment performance for different metals, some of which have been discussed in earlier studies (White et al. 2012). The precipiation of copper phases is typically unaffected by low temperatures; however, reaction kinetics in cold conditions are reduced and can result in slower formation of certain minerals. As such, it is possible that a longer-term study of a similar design might detect new mineral phases not identified in this study. Another important consideration surrounding the treatment of lead, particularly with orthophosphate is the solubility of

reaction products formed during treatment. In many cases the products produced by treatment of lead with orthophosphate under cold conditions are more soluble, less complete and less stable than those produced upon reaction between orthophosphate and other metals e.g. copper, under cold conditions (White et al. 2012; Ossorio et al. 2013). The treatments were less effective at immobilising ZnO, possibly due to the lower solubility of zinc leading to the formation of fewer, less soluble mineral products (White et al. 2012).

Other factors independent of the type of metals requiring treatment may also affect the performance of chemical treatments. Orthophosphate in the form of triple super phosphate is naturally acidic and requires pH buffering in acidic soils prior to treatment to maintain an environment with a pH suitable for mineral formation without causing acidification or mobilising metals or metalloids (Hafsteinsdóttir et al. 2015). With respect to silica treatments, the solubility of silica dramatically decreases in environments where pH is below 7-8. This requires the development of highly alkaline treatment solutions to ensure that silica remains in solution long enough to react with contaminants prior to precipitation (Camenzuli and Gore 2013). After treatment a mildly acidic solution is required to reduce pH to a level suitable for mineral formation and restore the system to an environmentally suitable pH. Salinity may also affect mineral production and the stability of minerals, for example the stability of bassanite increases with increasing salinity (Doner and Lynn 1989). The reverse effect is also possible for other mineral products and has the potential to reduce the effectiveness of remediation (Ossorio et al. 2013). Temperature also plays an important role by reducing the speed of reaction kinetics, but can also change the mineral composition of treated materials, for example the more stable thenardite transforms into mirabilite at lower temperatures (-8.2-1.2 °C) (Doner and Lynn 1989; Marion et al. 1999; Warren 2010; Hafsteinsdóttir et al. 2011). This also highlights the importance of natural freeze-thaw cycling in cold environments as mineral products can be altered by temperature or as a result of desiccation upon thawing (Hafsteinsdóttir et al. 2011, 2013).

Although this study provides new information supporting the application of orthophosphate, silica and coupled orthophosphate-silica treatments in cold regions, it is limited in several ways. Firstly, the relatively short time frame of the experiment (114 days) does not provide for a detailed understanding of the longer term stability of these reactant products, nor does it an allow for a characterisation of mineral products which form over longer times. This is particularly relevant to these results as the entire experiment was undertaken under cold conditions which reduces the speed of reaction kinetics significantly. Further, this study did not examine the effects of natural freeze-thaw cycling. Freezing and thawing might change the mineral products formed, or result in hydration and dehydration of minerals, which might affect the stability of reaction products formed during treatment (Hafsteinsdóttir et al. 2011, 2013). This also influences the long-term efficacy of in situ application of such treatments and represents an important consideration when applying this technique in cold

regions. Another limitation of this study is that it assessed only three metal species ($PbSO_4$, CuO and ZnO), and an assessment on a wider range of contaminants would be beneficial and provide a better indication of the overall performance of this technology for management of metal contaminated sites.

12.5: Conclusion

This study characterised the mineral products formed upon reactions between $PbSO_4$, CuO and ZnO with orthophosphate, silica and a coupled orthophosphate-silica treatment under cold conditions. Detectable minerals formed within all systems and these remained stable over the study period indicating that these treatments have the potential to immobilise metals and prevent contaminant migration at contaminated sites in cold regions. However, further studies are required before the safety and efficacy of the treatments trialed in this experiment can be considered safe for on-site or in situ application.

This study examined the performance of four treatments at immobilising metals in reagent grade chemical systems in order to characterise mineralogy. In natural soil environments, porosity, grain and soil pore size, organic content and competing ions all affect treatment performance. Therefore, studies which consider the impact of these natural factors should be undertaken before this technology is implemented on-site or in situ at metal contaminated sites. To achieve this, long-term batch and field based experiments trialing additional treatment compositions on a wider range of materials and soil types are required. Such experiments should assess treatment performance by measuring the total concentrations of metals in soil and leachate and should monitor soil pH, salinity and oxidation-reduction state.

12.6: Acknowledgements

D. Camenzuli thanks Russell Field for training on X-ray diffractometry techniques and analyses and assistance in the laboratory, and Marek Roullion and the reviewers for feedback on the manuscript.

12.7: References

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Chapter 13: Treatment of soil co-contaminated with metals and petroleum hydrocarbons using silica treatments

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Submitted for publication in the Journal of Hazardous Materials: 7 August 2015 (Manuscript number: 15-03271)

Abstract

Successful remediation of contaminated land in cold regions is challenged by freeze-thaw cycling, slow rates of natural hydrocarbon attenuation, extreme weather and logistical constraints. At sites co-contaminated with metals and petroleum hydrocarbons, microbial activity is suppressed and biodegradation of petroleum hydrocarbons is slowed further. This study assesses the performance of eight silica treatments for immobilising inorganics (Al, Cr, Fe, Ni, Cu, Zn, As, Cd and Pb) and reducing the concentrations of petroleum hydrocarbons in co-contaminated soil at 2 °C. Treatments containing orthophosphoric acid immobilised Cu, Zn, Cd and Pb, but mobilised As. The formation of hydroxypyromorphite, sodium aluminosilicates and calcium bearing minerals were observed following treatment, demonstrating the potential for successful immobilisation of inorganics using silica treatments. Silica treatments were less effective at reducing concentrations of petroleum hydrocarbons in soil relative to inorganics, indicating that further research is required to optimise treatment performance in materials co-contaminated with inorganics and petroleum hydrocarbons.

Keywords: Remediation; Pollution; Silica; Stabilisation; Encapsulation.

13.1: Introduction

Soil and sediment contaminated with inorganics and petroleum hydrocarbons, associated with urbanisation, industrialisation, resource extraction and waste disposal, can create widespread environmental and human health problems (Poland et al. 2003; Martin and Ruby 2004; Dong et al. 2013). Methods for managing inorganics or petroleum hydrocarbon contaminated soil are well described (Martin and Ruby 2004; Filler et al. 2006; Kumpiene et al. 2008; Camenzuli et al. 2014). However, managing soils co-contaminated with inorganics and petroleum hydrocarbons is more complicated due to the diverse chemical processes and remediation technologies required by individual contaminants for effective remediation (Dong et al. 2013). Biodegradation of petroleum hydrocarbons in soil can also be suppressed in the presence of elevated concentrations of metals in soil (Dong et al. 2013). For example, Co, Ni, Cu, Zn, Cd and Pb can inhibit the activity of degrading bacteria (Al-Saleh and Obuekwe 2005; Sprocati et al. 2006; Alisi et al. 2009; Dong et al. 2013).

Managing contaminated sites in remote, cold regions involves multiple challenges (Poland et al. 2003; Filler et al. 2006; Camenzuli et al. 2014). Contaminants can be solubilised due to freeze-thaw cycling and can rapidly disperse off-site (Filler et al. 2006; White et al. 2012; McDonald and Knox 2014). The mobilisation of some contaminants (e.g. As) due to a change in pH or redox conditions also requires monitoring (Basta and McGowen 2004; Sprocati et al. 2006; White et al. 2012; Dong et al. 2013). Furthermore, terrestrial and marine wildlife in cold regions such as Antarctica show increased sensitivity when exposed to contaminants and experience slower rates of recovery relative to temperate species (Bargagli 2005; Mooney et al. 2013; Payne et al. 2014). Rates of petroleum hydrocarbon volatilisation and biodegradation are also slower in cold regions and are hindered by cold related decreases in microbial metabolic activity, which can prolong remediation (Filler et al. 2006; McDonald and Knox 2014). Finally, the logistical and financial constraints associated with operating in remote, cold regions renders many of the traditional approaches to remediation such as dig and haul, less suitable in areas of freezing ground than most temperate areas (Filler et al. 2006; Camenzuli et al. 2014; McDonald and Knox 2014).

Silica treatments have potential for concurrent remediation of inorganics and petroleum hydrocarbons in soil (Mitchell et al. 2000a, b; Camenzuli and Gore 2013). As a low-cost, low maintenance technology that can be applied in-situ, silica treatments demonstrate high suitability for use in both temperate and cold regions (Mitchell et al. 2000a, b; Camenzuli and Gore 2013; Camenzuli 2015). Silica treatments immobilise inorganics via the formation of hydroxides, metal silicates or polymerised silicates which encapsulate metals or provide active sites for the adsorption of metals (Naja and Volesky 2009; Camenzuli and Gore 2013, Camenzuli 2015). Encapsulation of petroleum hydrocarbons using silica can be achieved within three hours during a two-stage reaction (Mitchell et al. 2000a, b; Hill and Ross 2012; Camenzuli and Gore 2013). The first stage requires the application of an emulsifier to desorb

petroleum hydrocarbons from soil (Mitchell et al. 2000a, b; Camenzuli and Gore 2013), and is followed by the application of a strongly alkaline silica solution (McDowell 1994; Camenzuli and Gore 2013). An acid-base reaction occurs between the silica solution and the emulsifier micelle, forming microscopic silica shells that encapsulate petroleum hydrocarbons (McDowell 1994; Mitchell et al. 2000a, b; Camenzuli and Gore 2013). Alternatively, a strongly alkaline-based silicate solution can be applied first, followed by an acidic solution (Billings and Burns 1997; Camenzuli and Gore 2013). The application of an acidic solution immediately after the addition of an alkaline silica solution rapidly reduces the pH of the treatment solution to prompt faster and more complete immobilisation and encapsulation of contaminants (Billings and Burns 1997; Camenzuli and Gore 2013).

The potential for silica treatments to remediate soil contaminated with inorganics or petroleum hydrocarbons has been demonstrated (McDowell 1994; Mitchell et al. 2000a, b; Mbhele 2007; Camenzuli et al. 2015). However, no studies have evaluated the performance of silica treatments on soil co-contaminated with inorganics and petroleum hydrocarbon sunder cold conditions. As a consequence, there are insufficient data to determine whether or not silica treatments can immobilise inorganics and encapsulate petroleum hydrocarbons rapidly enough to prevent contaminant migration (Camenzuli and Gore 2013), or whether or not the reaction products formed during treatment are safe and stable enough for long-term remediation (Camenzuli 2015).

This study investigates the performance of silica treatments at immobilising inorganics and encapsulating petroleum hydrocarbons in co-contaminated soil under cold conditions. The performance of eight silica treatments was assessed by measuring the following parameters pre- and post- treatment: concentrations of leachable metals using the Toxicity Characteristic Leaching Procedure (TCLP), concentrations of C_9-C_{18} petroleum hydrocarbons, pH, electrical conductivity (EC) and oxidation-reduction potential (ORP) in soil. The formation of mineral products and polymerised silicates was also observed using scanning electron microscopy (SEM) and characterised by X-ray diffractometry (XRD). All results obtained from treated soils were benchmarked against results obtained from untreated soil. The experiment was undertaken at laboratory scale under cold conditions (2 °C) to simulate remediation under cold conditions and provide a controlled evaluation of treatment performance.

13.2: Materials and methods

13.2.1: Experimental design

Eight silica treatments were applied to five replicates in 473 mL Teflon lined, sealed glass jars containing 250 g of contaminated soil obtained from an abandoned Pb-Ag-Zn mine in Sunny Corner, New South Wales (n=40). The total concentrations of Cr, Fe, Cu, Zn, As, Cd and Pb before treatment were 106, 280, 500, 3680, 2036, 21,300, 33 and 108,300 mg/kg, respectively, as determined by X-ray

Fluorescence spectrometry. The site is dominated by volcanogenic massive sulphides with mineralisation comprising pyrite, sphalerite, galena, chalcopyrite (Seccombe 1984; GCR 2012) and some As-bearing minerals (Lech et al. 2002). The soil was homogenised, sieved to <2 mm and spiked with 2 wt% Special Antarctic Blend (SAB; a winterised diesel) diesel prior to treatment. This diesel product is the most commonly used fuel at Australian Antarctic stations and consists primarily of *n*-C_9-C_{14} alkanes and trace level concentrations of *n*-C_{15}-C_{23} (Snape et al. 2006). Following the addition of SAB, the soil was cooled to 2 °C in a Sanyo MIR-253 incubator. A further five 473 mL Teflon sealed, glass jars containing 250 g of sieved soil were spiked with 2 wt% SAB and cooled to 2 °C, but remained untreated for use as experimental controls.

The eight silica treatments were applied by mixing calcium carbonate ($CaCO_3$) and titanium dioxide (TiO_2) powder reagents with soil on a platform shaker for 10 minutes at 100 rpm, followed by the application of reagent grade sodium metasilicate dissolved in deionised water (resistivity of 18.2 mΩ; Milli-Q, Millipore). The silica treatments were comprised of dissolved sodium metasilicate (Na_2SiO_3) or sodium metasilicate, propylene glycol ($C_3H_3O_2$) and sodium lauryl sulphate **(**$C_{12}H_{25}NaO_4S$) (Table 13.1). The composition and doses of these treatments were adapated from earlier studies (Arocha et al. 1996; Fytas et al. 1999; Camenzuli and Gore 2013; Camenzuli et al. 2015). Treatments T3-T8 were adjusted to pH 10 prior to application using nitric acid (85% concentration). Orthophosphoric acid (H_3PO_4) (85% concentration) was applied to T5-T8 treated soil after the application of dissolved sodium metasilicate to encourage faster polymerisation of soluble silicates (Mbhele 2007; Camenzuli and Gore 2013). After 7 days, samples were obtained from each batch of treated and untreated soil for concentrations of leachable metals and petroleum hydrocarbons (C_9-C_{18}), pH, EC and ORP measurements, and mineral formation by SEM and XRD.

Table 13.1: Composition of assessed silica treatments.

	Powder reagent		**Silica solution**				**Acidic solution**	
Treatment	**$CaCO_3$ (wt%)**	**TiO_2 (wt%)**	**Na_2SiO_3 (wt%)**	**$C_3H_8O_2$ (wt%)**	**$C_{12}H_{25}NaO_4S$ (wt%)**	**Deionised water (wt%)**	**H_3PO_4 (wt%)**	**Deionised water (wt%)**
Untreated	0.0	0.0	0	0	0	0	0	0
T1	0.1	0.0	40	0	0	60	0	0
T2	0.1	0.5	40	2	2	56	0	0
T3	0.1	0.0	40	0	0	60	0	0
T4	0.1	0.5	40	2	1	57	0	0
T5	0.1	0.0	40	0	0	60	30	70
T6	0.1	0.5	40	2	1	57	30	70
T7	0.1	0.0	50	0	0	50	40	60
T8	0.1	0.5	50	5	2	43	50	50

13.2.2: Analysis of the concentrations of leachable metals in soil

The TCLP extraction (US EPA method 1311) simulates contaminant leachability of metals from soil under municipal landfill conditions, and can be used to estimate mobility of metal contaminants (US EPA 1992; Stark et al. 2005, 2008). TCLP extractions were performed on 100 g soil samples (n=60) collected from experimental control batches (n=5), and on soil samples collected pre- (n=15) and post- (n=40) treatment. Soil samples were extracted using an acetic acid and sodium hydroxide solution (pH 4.93) for 18 hours in accordance with AS 4439 (Standards Australia 1997) and US EPA method 1311 (US EPA 1992). Extracts were analysed using a Varian 730-ES Inductively Coupled Plasma-Optical Emission Spectrometer at EnviroLab Services in Sydney. Analytical duplicates returned relative standard deviations for all analytes of <0.5%. Mean analyte recovery was measured using matrix spikes (n=7) and was 99, 103, 100, 101, 102, 105, 106, 107 and 99% for Al, Cr, Fe, Ni, Cu, Zn, As, Cd and Pb, respectively.

13.2.3: Analysis of total petroleum hydrocarbons in soil

To assess the performance of silica treatments for the management of petroleum hydrocarbons, 50 g soil samples (n=65) were obtained prior to the addition of 2 wt% SAB (n=5), after the addition of 2 wt% SAB (n=15), after treatment with silica (n=40) and from experimental control batches (n=5). Soil samples were analysed for petroleum hydrocarbons (C_9-C_{18}) by firstly mixing with sodium sulphate followed by extraction using a 1:1 dichloromethane and acetone solvent mixture according to US EPA Method 8015 and NMI's internal method NGCMS 11.12. Extracts were analysed using an Agilent 7890 Gas Chromatograph fitted with a Flame Ionization Detector at the National Measurement Institute in Sydney. Analytical duplicates returned relative standard deviations for all analytes of <0.1%. Mean recovery percentages of laboratory control samples and matrix spikes (n=4) were 91 and 72%, respectively.

13.2.4: Pre- and post- treatment soil pH, EC and ORP

The pH and ORP of pre- (n=30) and post- (n=60) treatment soil samples, and experimental controls (n=5) was measured in an aqueous suspension with a 1 g: 5 mL soil: water ratio using TPS probes attached to a Denver 250 pH/ORP meter. Electrical conductivity was measured using a Eutech EcoScan Con 6 conductivity probe and meter in an aqueous suspension with a 1 g: 5 mL soil: deionised water ratio agitated for 1 hour.

13.2.5: Scanning Electron Microscopy

To observe and identify the formation of metal-silicates and polymerised silicates, pre- (n=15), post- (n=40) treatment and untreated soil samples were dried for 24 hours at 32 °C, mounted onto adhesive double-sided carbon tabs (ProSciTech Pty Ltd) and positioned onto 9 port stub holders for SEM imaging. Micrographs were obtained using a Hitachi Analytical Table Top SEM T3030 with EDS and

Bruker Quantax 70 software. Pre- and post- treatment samples were examined under 15 kV acceleration voltages to allow the use of all four primary detectors to provide a compositional back-scatter electron (BSE) image, where heavier elements scatter strongly, while providing clear contrast for visual inspection. The EDX mode also used the maximum acceleration voltage of 15 kV to excite X-rays for compositional analysis. Calibration of the Bruker Quantax 70 EDS software requires a pure elemental standard to align the X-ray spectral emission lines to individual elements. We used a copper stub to calibrate the detector using the Cu Kα and K β X-ray emissions.

13.2.6: Characterising minerals formed during treatment using X-Ray Diffractometry

Soil samples were milled to <10 µm and top loaded into stainless steel sample holders for analysis by XRD. Prior to treatment, untreated soil samples (n=15) were analysed as experimental controls to benchmark pre- and post- treatment comparisons. Seven days after the experiment commenced, post-treatment analyses (n=40) and analyses of experimental controls (n=5) were undertaken using the same instrument conditions. All diffractograms were collected from 5 to 90° 2Θ with a PANalytical X'Pert Pro MPD diffractometer, using conditions of 45 kV, 40 mA, CuKα radiation, X'Celerator detector, Bragg Brentano geometry, and a slew rate of 5° 2Θ per minute. Mineral identification was achieved using PANalytical's Highscore Plus software v2.2.4, with ICDD PDF2 and PAN-ICSD databases.

13.3: Results and discussion

13.3.1: Concentration of leachable metals in soil

Pre- and post- treatment concentrations of leachable metals in soil (Table 13.2) show that treatments containing orthophosphoric acid (T5-T8) were highly effective at immobilising Cu, Zn, Cd and Pb, but mobilised As. Treatments not containing titanium dioxide (TiO_2), sodium lauryl sulphate ($C_{12}H_{25}Na_{O4}S$), propylene glycol ($C_3H_8O_2$) or orthophosphoric acid (H_3PO_4) (T1, T3) were less effective at immobilising inorganics. Alternatively, treatments containing TiO_2, $C_{12}H_{25}Na_{O4}S$ and $C_3H_8O_2$ without orthophosphoric acid (T2, T4) resulted in significant mobilisation of Pb. Fe was mobilised in all soils, except soil treated with T3 (Table 13.2). The inclusion of TiO_2, $C_{12}H_{25}Na_{O4}S$ and C_3H_{8O2} in treatments containing orthophosphoric acid (T6, T8) did not improve immobilisation efficacy.

Table 13.2: Pre- and post- treatment concentrations of leachable analytes (mg/L). Reported values are mean ± standard deviation.

	Pre- treatment (mg/L)						
	Al	**Fe**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
	0.20± 0.03	0.03± 0.02	0.06± 0.02	3.7± 1.3	<0.05± 0.00	0.02± 0.01	110± 16
	Post- treatment (mg/L)						
Treatment	**Al**	**Fe**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
Untreated	0.20± 0.00	0.19± 0.10	0.04± 0.01	2.5± 0.15	<0.06± 0.01	0.02± 0.01	82± 7.6
T1	0.30± 0.06	0.28± 0.18	0.07± 0.08	1.4± 1.2	2.6± 5.3	0.01± 0.01	90± 120
T2	0.10± 0.05	0.10± 0.05	0.02± 0.00	1.1± 0.10	0.06± 0.02	0.01± 0.00	410± 34
T3	<0.01	0.04± 0.02	0.02± 0.01	1.6± 0.61	<0.05	0.01± 0.01	86± 41
T4	0.30± 0.14	0.76± 0.47	0.04± 0.01	2.9± 0.21	0.14± 0.01	0.02± 0.00	400± 190
T5	0.28± 0.10	0.13± 0.07	0.02± 0.00	0.18± 0.05	8.4± 0.88	<0.01	0.75± 0.12
T6	0.20± 0.00	0.28± 0.08	0.02± 0.01	0.18± 0.05	5.5± 1.3	<0.01± 0.00	1.7± 0.69
T7	0.47± 0.31	0.24± 0.23	0.02± 0.01	0.05± 0.03	19± 4.9	<0.01	1.0± 0.33
T8	0.50± 0.29	0.21± 0.14	0.02± 0.01	0.04± 0.02	16± 0.71	<0.01	0.55± 0.10

The increased immobilisation efficiency of T5-T8 is attributed to the addition of orthophosphoric acid which encouraged the formation of metal-phosphate minerals and reduced pH to levels appropriate for the formation of polymerised silicates, metal-silicates and hydroxides (Amofah et al. 2011; White et al. 2012; Hafsteinsdóttir et al. 2011, 2013; Camenzuli and Gore 2013; Camenzuli 2015). One disadvantage of utilising orthophosphate is that competitive phosphate-arsenate (PO_4^{3}-AsO_4^{3}) interactions result in the mobilisation of As (Peryea 1991; Munksgaard and Lottermoser 2013; Camenzuli et al. 2015). This represents a major limitation of silica-orthophosphate based treatments which may be overcome by substituting orthophosphoric acid with small amounts of citric or acetic acid (Toeneboehn et al. 1992; Arocha et al. 1996). It is critical that only small amounts of an alternative acid are used to ensure that pH is dropped to a level sufficient for silica mineral precipitation, without inhibiting Cu, Zn and Pb immobilisation.

Understanding the causes of Fe mobilisation is more complex. Reductive dissolution (Chuan et al. 1996; Löhr 2010), fulvic acid or low pH environments can facilitate Fe dissolution. However, the pH and ORP data (Table 13.3) suggest that Fe was mobilised independent of these parameters. The inclusion of TiO_2, $C_3H_8O_2$, $C_{12}H_{25}NaO_4S$ or orthophosphoric acid also appear to have no influence on Fe mobility (Tables 13.1 and 13.2). One explanation is that Fe solubilising bacteria in the soil may have contributed to the dissolution of leachable Fe (Kalinowski et al. 2000). This has previously been observed in cold regions by Langdahl and Ingvorsen (1997) who reported on Fe dissolution by solubilising bacteria at 0 °C at an exposed sulphide ore deposit in Citronen Fjord, North Greenland. The mobility of P, Ni, Cu, Zn, As, Cd and Pb are also influenced in the presence of solubilising bacteria (Sheng and Xia 2006; Rajkumar and Freitas 2008; He et al. 2009; Mailloux et al. 2009; Rajkumar et al. 2009; Huang et al. 2010; Ghosh et al. 2011). While beyond the scope of this study, microbial community analyses would be required to ascertain whether or not the increase in concentrations of leachable Fe can be attributed to soil biology.

13.3.2: Concentration of petroleum hydrocarbons in soil

Soil concentrations of petroleum hydrocarbons in the SAB (C_9-C_{18}) range prior to and following the addition of 2 wt% SAB were <100 mg/kg and 17,300 mg/kg, respectively. Pre- and post- treatment concentrations of petroleum hydrocarbons in the SAB range (C_9-C_{18}) are in Figure 13.1. Although significant reductions in petroleum hydrocarbons were observed in all soils, there are few trends in the data. T1 and T7 reduced petroleum hydrocarbons (C_9-C_{18}) by approximately 70%. However, T1, T4 and T8 were less effective than the untreated systems at reducing concentrations of petroleum hydrocarbons (C_9-C_{18}). Addition of TiO_2, $C_3H_8O_2$ and $C_{12}H_{25}NaO_4S$ did not improve TPH removal, in fact treatments not containing TiO_2, $C_3H_8O_2$ and $C_{12}H_{25}NaO_4S$ (T1, T3, T5, T7) were more effective than treatments containing TiO_2, $C_3H_8O_2$ and $C_{12}H_{25}NaO_4S$ (T2, T4, T6, T8). Treatments containing orthophosphoric acid were marginally more effective on average, excluding T8, which is attributed to the large amount of surfactant ($C_{12}H_{25}NaO_4S$) in the treatment. The large reduction in TPH concentrations (C_9-C_{18}) in the untreated soil is partially attributed to the loss of volatiles during sampling and analysis and natural attenuation.

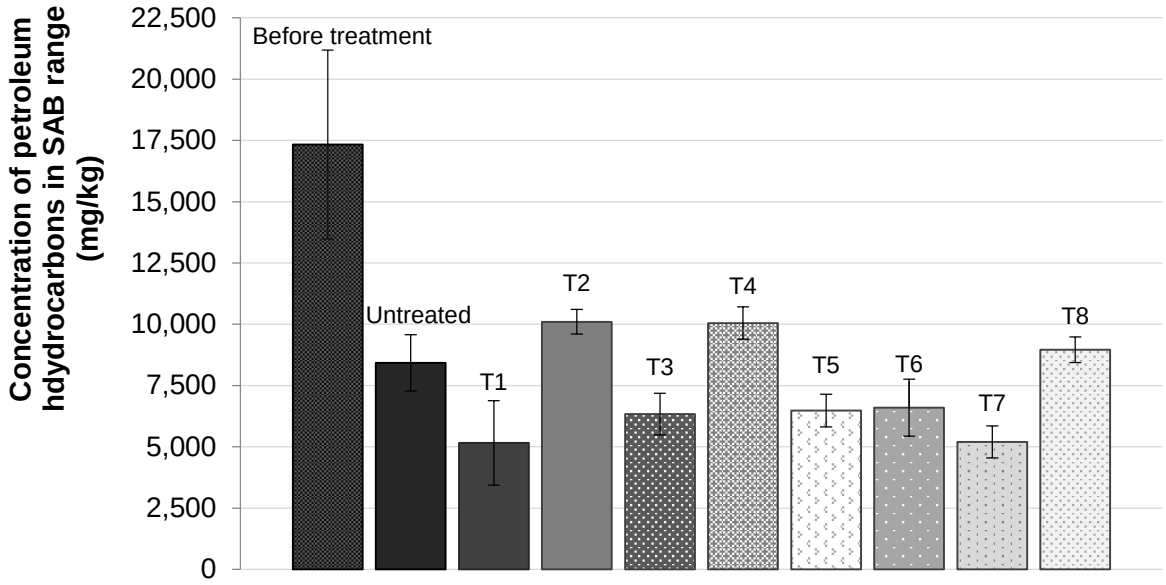

Figure 13.1: Pre- and post- treatment concentrations of petroleum hydrocarbons in SAB (C_9-C_{18}) range (mg/kg). Standard deviation is represented by error bars.

Although it is difficult to identify reasons for the ineffectiveness of T2, T4 and T8, three possible explanations exist. First, Arocha et al. (1996) found that two applications of silica doubled remediation efficacy when compared to a single application. As only single application treatments were assessed in this experiment, further studies comparing the effectiveness of single application treatments with multi-application treatments would be beneficial. This may be achieved by administering at least two low dose treatments per batch. Second, an assessment of silica treatments using a wider variety of reagents than used in this experiment should be undertaken to optimise treatment performance. In this experiment, orthophosphoric acid was the only acid assessed for polymerisation, since orthophosphate is a well-established method for metal immobilisation (Hafsteinsdóttir et al. 2014, 2015). However, Arocha et al. (1996) and Toeneboehn et al. (1992) successfully immobilised hydrocarbons using silica treatments containing acetic acid and citric acid. Finally, although reductions in petroleum hydrocarbons (C_9-C_{18}) in T2, T4 and T8 treated soil were less than reductions in untreated soil, evidence of encapsulation was observed during SEM imaging (Figures 2b and S2). This suggests that encapsulation occurred either was not complete, or was not robust enough to resist dichloromethane and acetone extraction prior to analysis. In either case, some uncertainty remains regarding its use in remediation projects that require complete and robust encapsulation.

The results suggest that applying no treatment was more effective at reducing concentrations of petroleum hydrocarbons (C_9-C_{18}) in the soil than treatments T2, T4 and T8. Presumably a portion of the hydrocarbons were lost in the untreated controls by volatilisation, which raises the concern that the immediate environmental and human health risks presented by exposure to elevated concentrations of petroleum hydrocarbons from contaminated soil can be significant (Khan 1990;

McDougal et al. 2000; Mehlman 2005; Davoodi and Claireaux 2007; Rekhadevi et al. 2010). Further studies focused on optimising the performance of silica treatments may produce more effective treatments for managing co-contaminated soil. Alternatively, technology coupling with alternative in-situ techniques (e.g. electrokinetic remediation, lining technologies or permeable reactive barriers) could facilitate more effective management of petroleum hydrocarbons at co-contaminated sites (Gore 2009, Mumford et al. 2013; McWatters et al. 2014; Camenzuli et al. 2014; Statham et al. 2015a,b).

13.3.3: Soil pH, electrical conductivity and oxidation-reduction state

The mean pH, EC and ORP of the soil before treatment was 3.2, 1.0 mS/cm and 240 mV, respectively. Significant changes in soil pH, EC and ORP occurred after treatment (Table 13.3). Sharp increases in soil pH followed the application of silica treatments not containing orthophosphoric acid. The pH of soil treated with T7 and T8 remained slightly acidic but closest to neutral after treatment. The optimum pH range for agricultural soil is 6.5 to 7.0 (Arshad and Martin 2002). Achieving the optimum pH range in treated soils is important for several reasons. Fe, Cu, Zn, Cd and Pb are generally less mobile under alkaline conditions (Chuan et al. 1996; McBride et al. 1997; Smith and Hyuck 1999). However, As becomes more mobile under alkaline conditions (Masscheleyn et al. 1991). Although metals are generally more mobile in strongly acidic environments, strongly alkaline environments can compromise soil structure, filtration and microbial health (Smith and Doran 1996; Butterly et al. 2012). Microbial activity is also affected by pH, with fungi, bacteria, protozoa and actinomycetes all preferring a pH range of 6-8 for survival and function (Smith and Doran 1996; Butterly et al. 2012). Since no treatments assessed in this study achieved the optimum pH range for soil post-treatment, further studies are required to optimise the treatments trialled in this experiment. Achieving the optimum soil pH may require applying a lower concentration acid after the silica solution, substituting orthophosphoric acid for a suitable alternative (Toeneboehn et al. 1992), or not adjusting the pH of the silica solution prior to application.

The redox state of the soil also changed after treatment (Table 13.3). Soil treated with silica treatments containing orthophosphoric acid typically generated an oxidising environment (with the exception of T7), while treatments not containing orthophosphoric acid generated reducing environments. This has important implications for contaminant mobility as Al, Cr, Fe, Cu, Fe, As and Pb are sensitive to redox conditions (Chuan et al. 1996; Smith and Hyuck 1999). In general, concentrations of dissolved metals are lower in reducing environments (María-Cervantes et al. 2011), whereas oxidising environments tend to solubilise metals (Hermann and Neumann-Mahlkau 1985; Otero and Macias 2002; Du Laing et al. 2009; Conesa et al. 2011; Hafsteinsdóttir et al. 2014). However, immobilised metals can be adsorbed onto Fe-Mn oxyhydroxide surfaces which can release under reducing conditions (Chuan et al. 1996; Löhr 2010). Reductive dissolution is likely to have contributed to the

significantly higher concentrations of metals (e.g. Pb) reported in the reducing soils treated with T1-T4 (Tables 13.2 and 13.3) (Elliot et al. 1989; Smith and Hyuck 1999). To increase understanding of the impact of redox state on the behaviour of silica treated soil, further studies assessing treatment performance under both dry and water-saturated conditions would be beneficial (Kumpiene et al. 2009). Electrical conductivity readings were significantly higher in silica treated soil relative to untreated soil (Table 13.3), due to the large amounts of reagent applied.

Table 13.3: Pre- and post- treatment soil pH, EC and ORP. Reported values are mean ± standard deviation.

	Pre- treatment (n=30)		
	pH	**EC (mS/cm)**	**ORP (mV)**
	3.2±0.021	1.0±0.084	240±17
	Post- treatment (n=60)		
Treatment	**pH**	**EC (mS/cm)**	**ORP (mV)**
Untreated	3.2±0.04	1.0±0.13	280±20
T1	10±0.33	29±7.0	-210±14
T2	9.5±0.53	26±3.1	-170±13
T3	8.8±0.46	23±5.7	-94±12
T4	10±0.14	20±2.5	-170±14
T5	5.7±0.25	28±5.1	25±6.0
T6	5.2±0.40	26±2.0	47±22
T7	6.2±0.68	25±3.8	-38±35
T8	6.0±0.40	22±3.1	11±7.0

13.3.4: Observation of minerals and polymerised silicates formed after treatment

The formation of metal-silicate and phosphate minerals in soil following treatment with silica was observed, photographed and characterised using SEM with EDS and is illustrated in Figure 13.2b, c and d. SEM imaging also provided evidence of the formation of polymerised silicates, appearing as colloidal chains enveloping the recently formed metal-silicate minerals (Figure 13.2b). Alternatively, polymerisation is absent and crystallinity is limited in Figure 13.2a, collected from untreated soil. EDS indicated the polymerised silica chains in Figure 13.2b as sodium aluminosilicates and the minerals in Figure 13.2c and 13.d, as Pb-silicates and Pb-phosphates (Figures S13.1-S13.4). Sodium aluminosilicates have been demonstrated as an effective sorbent for aflatoxins, indicating that treatment with silica may provide secondary benefits not previously considered (Phillips et al. 1988; Ramos and Hernández 1996; Ledoux et al. 1999).

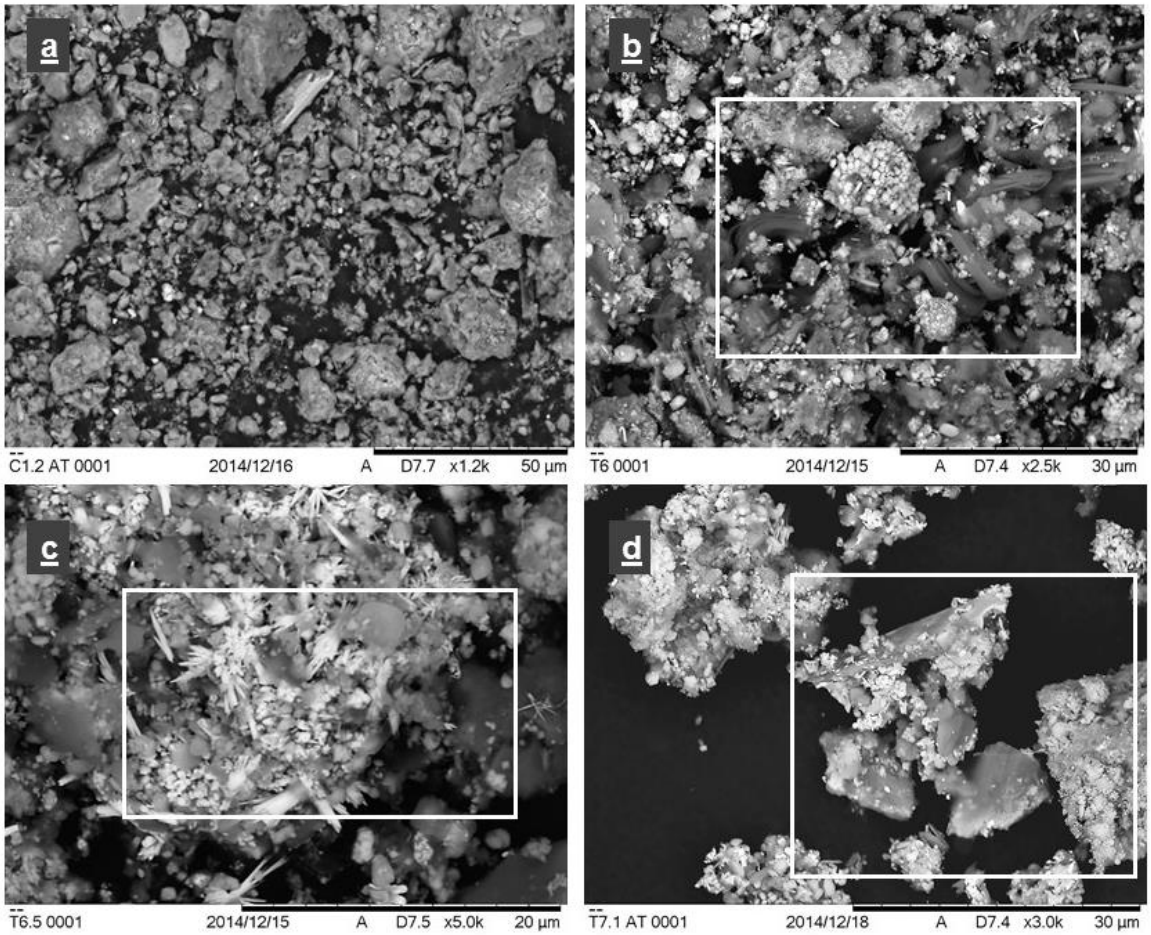

Figure 13.2: SEM images of untreated and treated materials. SEM micrograph of: (a) untreated material, (b) colloidal polymerised silicate chains formed after treatment with T6, (c) Pb phosphates and sodium aluminosilicates formed after treatment with T6, (d) Metal phosphate and silicate minerals formed after treatment with T7. Elemental characterisation by EDS for these images is provided in Figures S13.1-S13.4.

13.3.5: Characterisation of minerals formed after treatment

The mineral phases observed after treatment (Table 13.4) are consistent with those reported by White et al. (2012), Hafsteinsdóttir et al. (2011, 2013) and Camenzuli (2015). Prior to treatment, the dominant minerals identified in soil by XRD were quartz, segnitite, anglesite, beudantite and muscovite. Post-treatment analyses revealed these same minerals, with the formation of several new mineral phases, with the most significant changes occurring in soil treated with T4-T8. The formation of hydroxypyromorphite, hydroxylapatite, fluoroapatite, sodium aluminosilicates and calcium bearing minerals within 7 days of treatment with T5-T8 demonstrate the potential of this technology for the immobilisation of metals in low temperature environments. The formation of coesite is interesting as it is often considered a high pressure polymorph of silicon dioxide, although xerogel materials can crystallise coesite at ambient pressures and temperatures of 565 °C (Martínez et al. 2008). The lowest temperature at which coesite might form via this reaction pathway has not yet been constrained.

Table 13.4: Mineral phases identified after treatment with silica using XRD.

Treatment	Mineral	Chemical formula
Untreated	Quartz	SiO_2
	Segnitite	$PbFe^{3+}{}_3(AsO_4)_2(OH,H_2O)_6$
	Anglesite	$PbSO_4$
	Beudantite	$PbFe^{3+}{}_3(AsO_4)(SO_4)(OH)_6$
	Muscovite	$KAl^3Si_3O_{10}(OH)_2$
T1	Quartz	SiO_2
	Coesite	SiO_2
	Segnitite	$PbFe^{3+}{}_3(AsO_4)_2(OH,H_2O)_6$
	Muscovite	$KAl^3Si_3O_{10}(OH)_2$
	Cuprite	CuO
	Thenardite	Na_2SO_4
T2	Quartz	SiO_2
	Beudantite	$PbFe^{3+}{}_3(AsO_4)(SO_4)(OH)_6$
	Muscovite	$KAl^3Si_3O_{10}(OH)_2$
	Thenardite	Na_2SO_4
T3	Quartz	SiO_2
	Anglesite	$PbSO_4$
	Beudantite	$PbFe^{3+}{}_3(AsO_4)(SO_4)(OH)_6$
	Muscovite	$KAl^3Si_3O_{10}(OH)_2$
	Coesite	SiO_2
T4	Quartz	SiO_2
	Coesite	SiO_2
	Albite	$NaAlSi_3O_8$
	Beudantite	$PbFe^{3+}{}_3(AsO_4)(SO_4)(OH)_6$
	Muscovite	$KAl^3Si_3O_{10}(OH)_2$
	Wüustite	FeO
	Anorthite	$Al_2Ca_{10}Si_8$
	Potassium aluminium silicate	
T5	Quartz	SiO_2
	Anglesite	$PbSO_4$
	Coesite	SiO_2
	Segnitite	$PbFe^{3+}{}_3(AsO_4)_2(OH,H_2O)_6$
	Hydroxylapatite	$Ca_5(PO_4)_3OH$
	Muscovite	$KAl^3Si_3O_{10}(OH)_2$
	Hydroxypyromorphite	$Pb_5(PO_4)_3OH$
T6	Quartz	SiO_2
	Calcite	$CaCO_3$
	Anglesite	$PbSO_4$
	Beudantite	$PbFe^{3+}{}_3(AsO_4)(SO_4)(OH)_6$
	Muscovite	$KAl^3Si_3O_{10}(OH)_2$
	Segnitite	$PbFe^{3+}{}_3(AsO_4)_2(OH,H_2O)_6$
	Hydroxylapatite	$Ca_5(PO_4)_3OH$
	Fluoroapatite	$Ca_5(PO_4)_3F$
T7	Quartz	SiO_2
	Anglesite	$PbSO_4$
	Beudantite	$PbFe^{3+}{}_3(AsO_4)(SO_4)(OH)_6$
	Muscovite	$KAl^3Si_3O_{10}(OH)_2$
	Segnitite	$PbFe^{3+}{}_3(AsO_4)_2(OH,H_2O)_6$
	Hydroxylapatite	$Ca_5(PO_4)_3OH$
	Fluoroapatite	$Ca_5(PO_4)_3F$
	Sodium aluminium silicon phosphate	
T8	Quartz	SiO_2
	Calcite	$CaCO_3$
	Anglesite	$PbSO_4$
	Beudantite	$PbFe^{3+}{}_3(AsO_4)(SO_4)(OH)_6$
	Muscovite	$KAl^3Si_3O_{10}(OH)_2$
	Segnitite	$PbFe^{3+}{}_3(AsO_4)_2(OH,H_2O)_6$
	Hydroxylapatite	$Ca_5(PO_4)_3OH$
	Sodium calcium aluminium silicate	$NaCaAl_2Si_2O_8$
	Kintoreite	$PbFe_3(PO_4)_2(OH,H_2O)_6$

The increased immobilisation efficiency of T5-T8 demonstrates the effect of applying orthophosphoric acid after dissolved sodium metasilicate which prompts the formation of metal-

phosphate minerals and reduces the pH of soil, thereby encouraging faster and more complete reactions between silica and inorganic contaminants (Camenzuli and Gore 2013; Camenzuli 2015). Furthermore, the formation of calcium bearing minerals demonstrates that the inclusion of calcium carbonate was effective at promoting mineral precipitation and the subsequent immobilisation of contaminants.

Reaction kinetics and mineral formation are typically slower in cold environments (White et al. 2012; Hafsteinsdóttir et al. 2011, 2013, 2014; Camenzuli 2015), therefore a longer term study may be beneficial for the characterisation of minerals which may form over a longer experiment. A long-term study may also provide an assessment of the long-term stability of minerals formed by treatments under cold conditions where hydration and dehydration reactions, freeze-thaw and temperature can significantly affect the stability of minerals formed during treatment (Hafsteinsdóttir et al. 2011, 2013; Camenzuli 2015).

13.4: Conclusion

This study assessed the performance of eight silica treatments for the management of soil co-contaminated with inorganics and petroleum hydrocarbons under cold conditions. Significant reductions in the concentrations of leachable metals and the formation of silicates, calcium and phosphate bearing minerals in treated soils suggests that silica treatments may be a viable remediation technology in cold regions. Treatments containing orthophosphoric acid immobilised Cu, Zn, Cd and Pb, but mobilised As, indicating that further research is required to develop a treatment capable of achieving the optimum pH range for soil without mobilising As. Fe was also mobilised by all treatments except T3, but no conclusive explanation for this was found. One possible explanation is that Fe mobilisation may have been instigated by Fe solubilising bacteria.

Silica treatments were less effective at reducing concentrations of petroleum hydrocarbons, indicating that further research is required to optimise treatments for use at petroleum hydrocarbon or co-contaminated sites. In the interim, silica treatments should only be used at metal contaminated sites or in conjunction with a technology capable of managing petroleum hydrocarbons.

13.5: Acknowledgements

This work was performed in-part at the OptoFab node of the Australian National Fabrication Facility, using NCRIS and NSW state government funding. We thank the Australian Antarctic Division for funding (grant 4029), and Benjamin Freidman for feedback on the manuscript.

13.6: Addendum

13.6.1: Additional notes on soil preparation and volatilisation

The soil material used in this experiment was prepared by first being homogenised, sieved to <2 mm and then cooled for 48 hours in a Sanyo MIR-253 incubator set to 2 °C. Soils were removed from the incubator and spiked with 2 wt% Special Antarctic Blend (SAB; a winterised diesel) prior to treatment. Once treated, the soils were immediately returned to the incubator for the remaineder of the experiment.

The results reveal that volatilisation of SAB was significant for all treatments. This is likely to be an unfortunate consequence of the transport procedures involved in undertaking the required analyses (Figure 13.1). The samples were couriered to Tasmania for TPH analysis at the Australian Antarctic Division. The methods used at the Australian Antarctic Division in Hobart did not result in successful extraction. The samples were transferred back to Sydney for analyses at the National Measurement Institute. Although every best effort was made to ensure that the samples remained refrigerated during the transfer of samples, the samples were not refrigerated during their return from Tasmania to Sydney due to a failure in-transit. The observed volatilisation is likely to be a result of this and highlights the advantages of internal or local laboratory analyses, where the requirement for transporting samples across long distances can be reduced. Additional data regarding the total concentration of leachable hydrocarbons (possibly due to immobilisation) would have been beneficial in developing a detailed understanding of the immobilised fraction of hydrocarbons relative to the volatilised portion. However, the small amount of soil material available for this experiment did not leave enough material to facilitate such analyses.

13.6.2: Additional notes on TPH extraction method

10 g soil samples (n= 65) were extracted with 20 mL of 1:1 dichlormethane and acetone via tumbling for 2 hours. Matrix spikes were prepared by adding 500 mk/kg of diesel to the soil material. The GC parameters used are summarised below:

Instrument: Agilent 7890 GC-FID

Injector: Agilent split/splitless capillary with salinised glass liner

Injector mode: Split. Split ratio 10:1

Injector temperature: 250 °C

Injection volume: 2 µL

Column: BPX5 0.32 mm (i.d.) x 12 m column (0.25 µm film thickness)

Carrier gas: Hydrogen 2.2 mL/min constant flow

Detector temperature: 320 °C.

13.6: References

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13.7: Supplementary

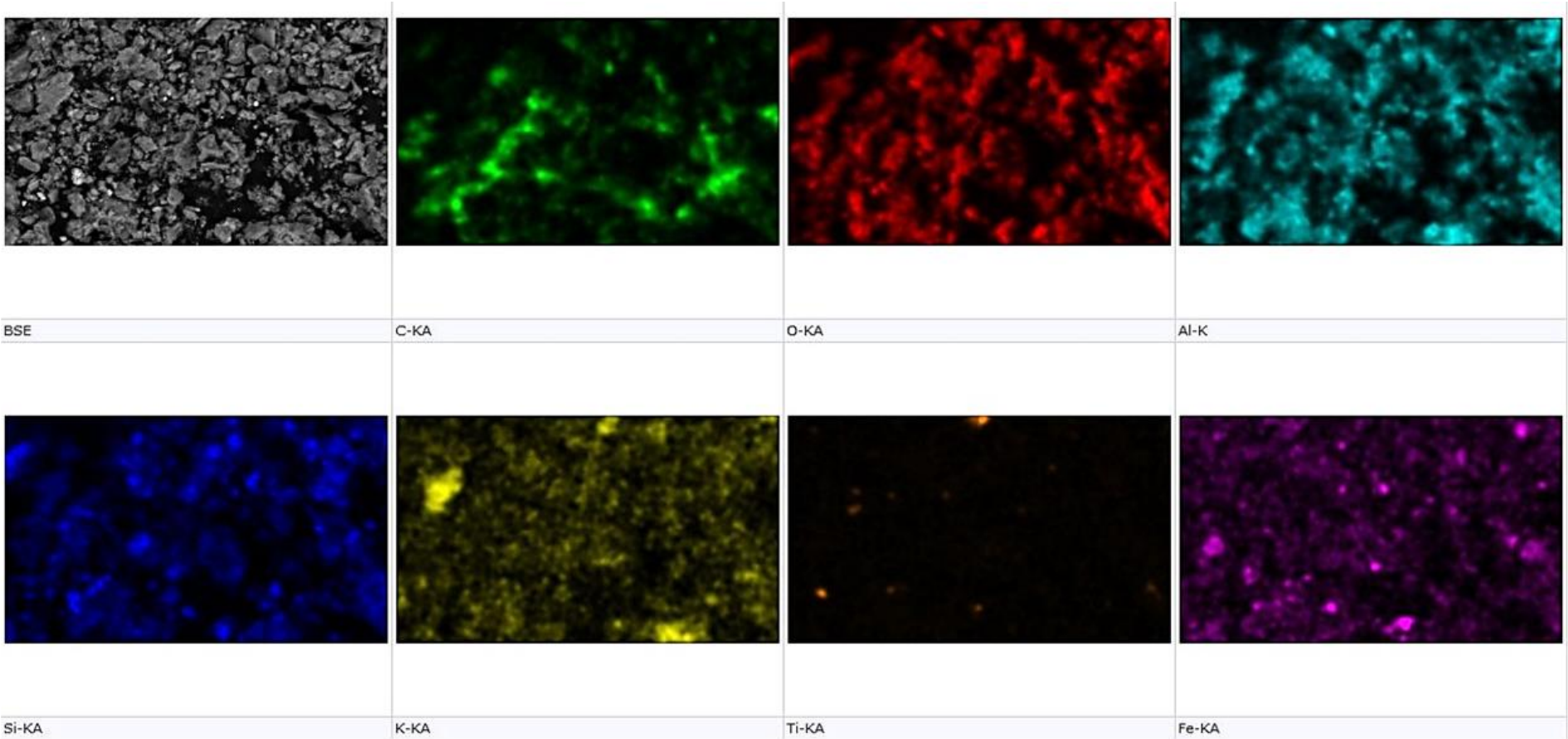

Figure S13.1: Elemental characterisation of untreated soil using SEM-EDS.

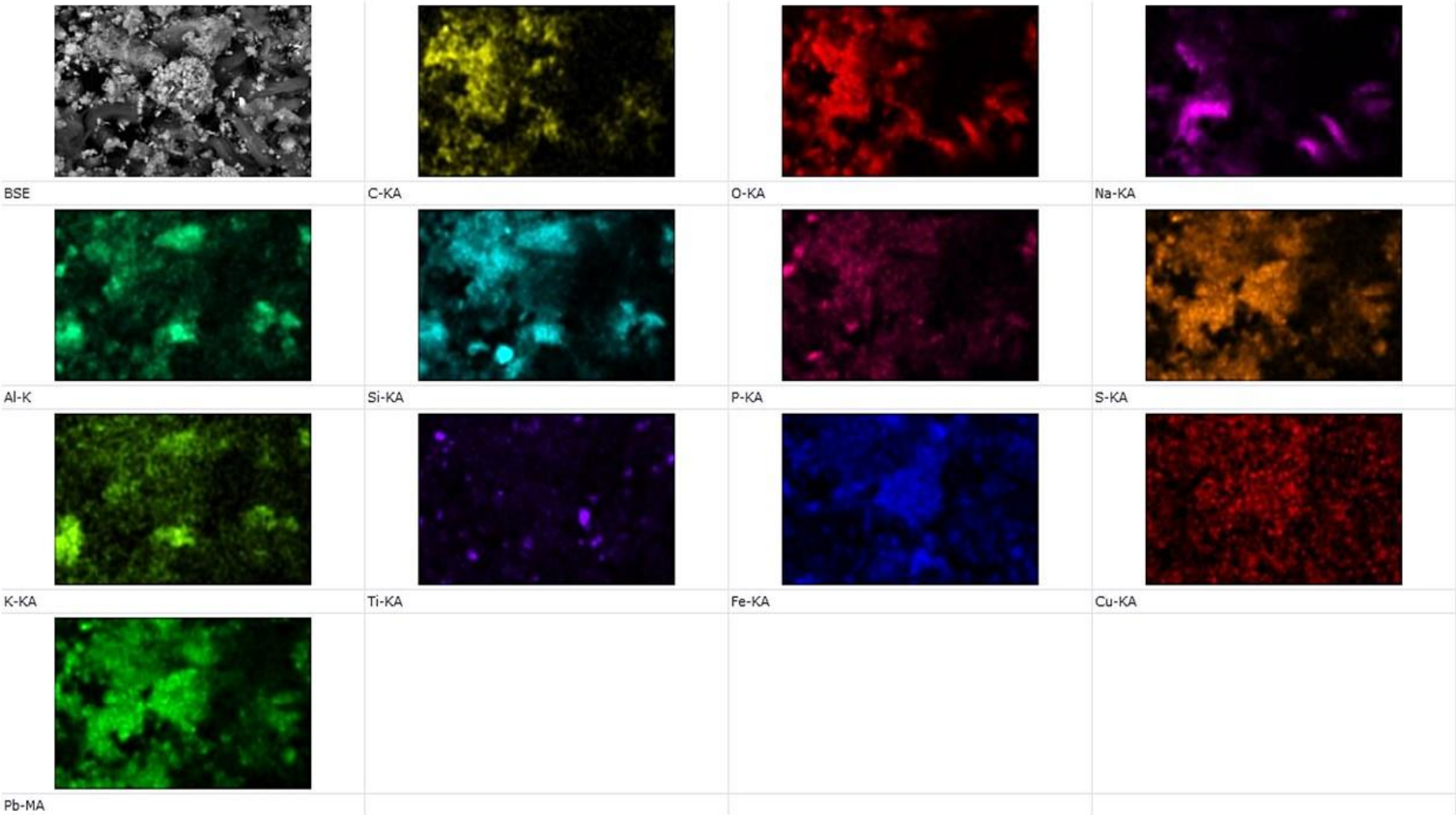

Figure S13.2: Elemental characterisation of polymerised silicates formed in soil treated with T6 using SEM-EDS.

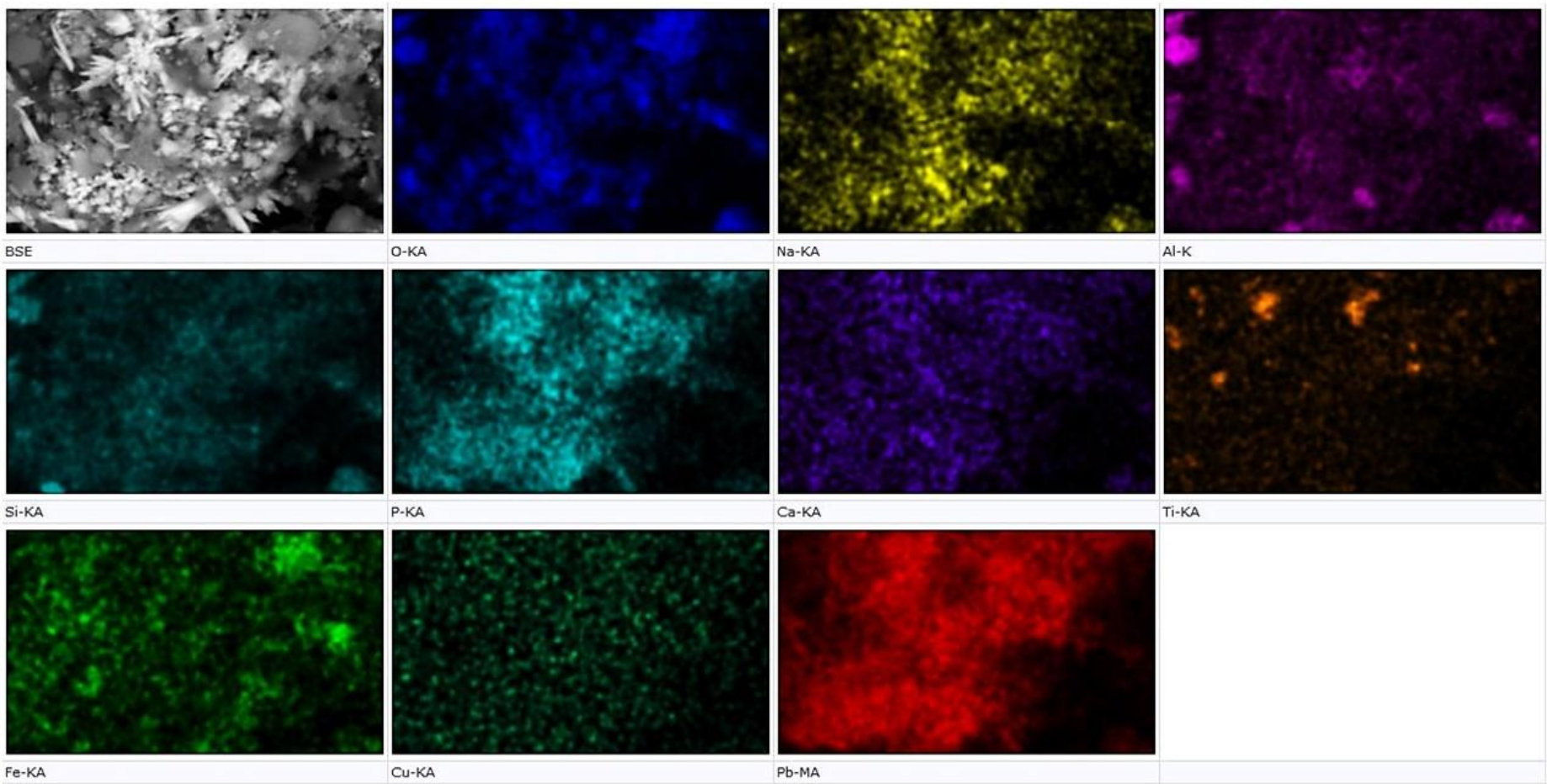

Figure S13.3: Elemental characterisation of minerals formed in soil treated with T6 using SEM-EDS.

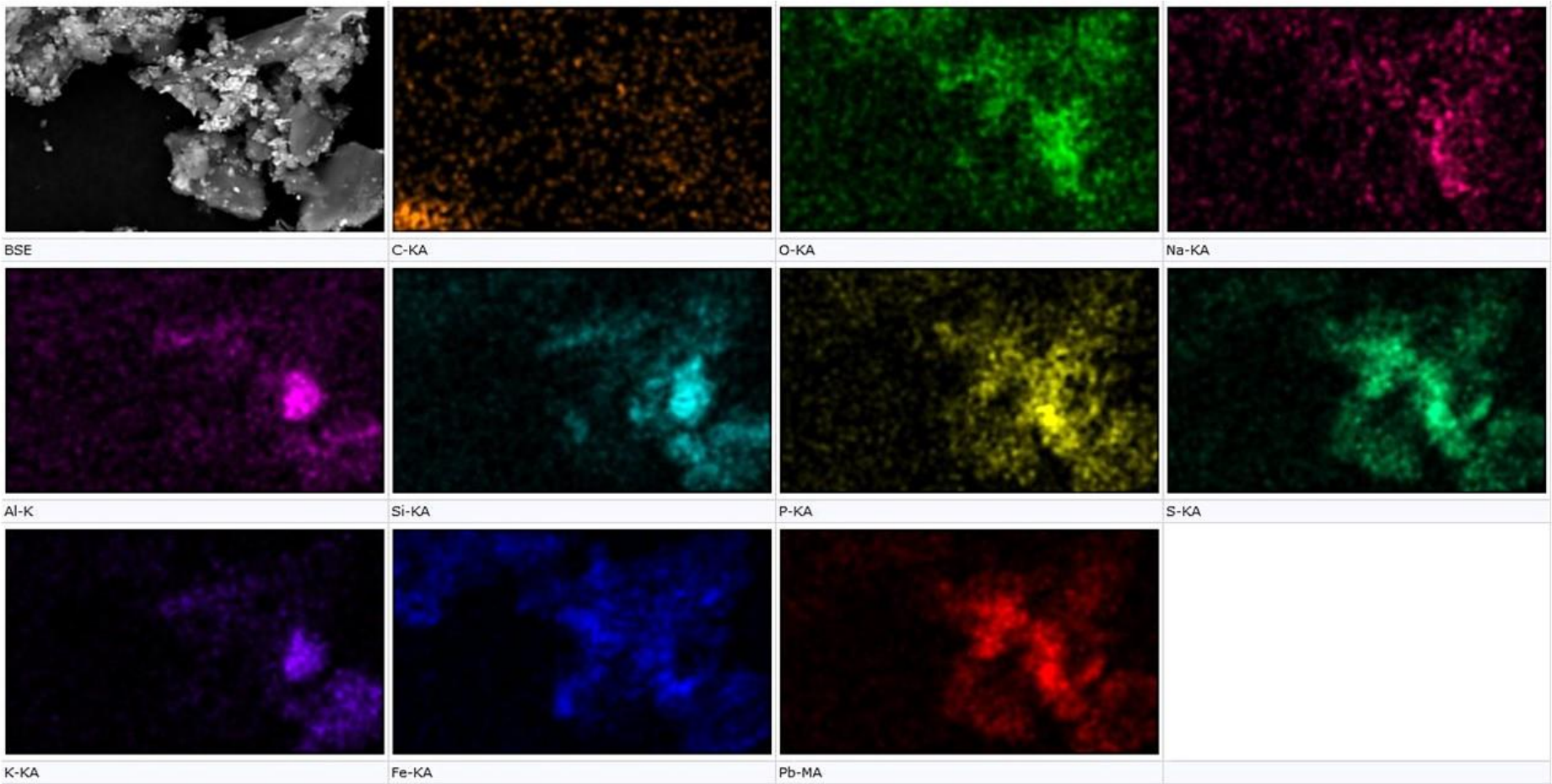

Figure S13.4: Elemental characterisation of minerals formed in soil treated with T7 using SEM-EDS.

Section 6: Synthesis

Chapter 14: Discussion

14.1: Research overview

The chapters of this thesis form a study that assessed the suitability of orthophosphate and silica treatments for the management of environmental contaminants at Wilkes. The context for this research was provided in Sections 1 and 2, and the research objectives of the thesis were provided in Section 3. These research objectives were addressed in Sections 4 and 5.

The research objectives of this thesis were;

1) To delineate the ice-covered landfill at Wilkes using a non-invasive geophysical method,

2) To investigate the effectiveness of orthophosphate and silica treatments for immobilising metal contaminants in Antarctic landfill materials,

3) To develop an understanding of the effects of applying treatments homogenously at contaminated sites, where zones of low-level metal contamination exist,

4) To observe the products which form when metals react with orthophosphate, silica and orthophosphate-silica mix treatments under cold conditions; and

5) To assess the remediation potential of silica treatments on soil co-contaminated with metals and petroleum hydrocarbons, under cold conditions.

A discussion and summary of the key findings is included in the sections following this discussion.

14.2: Summary of findings

14.2.1: Delineating ice covered landfills in Antarctica

The location and distribution of legacy waste at ice-covered sites in Antarctica is often poorly documented and is difficult to characterise (Snape and Riddle 1998; Stark et al. 2006; Fryirs et al. 2013, 2015; Chapter 9). Several papers discuss the challenges associated with assessing and remediating contaminated land in Antarctica (Snape et al. 2001a; Poland et al. 2003; Rutter et al. 2003; Chapters 2, 3 and 9). For instance, logistical constraints and ice cover can make access to sites and completing site assessments difficult (Chapters 2, 3 and 9). Contaminants can be solubilised during freeze-thaw cycling and migrate off-site, and rates of petroleum hydrocarbon volatilisation and biodegradation are slower in cold regions, which can prolong the timeframes of remediation (Filler et al. 2006; White et al. 2012; McDonald and Knox 2014; Chapters 11, 12 and 13). Furthermore, terrestrial and marine wildlife in cold regions such as Antarctica show increased sensitivity to contaminants and experience slower rates of recovery relative to temperate species (Bargagli 2005; Mooney et al. 2013; Payne et al. 2014). Finally, the logistical constraints and financial costs associated with undertaking remediation operations in

remote, cold regions renders many of the traditional approaches to remediation such as dig and haul impractical or unaffordable in areas of freezing ground (Stark et al. 2003; Filler et al. 2006; McDonald and Knox 2014; Chapters 2, 3, 10 and 13). Despite these challenges, the efficiency of remediation can be improved by rigorous, preliminary site investigations which form strategic and effective approaches to remediation (Gibson et al. 1996; Chapter 9). Preliminary site investigations typically require an assessment of the type, speciation, distribution and extent of contaminants, but rarely provide a holistic approach to site assessment that also considers the protection of cultural heritage value (Ferguson 1999; Stark et al. 2003; Bridgen 2009; Chapters 8 and 9).

The first objective of this research was to apply a non-invasive tool for delineating the ice-covered landfill at Wilkes to prevent unnecessary excavation, environmental disturbance and the risk of damage to ice-covered cultural heritage items (Monier-Williams et al. 1997; Stark et al. 2006; Evans 2007, 2011; Chapter 9). Previous geophysical investigations at Wilkes have been undertaken using ground penetrating radar coupled with geographical information systems (Babicka 2000; Chapter 9), but that study provided only reconnaissance-scale information on the spatial distribution of remnant waste at Wilkes. To address this research objective and characterise the spatial extent and depth of electrically conductive metal (particularly iron and steel) at the ice covered landfill at Wilkes, a two-part ground magnetometry survey was undertaken (Chapter 9).

Magnetic anomalies collected during the survey were used to successfully characterise the spatial distribution of the landfill, identify buried materials and map the landfill boundaries (Chapter 9). The survey results showed that the landfill boundary is aligned north-west to south-east along Newcomb Bay, and is potentially migrating seaward (Chapter 9). The area and volume of the landfill was estimated to be 6,250 m^2 and 17,000 m^3, respectively (Chapter 9). The composition of the landfill was characterised by large magnetic anomalies, indicative of variable material orientation and random dumping (Chapter 9). Buried drums and intermingled smaller metallic materials were also identified in the northern part of the landfill (Chapter 9). The unevenly configured fall-off rate and asymmetry of the magnetic peaks identified as drums suggests that the drums were either empty at the time of disposal or have since discharged fuel (Barrows and Rocchio 1990; Breiner 1999; Chapter 9). The remaining amount of fuel in drums must be considered to prevent further fuel seepages if excavation is required during remediation (Chapter 9).

The survey also highlighted some additional considerations relating to the application of ground magnetometry in Antarctica. Firstly, smaller waste items may be masked by complex interactions between buried ferrous objects and geology (Barrows and Rocchio 1990; Butler 2003; Prezzi et al. 2005; Chapter 9). Therefore, the independent use of ground magnetometry may not be sufficiently accurate for site assessment at certain sites (Barrows and Rocchi 1990). At such sites, the use of complementary tools (e.g. resistivity techniques or ground penetrating radar) for comprehensive

assessments is recommended. Secondly, discrepancies in the magnetic intensity data collected on different survey dates provides insight into the influence of overlying snow and ice thickness on survey data (Chapter 9). Although inconsistencies in the dGPS measurement accuracy between the two survey dates may have contributed to discrepancies in magnetic intensity, higher amplitude anomalies are likely to be the result of previously buried materials becoming exposed during periods of melt. As a result, variable measurements in magnetic intensity are expected both within and between seasons (Chapter 9).

To complement the two-part ground magnetometry survey undertaken to delineate the ice covered landfill at Wilkes, a resistivity survey was undertaken collaboratively with researchers from The University of Melbourne (Appendix II). A Geometrics OhmMapper TR1 was used to complete the resistivity survey, but did not achieve sufficient two- or three- dimensional definition between the landfill material and the surrounding environment (Statham 2014). Allred et al. (2008) discussed the challenges associated with applying resistivity techniques at dry and frozen ground surfaces due to contact resistance, which prevents the transfer of electric currents between the instrument electrode and ground surface. Consequently, Allred et al. (2008) argued that resistivity surveys are not suitable at locations such as Antarctica, where ice cover and extremely dry conditions will reduce the suitability of this technique. OhmMappers have been successfully used in previous survey where the geometry and subsurface conditions of landfills were mapped in temperate (Roe et al. 2011; Stierman et al. 2012) and cold regions (Oldenborger 2010; LeBlanc et al. 2011). However, these studies found that the OhmMapper was most effective for two-dimensional surveys and when coupled with drilling wells, piezometers, GPR and geomorphic mapping (Roy et al. 2009; Oldenborger 2010; LeBlanc et al. 2011; Roe et al. 2011). It is possible that dryness hindered the results of this resistivity survey at Wilkes, indicating that seasonality may play an important role in the performance of this technique in Antarctica.

In summary, of the two non-invasive geophysical techniques used in this research, only ground magnetometry provided a detailed understanding of the geometry of the abandoned landfill at Wilkes. In addition to offering an effective tool for mapping ice-covered landfills, ground magnetometry can identify the type and location of buried materials, prevent disturbance associated with unnecessary excavation and reduce the risk of damage to concealed cultural heritage items (Prezzi et al. 2005; Evans 2007, 2011; Chapter 9). Finally, the data collected during the magnetometer survey provides a platform for the identification of priority areas for remediation and the development of a co-ordinated, strategic plan for the management of contaminants at Wilkes. However, this technique may not be appropriate for use at all landfills concealed by ice (e.g. at sites with complex, or strongly magnetic geologic settings), and in some instances the addition of complementary methods may be required for more

comprehensive site assessments (Roy et al 2009; Oldenborger 2010; LeBlanc et al. 2011; Roe et al. 2011; Chapter 9).

14.2.2: Laboratory testing

Several research gaps surrounding orthophosphate and silica treatments and their suitability for contaminated sites in cold regions were identified in Chapters 4 and 5. These research gaps formed the basis of the research objectives outlined in Section 3. To address these research objectives, four laboratory-based experiments were undertaken and included in Section 5.

The immobilisation of Cu, Zn and Pb was a key focus of laboratory studies included in this thesis, due to identification of these elements as forming the primary contaminants of concern at Thala Valley and Wilkes landfills in previous studies (Deprez et al. 1999; Snape et al. 2001a, b; Stark et al. 2006; Thums et al. 2010; Fryirs et al. 2013, 2015; Hafsteinsdóttir et al. 2014). All laboratory experiments in Section 5 were undertaken at 2 ºC to simulate East Antarctic summer temperature conditions, with the exception of one pilot study undertaken at ambient temperature (22 ºC), presented in Chapter 10. This trial was undertaken at ambient temperature for two reasons. Chemical reactions are faster in temperate environments, enabling a quicker decision about the feasibility of the technique for further, more detailed research (Chapter 4). Second, undertaking experiments under both temperate and cold conditions will allow for additional studies which compare treatment performance under different temperature conditions (Chapter 15).

This study assessed the potential of silica and coupled orthophosphate-silica treatments for immobilising Cu, Zn, Pb and As in soil material obtained from Thala Valley landfill (Chapter 10). The compositions and doses of the treatments applied in this study were adopted from Arocha et al. (1996), Fytas et al. (1999) and Hafsteinsdóttir (2012) because of their proven efficacy. The coupled orthophosphate-silica treatment was most effective and reduced the leachable concentrations of Cu, Zn, and Pb by 94, 96 and 99%, respectively, relative to untreated soil (Chapter 10). Two silica treatments composed of sodium metasilicate and calcium carbonate also reduced leachable concentrations of Cu and Zn after treatment (Chapter 10). The lower dose sodium metasilicate and calcium carbonate treatment was also effective at reducing leachable concentrations of Pb (Chapter 10). Concentrations of As were increased by all treatments, most significantly by the coupled orthophosphate-silica treatment which increased the leachable concentration of As from 0.01 to 0.03 mg/L (Chapter 10). Leachate samples were also collected on the first 10 days of the experiment to provide additional data regarding the performance of treatments. However, the samples polymerised into a silica gel prior to analysis and consequently were not able to be analysed.

This pilot trial provided preliminary data demonstrating the potential of coupled orthophosphate-silica and silica treatments at immobilising metal contaminants in soil. However, several areas requiring

further research were identified, including studies which: (i) monitor the effect of treatment on EC, pH and ORP; (ii) investigate the reaction products formed during treatment; (iii) compare the effectiveness of coupled orthophosphate-silica and orthophosphate treatments to distinguish the remedial effects of orthophosphate from silica; (iv) examine treatment performance by assessing a wider range of analytes; and (v) investigate the adverse effects of treatments (Chapter 10). These elements were incorporated into the research design of the experiments in Chapters 11-13.

A final limitation of this study was the absence of collected pH data. This data was not collected due to the preliminary nature of the pilot trial. However, the same soil material and similar treatments were applied in Chapter 11. In Chapter 11, the pH of soil before treatment was 8.22±0.1. After treatment, the pH of untreated, orthophosphate, silica 1, silica 2 and coupled orthophosphate-silica treated soil was 8.35±0.1, 10.55±0.1, 10.02±0.0 and 9.37±0.1, respectively. In Chapter 13 different soil material and silica treatments were used, but the pH of soil also increased after treatment. The alkalising effect of silica on treated soil was observed in all of the experiments conducted as part of this research and highlights the importance of tailoring treatment composition and dose according to site specific factors such as soil character and the contaminants of interest (Chapter 11).

To increase understanding of the environmental safety of orthophosphate and silica treatments and potential impacts of treatment overdose, soils characterised by low concentrations of Cr, Fe, Ni, Cu, Zn, As, Cd and Pb were treated with high dose orthophosphate, silica or coupled orthophosphate-silica treatments under cold conditions (2 ºC) (Chapter 11). Silica treatments effectively reduced concentrations of Fe, Ni, Cu, Zn, Cd and Pb in soil, despite being ineffective at reducing concentrations of As (Chapter 11). Orthophosphate and coupled orthophosphate-silica treatments also reduced leachable concentrations of Fe, Cu, Zn, Cd and Pb, but were ineffective at reducing leachable concentrations of Cr, Ni and As (Chapter 11). Concentrations of P remained above environmentally safe levels in soils where treatments containing orthophosphate were applied, throughout the experiment (Chapter 11). This is consistent with previous studies that reported elevated concentrations of P after treatment with orthophosphate and highlights the importance of balancing treatment dose with contaminant concentration (Cao et al. 2003; Chrysochoou et al. 2007; Mignardi et al. 2012; Hafsteinsdóttir et al. 2014). Alternatively, lining technologies or geocomposite barriers may be used to prevent excess P from entering the environment (Bathurst et al. 2006; Rowe et al. 2010)).

At the completion of the experiment, the EC of leachate collected from untreated and orthophosphate treated systems had stabilised; however, the silica and coupled orthophosphate-silica treated systems remained highly saline (Chapter 11). This is attributed to reagent overdose of low-level metal contaminated soil (Hafsteinsdóttir et al. 2014; Chapter 11), and has important implications for remediation as metal availability increases with salinity due to competition for sorption sites by major

cations, resulting in the solubilisation of metals such as Ni (Du Laing et al. 2009; Li et al. 2010; Hafsteinsdóttir et al. 2014; Chapter 11). This effect was observed in all treated systems, shown by the distinct increase in EC and concentrations of metals in leachate, which gradually decreased over 185 days (Chapter 11). The ORP of leachate collected from the untreated and orthophosphate treated soil maintained an oxidising state throughout the experiment, whereas the silica treated soil produced strongly reducing leachate for the first 30 days of the experiment (Chapter 11). After day 30, the silica treated systems transitioned into an oxidising state for the remainder of the experiment. The concentrations of metals in leachate and leachable metals in soil did not increase, despite ORP transitioning into an oxidising state (Chapter 11). The pH of soil and leachate from untreated systems remained within the healthy range (6.5-8.5; von Gunten 2003; US EPA 2009) for groundwater throughout the duration of experiment (Chapter 11). The pH of soil and leachate from orthophosphate treated systems also stabilised to within the healthy range for groundwater after 30 days (Chapter 11). The pH of soil and leachate from silica and coupled orthophosphate-silicate treated systems were persistently highly alkaline (Chapter 11), indicating that a greater volume of acid was needed following treatment with silica to reduce soil pH to within the healthy range (von Gunten 2003; US EPA 2009; Chapter 11).

A final important aspect of this study was the emphasis on soil heterogeneity. Managing heterogeneity is an important consideration which must be addressed prior to applying stabilisation techniques in situ. The effects of heterogeneity were observed in both Chapter 10 and 11, evidenced by the large standard deviations in the TCLP results. This is due to both the heterogeneous nature of landfill material and difficulties in applying treatments homogeneously. Consequently, the importance of managing natural heterogeneity was considered in depth in Chapter 11. To manage heterogeneity, Chapter 11 highlights the importance of undertaking detailed characterisation of contaminated sites and pilot scale experimentation of dose suitability before in situ application. At highly heterogenous sites, safe and effective remediation using this technique may require more detailed zoning, with areas of varying contaminant concentrations being treated as several, smaller contaminated sites. Customised treatments and doses may be applied across different zones of contamination, or the soil material may need to be blended prior to treatment (Chapter 11). Heterogeneous soil materials may also require additional monitoring to ensure that the long-term effectiveness of treatments, or coupling with additional technologies to contain or treat different types and concentrations of contaminants (Chapter 11).

Studies observing the formation of metal-phosphates and silica minerals demonstrate that mineral formation during treatment is driven primarily by treatment composition and the contaminant species present (Hafsteinsdóttir et al. 2011, 2013; White et al. 2012; Chapters 12 and 13). Orthophosphate and coupled orthophosphate-silica treatments were the most effective immobilisers of Pb, evidenced

by the complete conversion of treatment reagents into metal-phosphate minerals and metal-silicates which remained stable over 114 days (Chapter 12). Orthophosphate treatments were also effective at immobilising Cu, with insoluble minerals forming within 14 days of treatment (Chapter 12). Treatment of Zn with orthophosphate was slower and less effective than Cu and Pb, which is consistent with earlier studies by Hafsteinsdóttir et al. (2011, 2013) and White et al. (2012).

Hydroxides, calcium silicates, sodium aluminosilicates and metal-silicate minerals formed upon treatment with silica (Chapters 12 and 13). Silica treatments effectively immobilised Cu, Zn and Pb (Chapters 12 and 13). The addition of an acidic solution after the application of sodium metasilicate reduced pH effectively to within the optimal range for the polymerisation of soluble silicates and initiated faster formation of insoluble metal-silicates (Chapters 5, 12 and 13). Several explanations accounting for the variation in the immobilisation efficiency were provided in Chapter 12. First, immobilisation of Cu is typically unaffected by temperature, despite the formation of Cu phases being slow (Hafsteinsdóttir et al. 2011, 2013; White et al. 2012). Second, the lower solubility of Zn and slowed reaction kinetics in cold regions tends to result in the slower formation of fewer minerals with lesser solubility (Hafsteinsdóttir et al. 2011, 2013; White et al. 2012). This warrants a longer-term experiment capable of identifying minerals that form over longer times. Salinity may also influence mineral formation, with the stability of some minerals (e.g. bassanite ($CaSO_4 \cdot 0.5H_2O$)) increasing with salinity (Ossorio et al. 2013). The reverse effect may also occur in highly saline soils and has the potential to reduce the effectiveness of remediation (Ossorio et al. 2013; Chapters 12 and 13).

The formation of metal-phosphate minerals such as hydroxypyromorphite and metal-silicate, sodium aluminosilicates and calcium bearing minerals is consistent with previous studies (Hafsteinsdóttir et al. 2011, 2013; Abdel-Hamid et al. 2012; White et al. 2012; Chapters 4 and 5), and demonstrates the effectiveness of this technology in low temperature environments. Since the products formed by treatment of metals with silica have not been previously characterised (Chapter 5), this study advanced knowledge of the processes responsible for the immobilisation of metals, the speed of mineral formation and the nature of products formed. However, further studies assessing the long-term stability of minerals formed by treatment with silica is recommended before in situ application of this technology can be considered safe and suitable for use in Antarctica (Hafsteinsdóttir et al. 2011, 2013; White et al. 2012; Chapters 12 and 13).

The final research component of this thesis involved assessing the potential of silica treatments for the remediation of co-contaminated soil. This was an essential component of assessing its suitability for Wilkes which is contaminated with both metals and petroleum hydrocarbons (Fryirs et al. 2013, 2015). This also represents an important component of understanding the wider applicability of this technology to other contaminated sites in cold regions (Sheppard et al. 2000; Margesin and Schinner 2001; Allen-Gil et al. 2003; Aislabie et al. 2006; Sanscartier et al. 2009).

The performance of eight silica treatments for managing metals and petroleum hydrocarbons in co-contaminated soil was evaluated in Chapter 13. Treatments containing orthophosphoric acid were effective at reducing leachable concentrations of Cu, Zn, Cd and Pb, but mobilised As (Chapter 13). The formation of hydroxypyromorphite, hydroxylapatite, fluoroapatite, sodium aluminosilicates, calcium bearing minerals and polymerised silicates in all soils after treatment with silica provided additional evidence for the immobilisation potential of silica treatments in low temperature environments (Chapters 12 and 13). Immobilisation is largely attributed to the formation of metal-phosphate minerals and reduction of pH to levels suitable for the formation of polymerised silicates, metal-silicates and hydroxides (Amofah et al. 2011; White et al. 2012; Hafsteinsdóttir et al. 2011, 2013; Chapters 4, 12 and 13). One disadvantage of using orthophosphate is that competitive phosphate-arsenate (PO_4^3-AsO_4^3) interactions result in the mobilisation of As (Peryea 1991; Munksgaard and Lottermoser 2013; Chapter 10). However, this may be overcome by substituting orthophosphoric acid with a suitable alternative such as citric or acetic acid (Toeneboehn et al. 1992; Arocha et al. 1996).

Silica treatments that did not contain titanium dioxide (TiO_2), sodium lauryl sulphate ($C_{12}H_{25}Na_{O4}S$), propylene glycol ($C_3H_8O_2$) or orthophosphoric acid (H_3PO_4) (T1, T3) were less effective at immobilising metals (Chapter 13). In contrast, treatments that contained TiO_2, $C_{12}H_{25}Na_{O4}S$ and $C_3H_8O_2$ but not orthophosphoric acid (T2, T4) resulted in significant mobilisation of Pb (Chapter 13). This is inconsistent with earlier studies which argued that the inclusion of a surfactant increased remediation efficiency (Arocha et al. 1996; Mbhele 2007).

Treatment of petroleum hydrocarbons using silica was less effective, despite evidence of silica polymerisation provided by SEM imaging (Chapter 13). Although significant reductions in petroleum hydrocarbons were observed in all soils, there were few clear trends in the experimental data. Two silica treatments (T1 and T7) reduced concentrations of petroleum hydrocarbons (C_9-C_{18}) by approximately 70% (Chapter 13). However, concentrations of petroleum hydrocarbons (C_9-C_{18}) were lower in untreated soil than in soil treated with T1, T4 and T8 (Chapter 13). The data indicate that the inclusion of TiO_2, $C_3H_8O_2$ and $C_{12}H_{25}NaO_4S$ did not improve the remediation efficiency of treatments. Treatments not containing TiO_2, $C_3H_8O_2$ and $C_{12}H_{25}NaO_4S$ (T1, T3, T5, T7) were more effective than treatments containing TiO_2, $C_3H_8O_2$ and $C_{12}H_{25}NaO_4S$ (T2, T4, T6, T8), suggesting that encapsulation of emulsified hydrocarbons was incomplete (Chapter 13).

Chapter 13 identified several possible reasons for the ineffectiveness of T2, T4 and T8. First, Arocha et al. (1996) found that remediation efficacy doubled when two lower dose applications of silica were applied compared with a single application. Chapter 13 only assessed single application treatments; therefore, additional studies comparing the effectiveness of single application treatments with multi-application of lower dose treatments would be beneficial. Second, an assessment of the performance of silica treatments using a wider variety of reagents than used in this thesis should be undertaken as

part of optimisation treatments. For instance, orthophosphoric acid was the only acid used in the experiments in this thesis because of its previously well-established immobilisation potential (Hafsteinsdóttir et al. 2014; Chapter 4). However, substituting orthophosphoric acid with a suitable alternative may provide new and more effective treatments that do not increase the risk of eutrophication (Chapter 13). Toeneboehn et al. (1992) and Arocha et al. (1996) immobilised petroleum hydrocarbons using silica treatments that contained acetic and citric acid, indicating that these may be viable alternatives.

In summary, the research included in this thesis demonstrates that orthophosphate, silica and coupled treatments may be feasible technologies for use at metal contaminated sites in cold regions. However, treatment of petroleum hydrocarbons using silica was less effective, indicating that further research is required to optimise treatments for use at co-contaminated sites (Chapter 13). Therefore, in the interim, silica treatments should only be used at metal contaminated sites or in conjunction with a technology capable of managing petroleum hydrocarbons at co-contaminated sites (Chapter 13).

14.2.3: Implications for remediation at Wilkes

To satisfy the requirements of Annex III to the Protocol on Environmental Protection to the Antarctic Treaty (1991) and resolution 5 (ATCM 2001), Wilkes and other work sites should be remediated using techniques which will not generate adverse environmental impacts, or risk damage to pre-1958 artefacts that may hold cultural heritage value (Fryirs et al. 2013, 2015; Chapter 8).

The future remediation of Wilkes represents a large logistical and financial operation, reflecting challenges due to environmental conditions, remoteness, items with heritage value remaining on-site and the wide distribution of legacy waste (Poland et al. 2003; Evans 2007, 2011; Fryirs et al. 2013, 2015). Despite these challenges, several possible strategies for effective management of contaminants at Wilkes exist.

The logistical and financial burden, and the risk of environmental damage to the Antarctic environment presented by a 'dig and haul' approach to remediation, justifies the implementation of an on-site or even an in situ approach to remediation (Hettiarachchi et al. 2000, 2001; Martin and Ruby 2004; White et al. 2012; Statham 2014). To remain compliant with the Madrid Protocol, an assessment of the potential environmental risks associated with each remediation technology should be undertaken during a preliminary site assessment (Snape et al. 2001a, b; Stark et al. 2006; Statham 2014). The results of this assessment should represent an important consideration in the selection of technologies used for the long-term management of environmental contaminants at Wilkes.

Removal of the 222 exposed drums, numerous batteries and other discarded waste items remaining on-site should be the first priority of remediation operations at Wilkes (Fryirs et al. 2013, 2015; Statham 2014). Once removed, these items may be transported to Australia for safe disposal (Statham

2014). The abandoned landfill at Wilkes represents a large concentrated area of legacy waste, presents an immediate environmental threat to the Antarctic environment and is a safe distance from the buildings and relics with heritage value remaining on-site (Fryirs et al. 2013, 2015, Chapters 7, 8 and 9). As such, it should be managed as the second highest priority in the remediation plan for Wilkes.

This study demonstrates that metal contaminants at the landfill can be effectively managed using orthophosphate, silica or coupled orthophosphate-silica treatments (Chapters 10-13). Treatments containing orthophosphate should be customised according to the concentrations of contaminants present to prevent eutrophication (Hafsteinsdóttir et al. 2014; Chapter 11), and the complex distribution of contamination at Wilkes may justify the use of several different doses for safe and effective remediation (Chapter 12). Chemical treatments successfully applied in temperate regions include pressure injection, ribbon blenders, surface application, and excavation with subsequent mixing on-site (McDowell 1994; Mulligan et al. 2001; Yang and Mosby 2006; Chapter 5). In cold regions these techniques may be hindered by ice cover and limited infrastructure and energy supply (Poland et al. 2003; Filler et al. 2009; Chapters 2 and 3). As such, remediation at Wilkes should be undertaken during summer thaw when the environmental conditions are more favourable for in situ remediation (Poland et al. 2003). Selecting the most appropriate application technique requires an assessment of the associated financial costs, logistical burden, ease of transport and potential for environmental damage, and warrants an independent study or investigation that should be included within a detailed site assessment (Filler et al. 2009; Chapters 2, 3, 4 and 5).

Arguably the greatest challenge associated with the use of this technique at Wilkes is preventing excess P, mobilised metal contaminants and petroleum hydrocarbon contaminated groundwater from entering the environment (Hafsteinsdóttir et al. 2014; Statham 2014; Chapters 11-13). As silica treatments were ineffective at reducing concentrations of petroleum hydrocarbons in co-contaminated soil, they require further assessment before implementation can be considered viable for the management of petroleum hydrocarbons (Chapter 13). Optimisation studies may produce a silica treatment capable of managing petroleum hydrocarbons. However, in the absence of such a treatment, coupling with a technology capable of managing petroleum hydrocarbon contaminanted soil (e.g. bioremediation or electrokinetic remediation) is required (McMeekin et al. 1993; Cavanagh et al. 1995; Suni et al. 2007; Dandie et al. 2010; Wang et al. 2015; Chapter 13).

Recent studies indicate that contaminated groundwater can be safely and effectively managed in cold regions using permeable reactive barriers (Snape et al. 2001b; Filler et al. 2006; Gore 2009; Kalinovich et al. 2012; Mumford et al. 2013, 2014; Hafsteinsdóttir et al. 2014; Statham 2015 a, b, c). Statham (2014) demonstrated that P, metal and petroleum hydrocarbon contaminated groundwater at Wilkes can be managed using permeable reactive barriers comprised of a granular activated carbon, zero valent iron, sand and clinoptilolite zeolite sequence. The most appropriate location for a permeable

reactive barrier at Wilkes is along the bedrock ridgeline, downslope of the landfill. This site is approximately 4 m above mean sea level and will prevent landfill leachate runoff from entering Newcomb Bay (Statham 2014). Statham (2014) demonstrated the feasibility of installing one large permeable reactive barrier adopting a funnel and gate design at Wilkes, which should be undertaken prior to on-site or in situ application of chemical treatments.

To ensure the stability of the immobilised metals after treatment at Wilkes, or other sites where field implementation may be achieved, a long-term monitoring strategy for mobile analytes, EC, ORP and pH in soil and groundwater should be maintained (Hafsteinsdóttir et al. 2014; Chapters 11, 12 and 13).

Managing localised contaminated soil and sediment within the station precinct represents the final priority in the long-term management plan of Wilkes. Fryirs et al. (2013, 2015) identified several contaminant hotspots within the station precinct; however, the study demonstrated that the environmental threat presented by these hotspots relative to the landfill site is small. Furthermore, Resolution 5 (ATCM 2001) prohibits the removal of pre-1958 historic artefacts and all construction activities at sites where pre-1958 historic remains exist unless the items have been appropriately recorded and evaluated by the ATCM (Chapter 8). Clark and Wishart (1989) described the location of on-site artefacts at Wilkes, but a comprehensive assessment by the ATCM of any remaining pre-1958 artefacts is required before remediation operations can be approved within the station precinct (Chapter 8).

14.2.4: International relevance

Challenges surrounding the management of contaminated land are not exclusive to Wilkes or Antarctica and represent a widespread technological and infrastructural problem of varying intensity and significance (Ferguson 1999; Juhasz et al. 2003; Rutter et al. 2003; Filler et al. 2006; Chapters 2 and 3). Managing contaminated land in both temperate and cold regions is challenged by financial costs, logistical constraints, technological limitations, high heterogeneity, co-occurring contaminants and competing interests (Filler et al. 2006; Evans 2007, 2011; Fryirs et al. 2013, 2015; Chapters 2, 3, 8, 12 and 13). Therefore, the development of technologies that are capable of managing environmental contaminants despite these challenges has international relevance, and the implications of this research extends beyond Wilkes.

Geophysics has previously been used in landfill investigations in temperate regions (Benson et al. 1984; Prezzi et al. 2005; Chapter 9), but its use in cold regions has been limited (Chaparro et al. 2007). Prior to the ground magnetometry survey included in Chapter 9, the use of this technology in polar regions has been limited to geological and archaeological investigations, or pollution monitoring (Chaparro et al. 2007; Hodgetts et al. 2011; Chapter 9). The application of ground magnetometry for

the delineation of landfills had previously not been achieved in Antarctica and its successful application demonstrates that it is a cost-effective, efficient and non-invasive technique for delineating ice-covered landfills. Furthermore, these results justify the application of this technique in further research studies, preliminary site assessments, cultural heritage assessments and remediation operations at ice-covered landfills in polar regions. Since abandoned landfills, subsurface drums and buried artefacts are common near some abandoned stations in polar regions, this research has important, widespread implications at ice-covered sites where the need for subsurface data co-exists with the desire to prevent disturbance associated with excavation (Lenihan et al. 1990; Risebrough et al. 1990; Crockett et al. 1995; Poland et al. 2003; Hafsteinsdóttir et al. 2014; Chapter 9).

Similarly to the use of ground magnetometry, silica treatments have not been previously applied in cold regions and the successful application of orthophosphate fixation in cold regions is limited to a small number of recent studies (White et al. 2012; Hafsteinsdóttir et al. 2013, 2014). Therefore, this research advanced current understanding of the suitability of these techniques to low temperature environments, providing a platform for future research and application.

This research also represents an important international scientific contribution to the development of techniques for in situ management of contaminated sites in Antarctica beyond the Australian stations. Previously remediation efforts by the USA, New Zealand and Russia in Antarctica have mostly adopted a 'do nothing' or 'dig and haul' approach to waste management (Crumrine 1992; Kohnen 1994; Chiang et al. 1997; Sheppard et al. 2000; Plato and Shears 2003; Webster et al. 2003; Stark et al. 2006; Lupachev and Abakumov 2013). Moreover, the assessment and management of contaminated land in Antarctica has rarely adopted a holistic, integrated approach to remediation which considers co-existing priorities and the benefits of technology coupling (Stark et al. 2006; Chapter 8). For example, remediation operations at McMurdo Station (USA), have relied on the removal of surface landfill material, with buried materials left in situ (Crumrine 1992; Chiang et al. 1997). This can become problematic if the buried materials become exposed by thaw, and is ineffective at ameliorating the environmental impacts of contamination on local ecosystems if the contaminants have been mobilised beyond the waste disposal site prior to remediation (Stark et al. 2006). Similarly, the initial clean-up of the Thala Valley landfill located adjacent to Casey Station relied on the removal of waste material for long-term storage off-site (Deprez et al. 1999). This resulted in the mobilisation and redistribution of metal contaminants, increased concentrations of contaminants in the active layer and increased the flux of contaminants into Brown Bay (Stark et al. 2006). In response, a staged approach to remediation was implemented in conjunction with an ongoing marine monitoring program to monitor the adverse impacts of clean-up operations on-site (Stark et al. 2006). Such incidences demonstrate the need for and benefit of improved remediation practices in Antarctica and justifies the development of cost-effective, environmentally sensitive alternatives to 'do nothing' or 'dig and haul' remediation strategies.

The research in this thesis is also relevant to the management of contaminated soil and landfills in other cold, remote regions including the Canadian Arctic, Alaska, Sweden and Russia (Poland et al. 2001; Hogland et al. 2004; Filler et al. 2006; Manion et al. 2010; Rowe et al. 2010; Kalinovich et al. 2012; Kolesnikov et al. 2013). Furthermore, the technology can also be easily adapted to temperate environments and is particularly suited to developing countries where financial and logistical constraints present obstacles to remediation (Taiwo 2011).

14.2.5: Limitations and future research

The results of the laboratory studies in Section 5 demonstrate the potential for immobilisation of metals using silica and orthophosphate treatments. However, further research into treatment optimisation is required before remediation of metals and petroleum hydrocarbons in co-contaminated soil using silica can be considered safe and viable in Antarctica. Despite addressing several research objectives, this study was limited in several ways.

The principal limitation of this study is the absence of field-based data. Although laboratory based studies are a vital component of technology development, they represent a simplified form of the natural environment. Site-specific factors including geology, climate, freeze-thaw cycling, the type and distribution of contamination and microbial activity can influence the performance of treatments substantially (Hettiarachchi et al. 2000, 2001; Kumpiene et al. 2007, 2008; Rayner et al. 2007; White et al. 2012; Hafsteinsdóttir et al. 2014). A field-based study would have provided a more detailed understanding of how these factors influence treatment performance in natural environments. Studies using a wider range of soil types with different contaminants and under varying temperatures would also be beneficial for the development of this technique. Although two Antarctic based field experiments were undertaken to validate the results of laboratory experiments as part of this research, results from these studies were unobtainable due to the samples being damaged beyond analytical use during their transfer from Antarctica to Australia (Appendix I).

The short timeframes of the experiments included in this thesis provide an understanding of the speed and effectiveness of treatments, and detail regarding the chemical reactions responsible for remediation (Kumpiene et al. 2008; Hafsteinsdóttir et al. 2011, 2013; White et al. 2012). However, longer-term studies are necessary to determine whether the mineral and polymerised silicates formed during treatment are safe, stable and suitable for long-term remediation. Such studies should focus on the potential for metals to become re-solubilised after treatment due to a change in environmental conditions such as pH and redox (Kumpiene et al. 2007, 2008; Hafsteinsdóttir et al. 2015), and investigate whether or not polymerised silicates degrade over time (Chapter 5).

Due to these limitations, several uncertainties surrounding orthophosphate and silica treatments remain unaddressed and are critical to the development of these technologies. Therefore, additional research in the areas listed below are suggested:

1- Field-based studies to validate the results of laboratory studies.
2- Optimisation studies investigating the performance of treatments on a wider range of soil and contaminant types to identify the most appropriate treatment composition for individual soil types and contaminants.
3- Optimisation studies concentrating specifically on the development of a silica treatment capable of managing petroleum hydrocarbon contaminated soil.
4- Studies assessing the long-term stability of minerals and polymerised silicates formed during treatment, under varying temperature conditions.
5- Studies assessing delivery techniques for in situ application of orthophosphate and silica treatments; and,
6- Studies investigating the effects of orthophosphate and silica treatments on microbial communities.

Finally, the environmental contamination problems described in this study are not unique to Wilkes, therefore significant potential for equivalent research at similarly contaminated sites exists in both temperate and cold regions.

14.3: References

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Chapter 15: Conclusion

This research focused on developing orthophosphate, silica and coupled orthophosphate-silica treatments for the management of contaminants at Wilkes. In addition, this research developed our understanding of the areas requiring treatment at Wilkes and will aid in the selection of technologies suitable for safe and effective remediation. Although this research was largely laboratory-based due to previously mentioned complications, the study results provide information relevant to Wilkes and other contaminated sites in remote, cold locations.

The results of laboratory experiments demonstrate that orthophosphate, silica and coupled orthophosphate-silica treatments are highly effective at immobilising Cu, Zn, Cd and Pb. However, managing petroleum hydrocarbons in co-contaminated soil using silica was less effective, indicating that further research is required to optimise treatments.

The complex distribution of contaminants and presence of potential heritage items at Wilkes warrants a staged approach to remediation. This study proposes that initial remediation efforts should concentrate on the removal of legacy waste, followed by remediation of the landfill site. Effective management of metal contaminants at the landfill may be achieved using orthophosphate, silica or coupled orthophosphate-silica treatments. However, to effectively manage P, As and petroleum hydrocarbon contaminated groundwater, the installation of a permeable reactive barrier downstream of the landfill is recommended. A rigorous monitoring program to detect for any adverse effects of treatment or re-solubilised metals should also be implemented.

Furthermore, several aspects of orthophosphate, silica and coupled orthophosphate-silica treatments require further assessment before in situ implementation at Wilkes can be considered safe and viable. Specifically, in situ application of treatments is not recommended prior to the completion of additional studies demonstrating the long-term safety and efficacy of treatments. In addition, further research is required to optimise silica treatments for application to petroleum hydrocarbon contaminated soil and soil co-contaminated with metals and petroleum hydrocarbons. Optimisation studies should also investigate alternative treatment compositions that do not increase the risk of waterway eutrophication or As mobilisation. Studies investigating the impact of treatments on microbial communities and assessing the stability of products formed after treatment with silica are also required to ensure that the products formed are safe and suitable for long-term remediation. Finally, as these research outcomes extend beyond Wilkes, equivalent research at similarly contaminated sites in both temperate and cold regions to demonstrate the performance of these technologies under a wider range of environmental conditions would be beneficial.

Appendix I

Field trials at Casey Station, East Antarctica

Overview

In addition to the research presented in Sections 4 and 5, two experiments were undertaken at Casey Station, East Antarctica to assess the efficacy of orthophosphate and silica treatments under field conditions. The samples collected during the experiment were compromised beyond analytical use during transport from Antarctic to Australia, consequently the desired research outcomes were not achievable. The experimental design of these two experiments are presented below to provide guidance for future, relevant field-based research.

Assessing the efficacy of orthophosphate for treatment of metals in soil co-contaminated with metals and petroleum hydrocarbons

A field-based experiment assessing the performance of orthophosphate treatments at immobilising metals in soil co-contaminated with metals and petroleum hydrocarbons commenced on 7 January 2013. The soil material used in the experiment was extracted from the now abandoned landfill at Wilkes. Six orthophosphate treatments (P1-P6) were applied in duplicate to 40 kg batches of contaminated soil (n=28), homogenised in a cement mixer (Table A1; Figure A1) and sampled over a 20 day period. The overarching objectives of the experiment was to evaluate the feasibility of orthophosphate treatments as a component in the long-term management plan for environmental contaminants at Wilkes. To achieve this, the following research questions were addressed:

i) What is the most appropriate dosage and most effective composition of treatment for the immobilisation of metal contaminants in soil?

ii) How effective are orthophosphate treatments in the presence of petroleum hydrocarbons?

iii) What is the effect of phosphate rock on treatment performance?

Table A1: Orthophosphate treatments trialled during 2012-13 field season. Four litres of feedwater was added to each treatment on day 1, followed by an additional 200 mL of feedwater on each day of sampling.

Batch ID	Treatment ID	TSP (wt%)	PR (wt%)	Emag (wt%)	SAB (wt%)
1	P1- US	2	1.33	1.33	0
2	P2- US	2	0	1.33	0
3	P3- US	3	2	2	0
4	P4-US	3	0	2	0
5	P5-US	4	2.66	2.66	0
6	P6-US	4	0	2.66	0
7	Control- US	0	0	0	0
8	P1- US Duplicate	2	1.33	1.33	0
9	P2- US Duplicate	2	0	1.33	0
10	P3- US Duplicate	3	2	2	0
11	P4- US Duplicate	3	0	2	0
12	P5-US Duplicate	4	2.66	2.66	0
13	P6- US Duplicate	4	0	2.66	0
14	Control- US Duplicate	0	0	0	0
15	P1- S	2	1.33	1.33	4
16	P2- S	2	0	1.33	4
17	P3- S	3	2	2	4
18	P4- S	3	0	2	4
19	P5- S	4	2.66	2.66	4
20	P6- S	4	0	2.66	4
21	Control – S	0	0	0	4
22	P1 – S Duplicate	2	1.33	1.33	4
23	P2 – S Duplicate	2	0	1.33	4
24	P3 - S Duplicate	3	2	2	4
25	P4 – S Duplicate	3	0	2	4
26	P5 – S Duplicate	4	2.66	2.66	4
27	P6 – S Duplicate	4	0	2.66	4
28	Control – S Duplicate	0	0	0	4

- US indicate 'Unspiked'; S indicates 'SAB spiked'.

The sampling regime adopted for the field trial included soil samples collected pre- and post- treatment (n=84) and leachate samples obtained from each batch 4, 8, 12, 72, 120, 216, 264, 336, 384, 432 and 480 hours after treatment (n=308). Soil samples collected pre- and post- treatment were collected for analyses of total concentrations of metals, TPH, TCLP, pH, ORP, electrical conductivity and mineralogy. Leachate samples were collected for analyses of total concentrations of metals, TPH, pH, ORP and electrical conductivity.

Figure A1: Orthophosphate field trial experimental set-up.

Assessing the potential of silica treatments for the management of petroleum hydrocarbon contaminated soil

To assess the performance of silica treatments at managing petroleum hydrocarbon contaminated soil, a field experiment commenced on 17 December 2013. The soil material used in the experiment was obtained from the now abandoned landfill at Wilkes and spiked with 4 wt% Special Antarctic Blend diesel (SAB).

The petroleum hydrocarbon contaminated soil was homogenised in a cement mixer and separated into 5 kg batches (n=12) prior to treatment with one of 4 silica treatments (Table A2, Figure A2). An additional three 5 kg batches remained untreated for use as experimental controls. A further 5 kg of soil not contaminated with petroleum hydrocarbons remained untreated for use as a 'clean' control, and a stainless steel bucket containing 5 L of deionised water (no soil) was used as a water control, to detect for any cross contamination which may occur from exposure to the installed nylon extraction valves used throughout the experiment. After the application of silica treatments had been completed, each stainless steel bucket was stored in a 60 L wheelie bin to prevent contaminant migration and the loss of petroleum hydrocarbons in the volatile range (Figure A2).

Three soil samples from each batch (n= 48) were obtained pre- and post- treatment for TPH analyses (GC-FID) and analyses of mineralogy (XRD) and silica coatings formed by treatment (SEM). Leachate samples (n=170) were obtained after 24 hrs, 48 hrs, 72 hrs, 120 hours and weekly for a six week period. A complete leachate sample included 1 x 500 mL of leachate in a glass bottle for TPH analyses (GC-FID) and a 50 mL sample used for the monitoring of ORP, pH and EC.

Table A2: SME treatments for hydrocarbon contaminated soil.

Treatment ID	Powders (Step 1)		Solution 1 (Step 2)					Solution 2 (Step 3)		
	Calcium carbonate (wt%)	Titanium dioxide (wt%)	Sodium metasilicate (wt%)	Propylene glycol (wt%)	Sodium Laurel Sulphate (wt%)	DI water (wt%)	Solution volume (L)	Phosphoric acid (wt%)	DI water (wt%)	Solution volume (L)
SAB contaminated untreated control	0	0	0	0	0	100%	3	0	0	0
Clean untreated control	0	0	0	0	0	100%	3	0	0	0
Water blank control	0	0	0	0	0	100%	3	0	0	0
SME 1	0.04	0	40%	5%	5%	50%	3	15%	85%	1.5
SME 2	0.04	0	40%	5%	5%	50%	3	N/A	N/A	0
SME 3	0.04	3	45%	3%	2%	50%	3	15%	85%	1.5
SME 4	0.04	3	45%	3%	2%	50%	3	N/A	N/A	0

Figure A2: Silica field trial experimental set-up.

Appendix II

Resistivity survey at the abandoned landfill at Wilkes, East Antarctica

Overview

On 2 January 2014, a resistivity survey utilising a Geometrics TR1 OhmMapper was completed by undertaking a north-south orientated survey with the assistance of Benjamin Freidman, Tom Statham and Lachlan Mason from The University of Melbourne. Since the extent of the landfill had been previously mapped during a magnetometer survey (Chapter 9), the aim of this survey was to further delineate the central landfill area, identified during the magnetometer survey.

A grid system was adopted for the survey and consisted of 18 x 100 m parallel lines spaced 10 m apart, established in an east to west progression that spanned from the top of the landfill area seaward (Figure A3). Prior to commencing the survey, GPS readings were acquired at the start and end points of each survey line using a Trimble dGPS, with more central points generated through interpolation. This technique was implemented due to the limitation of the base station GPS battery life.

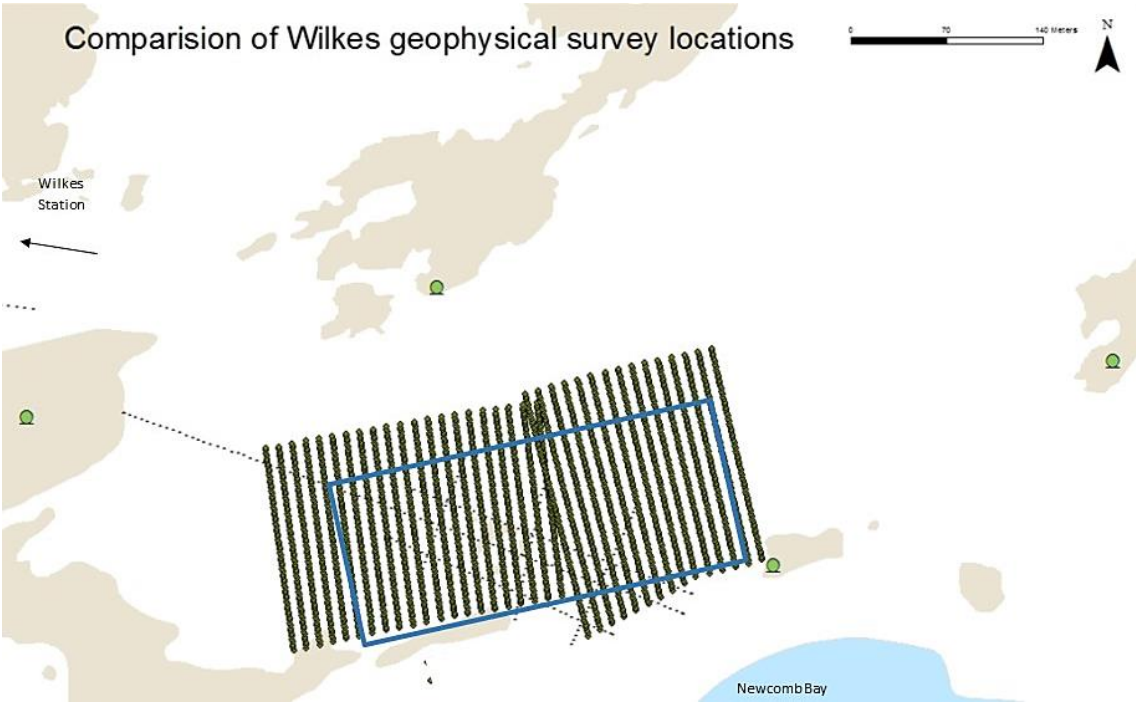

Figure A3: Approximate geometry and size of resistivity (OhmMapper) survey relative to magnetic survey (Magnetometer) undertaken at the abandoned landfill at Wilkes. The magnetomer survey dimensions are given by the dark vertical lines. OhmMapper survey dimensions are outlined by the blue rectangle.

To obtain resistivity data points and complete the survey, the OhmMapper was dragged by two people along the predetermined parallel survey lines. To improve contact between the OhmMapper and the frozen ground surface, the OhmMapper was dragged along a ski groove generated on top of each parallel survey line. The OhmMapper geometry utilised during the survey consisted of four receivers connected to the OhmMapper transmitter using 2.5 m dipole cables.

Analyses of collected data were undertaken in collaboration with Tom Statham and Lachlan Mason from the University of Melbourne and involved determining the locations of resistivity measurements using MAGMAP 2000 software. This software accessed the OhmMapper geometry and the GPS data collected prior to the survey to interpolate the location of each measurement position. Two dimensional data plotting was completed by Tom Statham and Lachlan Mason using Surfer 11 software. RES2DINV software was used to invert the data for presentation in a three dimensional format.

Analysis of collected resistivity data revealed that the survey failed to achieve sufficient two- or three-dimensional definition of the landfill material, or distinguish its resistivity signal from the surrounding environment (Statham 2014). As the data collected during this survey were unable to provide further detail regarding the geometry of the abandoned Wilkes landfill and were undertaken as a collaborative project, the data has not been included in this thesis, but are accessible online via the Australian Antarctic Data Centre (https://www1.data.antarctica.gov.au).

References

Statham T.M. 2014. *Zero-valent iron for the in situ remediation of Antarctic contaminated sites*. PhD thesis. The University of Melbourne, Australia.