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Research article

Application of controlled nutrient release to permeable reactive barriers

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ABSTRACT

The application of controlled release nutrient (CRN) materials to permeable reactive barriers to promote biodegradation of petroleum hydrocarbons in groundwater was investigated. The longevity of release, influence of flow velocity and petroleum hydrocarbon concentration on nutrient release was assessed using soluble and ion exchange CRN materials; namely Polyon™ and Zeopro™. Both CRN materials, assessed at 4 °C and 23 °C, demonstrated continuing release of nitrogen, phosphorus and potassium (N–P–K) at 3500 bed volumes passing, with longer timeframes of N–P–K release at 4 °C. Zeopro™–activated carbon mixtures demonstrated depletion of N–P–K prior to 3500 bed volumes passing. Increased flow velocity was shown to lower nutrient concentrations in Polyon™ flow cells while nutrient release from Zeopro™ was largely unchanged. The presence of petroleum hydrocarbons, at 1.08 mmol/L and 3.25 mmol/L toluene, were not shown to alter nutrient release from Polyon™ and Zeopro™ across 14 days. These findings suggest that Polyon™ and Zeopro™ may be suitable CRN materials for application to PRBs in low nutrient environments.

1. Introduction

Global extraction and transport of crude oil has resulted in the terrestrial environment being exposed to approximately 25,000 tonnes of crude oil every year as a result of damaged pipelines and storage vessels (McDonald and Knox, 2014). Permeable Reactive Barriers (PRBs) offer the potential to capture petroleum hydrocarbon contaminants in groundwater, minimising the transport of spills to uncontaminated terrestrial environments (Mumford et al., 2015). PRBs stand to significantly reduce remediation costs where soil remediation operations such as 'dig and haul' can influence petroleum hydrocarbon mobilisation through subsurface disturbance (Snape et al., 2001; Filler et al., 2006). Snape et al. (2001) and Ferguson et al. (2003) also emphasise the importance of coupling soil and groundwater remediation infrastructure to prevent contaminant migration in low organic, free-draining Antarctic soils.

The effectiveness of petroleum hydrocarbon adsorption materials such as granular activated carbon (GAC) in PRBs has been well reported (Karanfil and Kilduff, 1999; Arora et al., 2011; Mumford et al., 2015). However, in the absence of biodegradation, the finite adsorption capacity of GAC presents issues associated with breakthrough, regeneration and disposal as a hazardous material. The adsorption potential of GAC is also regulated by the hydraulic conductivity of a PRB which can be influenced by biomass growth and particle breakup with exposure to freeze–thaw cycling (Seki et al., 2006; Mumford et al., 2014). At contaminated sites in cold regions such as Antarctica, low nutrient groundwater has been shown to hinder microbial growth and biodegradation (Ferguson et al., 2003; Walworth et al., 2007). Simultaneous adsorption and biodegradation of petroleum hydrocarbons on GAC has been observed (Mason et al., 2000), suggesting the advantages of biofilms to the longevity of adsorption and degradation of heavy, long chained petroleum hydrocarbons (Mumford et al., 2015). Controlled release nutrient (CRN) materials are therefore important for the sustained delivery of essential nutrients to particle-attached

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biofilms in PRBs (Freidman et al., submitted for publication).

Mumford et al. (2013, 2014, 2015) report the first application of soluble and nutrient-amended zeolite CRN materials to promote biodegradation in a sequenced PRB at Casey Station, Antarctica. Total petroleum hydrocarbon concentrations, degradation indices and microbial analyses support the application of CRN materials to promote biodegradation within PRBs (Mumford et al., 2015). Due to logistical constraints associated with accessing contaminated sites in cold regions, the timeframes over which CRN materials will deliver essential nutrients will dictate the longevity and contribution of biodegradation to PRB performance.

In this study, timeframes of nitrogen, phosphorus and potassium (N–P–K) release from a polymer-coated and nutrient-amended zeolite CRN material under cold and temperate flow conditions were assessed. Cold flow conditions refers to water temperatures less than 5 °C that are characteristic of polar and alpine regions, while temperate flow conditions denote mild water temperatures in the range 15 °C–25 °C. This study compliments previous works that examine the influence of freeze–thaw cycling on nutrient release under batch conditions (Freidman et al., submitted for publication). While these batch tests are theoretically sufficient to predict nutrient release timeframes, in practice this understanding is not directly applicable to dynamic and fluctuating systems of flow through PRB media. Fluctuations within PRBs were also examined through the influence of changing flow velocity and petroleum hydrocarbon concentration on the rates of nutrient release. These findings will have significant implications for PRB design and longevity of biodegradation at contaminated sites in low nutrient environments.

2. Materials and method

2.1. Materials

A polymer-coated soluble fertiliser, Polyon™, and a nutrient-amended zeolite, Zeopro™, were examined in this study (Table 1). Similar to previous works, Zeopro™–GAC mixtures were also investigated (Freidman et al., submitted for publication). Additional CRN material information can also be found in previous works (Freidman et al., submitted for publication). All materials were sterilised with ethylene oxide prior to the commencement of flow cell experiments (Steritech).

2.2. Flow cell design

Flow cells were constructed from plexiglass with dimensions 130 × 50 × 40 mm (L × W × H). Inert ballotini ground glass (Potters Industries Inc. 25-40 US sieve) was placed in the front 1 cm of the flow cells to provide even flow distribution to the CRN materials. Deionised water (resistivity of 18.2 mΩ; Milli-Q, Millipore) was autoclaved at 121 °C for 100 min in 5 L glass Schott bottles and was delivered at 2.0 ml/min using multi-channel peristaltic pumps (IPC-12, ISMATEC) fitted with Norprene® L/S 14 tubing (Masterflex). Nalgene® 0.2 μm syringe filters (Sigma–Aldrich) were installed in the Norprene supply line as a secondary control to prevent microbial contamination. Polyon™ and Zeopro™ flow cells were duplicated at 23 °C and 4 °C. Zeopro™–GAC flow cells were only duplicated at 23 °C. These two temperatures were investigated to align with the upper and lower temperature range reported within Antarctic PRBs (Mumford et al., 2013).

Flow cells were operated to 3500 bed volumes (BV) passing (~318 days) at a flow rate of 11 BV passing/day. Nutrient concentrations remaining following 3500 BV passing and predicted times to depletion were determined by nutrient extractions and linear regression. The area under the concentration versus BV curves were calculated for N–P–K across each sampling interval until 3500 BV passing and extrapolation of release trends, coupled with nutrient concentrations remaining in the bed at 3500 BV passing, guided estimates of timeframes for depletion of N–P–K from Polyon™ and Zeopro™. Sterility was maintained in Polyon™ flow cells by flushing with 0.6 L of 0.5% (v/v) sodium hypochlorite (5 h sterilisation) every 500 BV passing. Flow cells containing Zeopro™ were flushed with 0.6 L of 70% (v/v) ethanol. These treatments were shown to have no effect on nutrient release from Polyon™ and Zeopro™. The low pH in Zeopro™–GAC flow cells also prevented microbial contamination.

Table 1
Nutrient material and flow cell operating characteristics. * indicates parameter not measured.

Flow cell characteristics	Polyon™	Zeopro™	GAC
Particle size (μm)	4000–2380	2380–1190	4000–2380
Bed porosity (%)	44.4	41.5	56.4
Particle roundness	Rounded	Sub-angular	Sub-angular
Particle density (g/cm^3)	0.96	0.85	0.34
BET surface area (m^2/g)	*	13	1302

Brunauer–Emmett–Teller (BET) surface area measurements were conducted using a Micromeritics ASAP 2010 (Micromeritics).

2.3. Influence of flow velocity

Nutrient release from Polyon™ and Zeopro™ was monitored within duplicated flow cells across 7 days at flow rates of 11, 27, 42, 55, 83, 111 and 166 BV passing per day at 23 °C. Polyon™ and Zeopro™ control cells were maintained at a flow rate of 11 BV/day across 7 days. Each flow velocity was applied for 24 h with three water sampling intervals at 3, 12 and 23 h within this period. Sampling of the flow cells after 3 h ensured that the material release mechanism in the bed had acclimated to the increased flow velocity; yielding more accurate nutrient concentrations. The 3, 12 and 23 h water sampling intervals were averaged to determine nutrient release at each applied flow velocity and as a function of exposure to increasing flow velocity. Flow velocity and control cells for Polyon™ and Zeopro™ were operated for 72 h at a flow rate of 11 BV/day prior to sampling to minimise inaccuracies associated with material wetting. Paired two-sample t-tests were conducted to assess the influence of flow velocity on nutrient release.

2.4. Influence of petroleum hydrocarbon concentration

The influence of petroleum hydrocarbons on nutrient release from Polyon™ and Zeopro™ was examined under stirred batch conditions and duplicated at 4 °C and 23 °C. The CRN material (10 g) was contacted with 1000 ml of sterilised deionised water in an Erlenmeyer flask and spiked with toluene (C_7H_8) (99.90%, Chem-Supply) at 1.08 mmol/L or 3.25 mmol/L at 4 °C and 23 °C. The solubility of toluene in water is 5.59 mmol/L at 23 °C (Arora et al., 2011). Toluene controls (1.08 mmol/L toluene with no CRN material) and controls (CRN material with no toluene) were established at 4 °C and 23 °C.

Flasks were capped with sterilised cotton wool and aluminium foil and shaken at 25 rpm for 14 days. A low shaking speed was employed to lower volatilisation rates of toluene from deionised water. Nutrient and toluene concentrations were sampled with glass syringes at 1, 4, 9 and 14 days in a sterile Pyramid Glove Bag (Cole Parmer). Checks for microbial contamination in the batch solutions were conducted at 14 days using the spread-plate technique and Tryptone Soy Agar (TSA) plates at 23 °C for 48 h (Oxoid). Microbial growth on the particles was checked by field emission