Chemosphere 77 (2009) 1121–1126

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Technical Note

Bioremediation of weathered petroleum hydrocarbon soil contamination in the Canadian High Arctic: Laboratory and field studies

David Sanscartier, Tamsin Laing, Ken Reimer *, Barbara Zeeb

Royal Military College of Canada, Kingston, Ontario, Canada

ARTICLE INFO

Article history:
Received 3 February 2009
Received in revised form 1 September 2009
Accepted 2 September 2009
Available online 24 September 2009

Keywords:
Remediation
Hydrocarbons
Landfarm
Contaminated soils
Cold and dry climate

ABSTRACT

The bioremediation of weathered medium- to high-molecular weight petroleum hydrocarbons (HCs) in the High Arctic was investigated. The polar desert climate, contaminant characteristics, and logistical constraints can make bioremediation of persistent HCs in the High Arctic challenging. Landfarming (0.3 m^3 plots) was tested in the field for three consecutive years with plots receiving very little maintenance. Application of surfactant and fertilizers, and passive warming using a greenhouse were investigated. The field study was complemented by a laboratory experiment to better understand HC removal mechanisms and limiting factors affecting bioremediation on site. Significant reduction of total petroleum HCs (TPH) was observed in both experiments. Preferential removal of compounds <nC16 was observed in both the field and the laboratory. In the laboratory, significant removal of compounds >nC16 occurred, whereas in the field, TPH reduction was mainly limited to removal of compounds <nC16. Slight removal of compounds >nC16 was observed in the fertilized field plots only. The greenhouse increased average soil temperatures and extended the treatment season but did not enhance bioremediation. Findings suggest that temperature and low moisture content affected biodegradation of HCs in the field. Little volatilization was measured in the laboratory, but this process may have been predominant in the field. Low-maintenance landfarming may be best suited for remediation of HCs compounds <nC16 in such conditions.

1. Introduction

Soil contamination by hydrocarbons (HCs) is recognized as a concern in the Arctic (AMAP, 1998). Treating contamination is difficult due to suboptimal environmental conditions, a very short treatment season, site remoteness and limited local infrastructure (Aislabie et al., 2006; Schiewer and Niemeyer, 2006). Bioremediation of HCs is now recognized as possibly the most attractive clean-up approach for Polar Regions (Aislabie et al., 2006). Research has focused on low- to medium-molecular weight compound mixtures such as diesel fuel and few studies have investigated high-molecular weight compounds such as motor oil (Snape et al., 2008). Numerous contaminated sites in Polar Regions have legacy contamination that is often associated with weathered contaminants that tend to be recalcitrant to bioremediation (Brassington et al., 2007).

There is growing interest in cold-region landfarming because it is a relatively inexpensive and effective method for dealing with contaminated soils in inaccessible areas (Paudyn et al., 2008). This technique has proven to be effective for removing low- to medium-molecular weight compounds in the Arctic (McCarthy et al., 2004; Chang et al., 2007; Paudyn et al., 2008). Reports of effective landfarming of higher-molecular weight compounds in cold climates are limited (Delille et al., 2004) and concerns remain about the effectiveness of this technology.

At Quttinirpaaq National Park (QNP), Ellesmere Island, NU, Canada, soil predominantly contaminated with weathered medium- to high-molecular weight HCs, provided an opportunity to assess the applicability of bioremediation under realistic High Arctic conditions. Bioremediation was investigated in the laboratory and the field. The study focused on the investigation of: (1) the potential for on-site bioremediation, (2) the removal of different HC fractions from soil, (3) the HC removal processes involved, and (4) the achievement of current HC fraction-based soil quality guidelines.

2. Materials and methods

2.1. Site description

The site under study is Tanquary Fiord, the main camp of QNP (81°24′ N, 76°53′ W). QNP is classified as a polar desert, receiving

* Corresponding author. Address: Environmental Sciences Group, Department of Chemistry and Chemical Engineering, Royal Military College of Canada, P.O. Box 17000 Stn Forces, Kingston, ON, Canada K7K 7B4. Tel.: +1 613 541 6000x6161; fax: +1 613 541 6596.
E-mail address: reimer-k@rmc.ca (K. Reimer).

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doi:10.1016/j.chemosphere.2009.09.006

an average of 60 mm of precipitation annually, with low temperatures (annual mean −15 °C) and short summers (about 3 months when daily temperature >0 °C). This remote park is mainly accessible by small aircraft via Resolute Bay, NU (~900 km away). There is very little infrastructure on site and electrical power is limited.

The soil is coarse grained (71% gravel, 29% sand), nutrient-poor (<2 mg kg^{-1} nitrate, nitrite, and ammonia, and <0.1 mg kg^{-1} orthophosphate), slightly alkaline (pH 7.6–8.0), and has a low total organic content (1.3 ± 1.1%). Weathered HC contamination resulted from spills of various petroleum products, such as diesel, jet fuels and motor oil, since the 1950s. HC-contaminated soil was collected in the field and kept refrigerated until used in the laboratory.

2.2. Experimental design

2.2.1. Solid-phase batch bioreactors

Two solid-phase batch bioreactors were built from 40-L sealed plastic boxes to test bioremediation in optimal conditions and to assess HC removal mechanisms. In each box, 18 kg of unsieved soil was incubated at room temperature (~22 °C) for 313 d. Both boxes received identical amendments. Fertilizers (urea and diammonium phosphate) were applied in a powder form to a C:N:P of 100:3.75:0.25. The surfactant Biosolve (Westford Chemical Corp.), an anionic biodegradable synthetic surfactant marketed as a bioremediation-enhancing agent, was added as a 3% solution at half of the recommended application rate. Application rates were chosen based on the results from previous experiments with Arctic soils (Reimer et al., 2003). Air was continuously injected in the soil at a rate of ~25 mL s^{-1}. A granular activated charcoal (GAC) filter captured HCs present in the air effluent from the bioreactor system. Soil moisture content was maintained at ~10% (wt). Three discrete soil samples were collected from each bioreactor at days 0, 41, 134 and 313, and analyzed for HCs and HC-degrading microbial counts (HC-degraders). After one month of treatment, three GAC samples were collected from the filters and analyzed for HCs. Soil respiration was measured weekly by closing the air inlet and outlet and monitoring the evolution of O_2 and CO_2 levels with a portable gas analyzer (ATX-620, Industrial Scientific). Cumulative O_2 depleted and CO_2 evolved were obtained by integrating under the respiration rate curves.

2.2.2. Field study

A landfarming experiment was carried out from July 2005–July 2008 in Tanquary Fiord. Because the site is rarely visited, a simple, low-maintenance remediation system was tested. Contaminated soil collected around the site was homogenized and divided into six, 0.3 m^3 plots (depth ~0.25 m). Plots were established within a bermed and lined area. Six treatments were tested: (1) C: Control – addition of water only, (2) S: addition of surfactant and water, (3) SF: addition of surfactant, fertilizers and water, (4) CGH: same as C inside a greenhouse, (5) SGH: same as S inside a greenhouse, and (6) SFGH: same as SF inside a greenhouse. The same fertilizers and surfactant as in the bioreactor experiment were applied at the same application rates. Water was applied to obtain ~10% (wt) moisture content. Amendments were applied at construction in 2005 and after sampling in the summer of 2007. The greenhouse enclosure (50-cm high wooden structure covered by a translucent tarpaulin) was erected to investigate the effects of passive solar heating. Soil temperature was monitored continuously from August 2006–July 2008 with thermocouples (105T, Campbell Scientific) inserted to a depth of 10 cm in plots. Outdoor temperature was obtained from Parks Canada weather station. All plots received minimal maintenance: watering and mixing with a rototiller three times per summer. Three discrete samples (10–20 cm) were collected from each plot at the start of the experiment and each summer thereafter and analyzed for HCs, nutrients and HC-degraders. Surface (0–10 cm) soil samples were collected from drainage holes made in the liner to assess leaching of HCs and nutrients.

2.3. Analytical methods

HC concentrations in soil were measured using two analytical methods. The total petroleum HCs (TPH) method with data analysis allowing for the identification of HC fractions by gas chromatography-flame ionization detection (GC-FID) was used for the laboratory experiment (US EPA, 1996, 2000). Contamination was divided into two HC fractions based on the retention time of hexadecane (nC16): <nC16 and >nC16. The Canada-Wide Standard for Petroleum Hydrocarbons in Soil (PHC CWS) reference method, a GC-FID based method, was only used for analysis of samples collected in the field due to the higher cost of this method and for the comparison of field results with the PHC CWS guidelines. This method defines four HC fractions as follows: F1: nC6–nC10, F2: >nC10 to nC16, F3: >nC16 to nC34, and F4: >nC34 (CCME, 2001). Compounds >nC28 were not identified with the TPH analytical method; thus a HC fraction for compounds >nC34 (as per the CWS analytical method) was not defined. The expression "TPH" refers to the total concentration of HCs obtained by both methods. For the CWS method, we defined TPH as the sum of F2, F3, and F4, as the F1 component was negligible (<3% in 2005 and not detected in subsequent years). The level of volatile HCs trapped on GAC samples in the bioreactors was determined by extraction of GAC with CS_2 (adapted from NIOSH, 2003) followed by analysis by GC-FID (same as TPH method).

HC-degraders were quantified by spread plate counts (Sanscartier et al., 2009a). NH_3, $NO_3^- + NO_2^-$ (reported as one compound), and PO_4^{3-} was determined on digested samples using methods 4500-NH3 G, 4500-NO3 H, and 4500-P (APHA, 2005). Laboratory results are reported per dry weight.

Quality assurance and quality control (QA/QC) consisted of the analysis of field and laboratory blanks, field and analytical duplicates and, in the case of HC soil concentrations, spiked controls. Criteria were met: blanks were below detection limit of respective methods, duplicate values were within 30% of one another and spiked controls were returned within 10% of target value. The CWS method prescribes comprehensive QA/QC procedures that were met (CCME, 2001).

2.4. Statistics

Statistical data analysis was carried out using non-parametric statistics with Systat ver.10 (Systat Software, Inc.). Statistical significance was accepted at $\alpha = 0.05$ (95% confidence level).

3. Results

3.1. Bench-scale bioreactors

Overall reductions of 66%, 81% and 61% were observed for TPH, compounds <nC16 and compounds >nC16, respectively (Table 1). Only compounds <nC16 were removed during the first 134 d. Significant removal of compounds >nC16 was observed after day 134. Volatile HCs (0.44 ± 0.27 g) were trapped during the first 30 d, equivalent to <1% of HCs initially present in soil. Volatilization was not measured thereafter. Nearly 99% of the volatile compounds trapped were <nC16.

Cumulative O_2 depleted and cumulative CO_2 evolved followed similar trends and reached 109 and 45 g, respectively (Fig. 1a). HC-degrader counts increased ~10-fold from an initial value of 3.7×10^5 CFU g^{-1}during the first 40 d and then dropped (Fig. 1a).