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# Petroleum hydrocarbon remediation in frozen soil using a meat and bonemeal biochar plus fertilizer

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## HIGHLIGHTS

- Laboratory-scale PHC degradation was investigated under frozen and thawed conditions using biochar and compost amendments.
- Under frozen conditions, F3-PHC degradation rate constants were higher in biochar-amended soils.
- Liquid water content increased in frozen soils amended with biochar, but not nutrient supply rates.
- Total PHC-degrading microbial populations were stimulated in frozen soils amended with biochar.
- Biochar applications at 3% (w/w) have the potential to increase PHC remediation rates in frozen soils.

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## ABSTRACT

Petroleum hydrocarbon (PHC) degradation slows significantly during the winter which substantially increases the time it takes to remediate soil in Arctic landfarms. The aim of this laboratory trial was to assess the potential of a meat and bonemeal (MBM) biochar to stimulate PHC degradation in contaminated soil collected from Iqaluit, Canada. Over 90 days, 3% (w/w) MBM biochar significantly increased F3-(equivalent $nC_{16}$-$C_{34}$) PHC degradation rate constants ($k$) in frozen soils when compared to the fertilizer (urea and monoammonium phosphate) control. Taking into consideration extensive variability within treatments and negative $k$ values, this difference may not reflect significant remediation. Decreasing $C_{17}$/Pr and $C_{18}$/Ph ratios in the frozen soil suggest that this reduction is a result of microbial degradation rather than volatilization. Amendment type and application rate affected the immediate abiotic losses of F2 and F3-PHC in sterile soils, with the greatest losses occurring in compost-amended treatments in the first 24 h. In frozen soils, MBM biochar was found to increase liquid water content ($\theta_{liquid}$) but not nutrient supply rates. Under frozen but not thawed conditions, genes for aromatic (*C2,3O* and *nahAc)* but not aliphatic (*alkB)* PHC degradation increased over time in both biochar-amended and control treatments but total viable PHC-degrading populations only increased in biochar-amended soils. Based on these results, it is possible that PHC degradation in biochar-amended soils is active and even enhanced under frozen conditions, but further investigation is required.



## 1. Introduction

Landfarming is the most common bioremediation method in cold regions but it is a slow and costly process that can be limited by extreme environmental conditions and remote locations (Mohn and Stewart, 2000). Conventional methods of petroleum hydrocarbon (PHC) remediation in landfarms rely on fertilizer additions and soil turning to stimulate the microbial community to catabolize organic contaminants; this approach, however, has yielded inconsistent results in cold environments (Powell et al., 2006; Paudyn et al., 2008). Current bioremediation strategies are targeted toward the short summer months (2–4 months/year); but this is often an insufficient amount of time to meet soil remediation targets and environmental criteria (Mohn and Stewart, 2000). Substantial bioremediation can occur at sub-zero temperatures and extending microbial degradation of PHC further into the winter months could reduce the amount of time required to clean

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landfarmed soil (Rike et al., 2003).

Biochar is a soil amendment that results from the heating of organic biomass under oxygen limited conditions, and has been used in environmental remediation to sorb organic pollutants and stimulate microbial degradation (Lehmann et al., 2011; Ogbonnaya and Semple, 2013). The type of feed stock and the conditions under which the pyrolysis is carried out, can drastically affect the chemical properties, elemental composition and overall suitability of the resulting biochar as a soil amendment (Amonette and Joseph, 2009; McLaughlin et al., 2009). Typical feed stocks include wood products, leaves, grasses, manures, sludges or crop residues. Biochars produced from meat and bonemeal (MBM) are less common but contain large amounts of calcium phosphate (Betts et al., 2013). Biochars derived from wood products generally have a higher carbon content, but lower ash, nitrogen, phosphorous, potassium, sulphur and micronutrient contents than biochars derived from bonemeal (Amonette and Joseph, 2009). There are advantages and disadvantages to the use of all feed stocks; however, utilization of an effective local source of the feed stock is ideal in that it can stimulate the economy while recycling waste materials. In northern climates, wood stocks can be limited, but there are often local sources of meat and/or bone available for use as a feed stock for biochar production.

Whereas biochar additions may contribute some nutrients to the soil (depending on the type of feedstock), a more important contribution is the ability of biochar to act as a driver for nutrient retention and transformation in the soil when supplemented with fertilizer (Glaser et al., 2002; Lehmann et al., 2003; Cantrell et al., 2012). The highly porous structure and large surface area of biochar alters nutrient retention, cation exchange capacity, aeration and hydrology within the soil pores (Atkinson et al., 2010). For example, when sandy soils are combined with biochar, the water holding capacity and liquid water ($\theta_{liquid}$) increases due to a net increase in surface area (Chan et al., 2007). Similarly, soil-biochar interactions increase the amount of liquid water in the soil, increasing nutrient supply rates (NSR), which in turn can increase degradation of PHCs (Harvey et al., 2012). In the presence of sufficient $\theta_{liquid}$, microorganisms capable of living at the critical interface of water and ice (i.e., eutectophiles) catabolize PHCs under frozen conditions (Deming, 2002). These microorganisms remain viable and metabolically active at low temperatures because the $\theta_{liquid}$ allows mass transfer processes to proceed.

In addition to changing the soil environment, biochar may also provide unique habitats for specialized microorganisms to thrive in much the same way as organic matter addition (Rivkina et al., 2000). The porous structure of biochar particles provides a suitable habitat for microorganisms by supplying nutrients and providing protection from desiccation. In turn, this promotes a larger microbial biomass, a greater abundance of culturable microorganisms and a higher metabolic efficiency relative to unamended soils (Thies and Grossman, 2006). Thus, there are two possible mechanisms by which biochar can increase microbial degradation in frozen soil; i) the biochar may alter nutrient and water diffusion rates and ii) the biochar may provide a suitable habitat for microorganisms that degrade PHCs (Thies and Rillig, 2009). Microbial colonization is dependent on pore size distribution within the biochar, as micropores are too small for most soil microorganisms, and habitable pores can become obstructed by soil or microbial components (Thies et al., 2015).

Few studies have been conducted on biochar-amended, PHC-contaminated soils under frozen conditions; therefore, the site-specific effectiveness of using biochar as a soil amendment and the mechanisms driving PHC remediation, are not well understood. The objectives of this study were to determine if MBM biochar additions could further enhance PHC degradation in fertilized, landfarmed soil from Iqaluit, Canada, and if so, to link this degradation to measureable chemical and microbial responses. We hypothesize that fertilizer plus the addition of MBM biochar has the potential to increase PHC remediation in cold regions—extending bioremediation rates into frozen months by manipulating $\theta_{liquid}$ to supply nutrients and stimulate microbial activity.

## 2. Materials and methods

### 2.1. Soil and biochar characterization

PHC contaminated soil from a landfarm in Iqaluit, Canada (63°45′N, 68°31′W) was used in a bench-scale laboratory trial to assess the effectiveness of MBM biochar and fertilizer to enhance PHC degradation in northern soils under frozen and thawed conditions. Iqaluit is located on the shores of Frobisher Bay, and experiences a typical dry Arctic climate with average monthly temperatures below freezing for eight months of the year and approximately 400 mm of annual precipitation. This area contains igneous Canadian Shield bedrock overlain by continuous permafrost.

The soil used in this study was a mixture of weathered PHC contaminated material (i.e., P50 arctic grade diesel fuel, hydraulic and heating oil) from Iqaluit and the surrounding area, which had an average PHC content of 653 mg $kg^{-1}$. Total PHC breakdown was as follows; F1: 3 mg $kg^{-1}$, F2: 156 mg $kg^{-1}$, F3: 478 mg $kg^{-1}$ and F4: 16 mg $kg^{-1}$. PHCs were extracted using Accelerated Solvent Extraction (ASE) and Canadian Council of Ministers of the Environment (CCME) column clean-up (see Section 2.4). According to Tier 1 CCME Canada-wide standards (CWS) for residential land use and coarse-grained soils (Supporting Information), F2-PHC concentrations already meet clean-up criteria (150 mg $kg^{-1}$) while F3-PHCs exceed criteria (300 mg $kg^{-1}$) by approximately 178 mg $kg^{-1}$.

The sandy soil (94% sand) had a near-neutral pH (7.5), was deficient in major nutrients [(i.e., N (1.43 mg $kg^{-1}$) and P (0.23 mg $kg^{-1}$)], and had low organic carbon (0.67%) and gravimetric moisture (9.81%) content. The MBM biochar (Titan Clean Energy Projects Corporation, Craik, SK) had a pH of 6.1, cation exchange capacity (CEC) of 35 $cmol_c$ $kg^{-1}$, Brunauer-Emmet-Teller (BET) surface area of 31 $m^2$ $g^{-1}$, average pore volume of 0.1003 $cm^3$ $g^{-1}$ and an average pore size of 11.83 nm (Betts et al., 2013). The major elements (present at concentrations >100 mg $kg^{-1}$) in the biochar were C (346 g $kg^{-1}$), Ca (135 g $kg^{-1}$), P (72.6 g $kg^{-1}$), K (18.2 g $kg^{-1}$), Na (10.7 g $kg^{-1}$), Fe (9.6 g $kg^{-1}$), Mg (53 g $kg^{-1}$) and Al (4.4 g $kg^{-1}$) (Betts et al., 2013). Composted sheep manure was locally sourced in Iqaluit and had a near neutral pH (7.4) and CEC of 90 $cmol_c$ $kg^{-1}$.

### 2.2. Experimental setup

Prior to start of the experiment, soil samples from various cells in the Iqaluit landfarm were sieved to remove large rocks, then combined and homogenized into the bulk starting material. Using a batch technique, the bulk soil was amended with urea (46-0-0) and/or monoammonium phosphate (MAP; 11-52-0) fertilizer and either compost or MBM biochar. Two levels were used for each amendment; compost at 5% or 10% (w/w) and biochar at 3% or 6% (w/w), to observe the effects at low and high amendment levels. Fertilizer additions (630 mg N $kg^{-1}$ and 70 mg P $kg^{-1}$ dry weight basis) were applied to maintain a C:N:P ratio of 100:9:1, which is considered optimal for Arctic sites (Chang et al., 2010). Whereas all treatments received nitrogen fertilizer, phosphorous fertilizer was only required for the control and compost treatments as biochar produced from bone is a potential source of calcium phosphate (ie., hydroxyapatite) and this particular MBM biochar contained enough