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A permeable reactive barrier (PRB) media sequence for the remediation of heavy metal and hydrocarbon contaminated water: A field assessment at Casey Station, Antarctica



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HIGHLIGHTS

- A sequenced PRB for heavy metal and hydrocarbon removal was constructed in Antarctica.
- Tracer testing, coring and water samples were used to assess performance over two summers.
- Enhanced phosphorus removal was achieved relative to existing PRBs at the site.
- Non-ideal flow was observed during the second summer.

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ABSTRACT

A field trial was conducted at Casey Station, Antarctica to assess the suitability of a permeable reactive barrier (PRB) media sequence for the remediation of sites containing both hydrocarbon and heavy metal contamination. An existing PRB was modified to assess a sequence consisting of three sections: (i) Nutrient release/hydrocarbon sorption using ZeoProTM and granular activated carbon; (ii) Phosphorus and heavy metal capture by granular iron and sand; (iii) Nutrient and excess iron capture by zeolite.

The media sequence achieved a greater phosphorus removal capacity than previous Antarctic PRB configurations installed on site. Phosphorus concentrations were reduced during flow through the iron/sand section and iron concentrations were reduced within the zeolite section. However, non-ideal flow was detected during a tracer test and supported by analysis of media and liquid samples from the second summer of operation. Results indicate that the PRB media sequence trialled might be appropriate for other locations, especially less environmentally challenging contaminated sites.

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1. Introduction

Global water-related risks, including contamination, are increasingly perceived as a major threat to society and the economy (WEF, 2013). To help address this problem there is a requirement to develop low-cost and sustainable treatment technologies for a wide range of contaminants. One such technology, a permeable reactive barrier (PRB), is an in situ treatment zone that passively treats a migrating contaminant plume preventing the pollutants

from reaching downstream receptors. Since the first PRB field installation in 1991 (O'Hannesin and Gillham, 1998) there has been over 200 PRBs installed worldwide; approximately 60% of these constructions utilise zero-valent iron (ZVI) (Henderson and Demond, 2007).

An important PRB design consideration is the selection of the reactive media. The choice of the reactive media is generally influenced by the type of contaminants requiring treatment, the hydrological and biogeochemical conditions of the aquifer, mechanical stability, and cost and availability of materials (Obiri-Nyarko et al., 2014). It is possible to remove numerous contaminants with the selection of a single medium or homogenised media

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(Obiri-Nyarko et al., 2014; Ludwig et al., 2009; Zhou et al., 2014). However, utilising sequenced media within a PRB can result in varied biogeochemical regions and hence enhanced remediation processes (Morkin et al., 2000; Conca et al., 2002; Plagentz et al., 2006; Mumford et al., 2013; Huang et al., 2015).

It has been proposed that design flaws have accounted for most PRB failures (Henderson and Demond, 2007). A comprehensive understanding of hydraulic conditions is required for the placement and selection of a PRB configuration (Henderson and Demond, 2007; Obiri-Nyarko et al., 2014). PRBs can be constructed using different configurations with consist of, but are not limited to, continuous trench (Thiruvenkatachari et al., 2008), funnel and gate (Mumford et al., 2013) or an array of passive wells (Bortone et al., 2013). While the mechanical configuration of a PRB is an important consideration, this is not discussed further as this study involved the utilisation of an existing PRB.

A thoroughly researched Antarctic remediation site is located adjacent to the Main Power House (MPH) at Casey Station (Snape et al., 2006). Here, in response to a fuel spill, a sequenced PRB was installed in 2005 (Mumford et al., 2013). The original design objective of this PRB was to capture petroleum hydrocarbons and accelerate their volatilisation and biodegradation. Various combinations of reactive materials were trialled in five parallel treatments. Each treatment contained a region for nutrient release, fuel sorption and capture of excess nutrients (Mumford et al., 2013).

Soil sampling completed at the MPH site in 2005 and 2010 indicated that since the original fuel spill minimal hydrocarbon degradation had occurred in the soil uphill of the PRB. As a management strategy, contaminated soil was excavated over the 2010/11 and 2011/12 summers and placed in biopiles (McWatters et al., 2012). Due to the removal of the source zone the risk of high concentrations of hydrocarbons flowing into the PRB was mitigated. During the 2011/12 southern hemisphere summer, 64 water samples were collected around the site after excavation and backfilling, and from within the PRB; only five of these samples contained reportable levels of C_9 – C_{40} hydrocarbons (Wilkins, 2014). However, owing to the risk of future spills the PRB remains as a preventative measure and for continued research.

The compartmentalised design of the PRB allows the replacement of media within each of the five parallel cages independently. During the 2012/13 summer, one of these cages (designated Cage 5 in Mumford et al., (2013)) was redesigned to assess a potential sequencing for the treatment of both hydrocarbon and heavy metal contamination. This sequencing consisted of three sections:

- 1. Nutrient release/fuel sorption (ZeoProTM and GAC);
- 2. Phosphorus and heavy metal capture (granular iron and sand);
- 3. Nutrient and excess iron capture (zeolite).

Assessment of the performance of the media sequence consisted of fluid dynamic tests (tracer or fluid age tests) and the analysis of media and water samples during the first two summers of operation. Lessons learnt from this new sequence can provide valuable information about how to best direct remediation efforts at other Antarctic contaminated sites that contain various components and offer an alternative approach for the treatment of polluted surface and groundwater in less operationally and climatic restrictive locations.

2. Methods

2.1. Barrier construction

The barrier was originally constructed during the 2005/06 Antarctic summer and media for all the cages was first replaced in

2009/10 (Mumford et al., 2014). The reactive gate consists of five modified Australian Antarctic Division (AAD) steel cage pallets with external dimensions 1.8 L x 1.1 W \times 0.75 H m (Mumford et al., 2013). Megaflo® (Geofabrics Australasia) was placed vertically across the entry face of the PRB and along the majority of the PRB funnel. Megaflo® is a high-density polyethylene (HDPE) subsurface panel drain that was installed to level the inflowing water height at the entry face of the five sequences of the PRB. This allows the hydraulic performance the different sequences to be compared. For further details on the design and construction of the PRB refer to a previous publication (Mumford et al., 2013).

The pre-existing PRB media in Cage 5 was excavated and refilled on the 16th of January 2013. In this process mixed media sections (as described) were homogenised within a cement mixer, batched, and then placed in the PRB. The heat trace, PRB inlet and outlet nylon mesh, temperature sensors and ¼ inch multiports from the original installation were reused. Six oxygen sensors (1-point calibrated Figaro KE-25) and additional temperature sensors (4-point calibrated Analog Devices AD592) were placed at set locations as the PRB was filled. Further information about the location of sensors and multiports (draw depths at 0.35, 0.45, 0.60 and 0.70 m) are shown in Fig. 1 and detailed in Supplementary Information (SI) Table S1.

2.2. Reactive media

The reactive media selected were commercially available, at relatively low cost, and have been investigated for the development of cold climate PRBs in supporting laboratory studies (Statham et al., 2015a, 2015d), complementary research aimed at hydrocarbon remediation (Mumford et al., 2013, 2014), or previous heavy metal removal studies (Woinarski et al., 2003, 2006). The particle size distribution of each material was determined by replicated sieving of 500 g samples on a sieve shaker (Endecotts Minor).

2.2.1. ZeoPro

ZeoPro™ (ZeoponiX, CO, USA; H-Plus 8–40 US mesh, 0.4–2.4 mm) is an ammonium and potassium loaded zeolite, coated with apatite (a calcium phosphate). As the apatite dissolves, calcium and trace elements exchange with ammonium and potassium cations within the pores of the zeolite. This process releases phosphorus and nitrogen into solution, the nutrients which limit microbial growth and hence bioremediation in Antarctic soils (Powell et al., 2006).

2.2.2. Granular activated carbon

GAC is an industry standard for the sorption of organic contaminants and chlorinated hydrocarbons. The GAC selected (PICA, OH, USA; Picabiol 6–12 US mesh, 1.7–3.4 mm) is derived from coconut husk and has a relatively high surface area.

2.2.3. Granular zero-valent iron

Granular zero-valent iron (ZVI) was selected for the removal of phosphorus and heavy metals from solution. Peerless iron (Peerless Metal Powders & Abrasive, MI, USA; cast iron aggregate 8–50 US mesh, 0.3–2.4 mm) was chosen to be consistent with laboratory based research (Statham et al., 2015a, 2015c).

2.2.4. Sand

Sand was selected to mix with ZVI to minimise reductions in porosity and hydraulic conductivity due to iron corrosion and aging processes (Noubactep and Caré, 2010; Statham et al., 2015c). Heat treated silica sand (*Stornoway*, TAS, Australia; 16 to 30 US mesh, 0.6—1.2 mm) was sourced from a Tasmanian quarry.

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