# PHYTOREMEDIATION OF PETROLEUM HYDROCARBON IMPACTED SOILS AT A REMOTE ABANDONED EXPLORATION WELLSITE IN THE SAHTU REGION, NORTHWEST TERRITORIES

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## ABSTRACT

Sub-arctic remote locations pose a challenge for remediation of petroleum hydrocarbons. Selecting the best method that considers and balances each of the social, economic and ecological factors that are associated with the problems can be difficult. Cost and logistical difficulties with conventional remediation by hauling hydrocarbon impacted material off-site from an abandoned exploration well site in the Sahtu Region of the Northwest Territories (NT) led to the decision to remediate the soils on-site through the use of phytoremediation with plant growth-promoting rhizobacteria (PGPR). PGPR perform many functions in the soil, e.g., increased nutrient uptake, enhanced germination and tolerance to toxic contaminants, which can lead to enhanced plant growth and subsequent breakdown of hydrocarbons in the soil. The site was seeded in 2012 with an annual northern tolerant species mix and fertilized. Biochar, a carbon-rich by-product of pyrolysis, was added to select grids to determine if a soil enhancing amendment would have a positive impact on soil fertility and stability in an otherwise inhospitable growing medium. Results from 2012 show decreases in concentrations of benzene, toluene, ethylbenzene, xylene, F1 and F2 hydrocarbons. Remediation below guidelines is anticipated by the end of summer 2014.

**Key Words:** Plant Growth-Promoting Rhizobacteria, Biochar, *Delftia Acidovorans*, Well Site.

## INTRODUCTION

Petroleum hydrocarbons (PHCs) are organic contaminants that can be persistent and are challenging to remediate to stringent environmental quality guidelines (EQG) using alternative techniques to conventional landfilling (Huang et al. 2005). Recently there has been extensive research on the use of phytoremediation utilizing plant growth-promoting rhizobacteria (PGPR) to enhance rooting zone biomass in plants; the PHCs are metabolized within the soil matrix. This approach allows the physical structure and biological properties to be preserved and soil fertility to be enhanced (Andreoni and Zaccheo, 2010). In addition, the use of phytoremediation at locations that are impractical to access by ground is an attractive remedial option to balance the economic, social and ecological factors of the project.

Cost and logistical difficulties with conventional PHC soil remediation (excavation, transport and landfill encapsulation off-site) led to a decision to remediate soils on-site by phytoremediation with PGPR at an abandoned exploration well site in the Sahtu Region of the Northwest Territories (NT). The abandoned well site is approximately 60 km south of Tulita, NT and is accessible only by air in the summer. In conjunction, as a secondary goal, this project is part of a research program to make PGPR a commercially viable and available product for consultants and industry to use on future reclamation and remediation projects. This paper presents the first year results of a phytoremediation program of PHCs at an abandoned well site in the Sahtu Region, NT.

## FACTORS AFFECTING REMEDIAL OPTIONS

Various factors were considered when determining the best remedial method for the site. Ensuring that an environmentally sustainable approach was implemented that encompassed the future protection of traditional harvesting areas, and that could be completed in a reasonable amount of time, and cost were important in the design of the overall remedial approach. Stakeholder engagement occurred with the local communities of Norman Wells and Tulita and the Sahtu Land and Water Board (SLWB). Aboriginal Affairs and Northern Development Canada (AANDC) aided in the overall plan development to ensure that any community and stakeholder concerns were addressed upfront. Significant consideration was given to the remoteness and air-only accessibility of the well site which prohibited the removal of impacted soil. Additionally, sourcing suitable clean fill would be difficult since it involves quarrying (disturbing more land), beyond the boundaries of the well site which was not acceptable to the stakeholders. Therefore, on-site remediation of impacted soils was selected.

## METHOD

### Phytoremediation Scientific Principals

Plants release nutrients into the soil which can be utilized as energy sources by microorganisms and biomass produced associated with plant roots/rootlets promotes and sustains microbial activity in the rhizosphere. If hydrocarbons are present in the rhizosphere, microorganisms will metabolize the hydrocarbons for energy (Atlas 1981). Biodegradation occurs as the microorganisms metabolize and use the carbon in the hydrocarbon chains as an energy source for cell production and growth; the hydrocarbon bonds are degraded and broken down into less harmful substances. Although biodegradation can occur naturally, the challenge is maintaining the microbial abundance and biomass in the rhizosphere under nutrient-deficient conditions in the presence of the contaminants (Huang et al. 2005).

Optimizing the phytoremediation process has included developing techniques that protect the plant from the contaminants that can arrest photosynthesis, plant respiration and metabolism resulting in reduced biomass production. When plants are stressed, they produce ethylene, a phytohormone, which invokes a stress response, leading to a reduction in plant and root growth and biomass in the rhizosphere (Saraf et al. 2011), which then inhibits microbial activity and, ultimately, hydrocarbon degradation.

PGPR increases the bacterial activity of 1-amino-cyclopropane-1-carboxylic acid (ACC) deaminase (an enzyme that catalyzes the removal from the plant of ACC, the immediate precursor to ethylene) in the rhizosphere which regulates the plants' production of ethylene (Bhattacharyya and Jha 2012; Saraf et al. 2011). PGPR also synthesizes and introduces other phytohormones consisting of auxins, gibberellins, cytokinin, and abscisic acid which regulate the growth of the plant (Bhattacharyya and Jha 2012; Saraf et al. 2011).

The combination of increased ACC deaminase activity and the production of auxins by the PGPR increases the plants' tolerance to contaminants; promotes increased plant and root growth and biomass production in the rhizosphere; and promotes the release of plant enzymes (e.g., oxidases and hydrolases) that breakdown PHCs, and exudates that stimulate microbial growth (Andreoni and Zaccheo 2010). The combination of these processes leads to a greater proliferation in microbial activity and a very active rhizosphere, which increases degradation and metabolism of hydrocarbons by the microorganisms. The hydrocarbon molecules are metabolized by the microorganisms for energy use which creates end products of carbon dioxide ($CO_2$), cell mass and water (Andreoni and Zaccheo 2010). PGPR also provide added protection to the plant against cold, drought and phytotoxic compounds that would otherwise inhibit plant and biomass production.

Implementation Logistics and Site Preparation

All equipment and materials for the remedial program needed to be heli-portable. Equipment, materials and fuel to construct a suitable pad and excavate the soils were not available locally, so were required to be trucked to Fort Simpson, NT then barged down the Mackenzie River to the closest staging area. A medium-lift helicopter was used to transport equipment, materials and personnel to the site. Local labourers, equipment operators and wildlife monitors were hired to support the program.

In the absence of a suitable quantity of low permeability clay deposits, and to limit the amount of disturbance to surface soils and re-vegetated areas at the well site, the phytoremediation pad was constructed from imported material, i.e., timber and a 30 mil linear low-density polyethylene (LLDPE) liner. The LLDPE liner was laid directly on the ground surface to contain the PHC-impacted soil during treatment and prevent impacted soils from cross-contaminating the underlying ground. At the edge of the liner, timber supports were constructed and erected to a height of about 1 m above ground level. The liner was extended over the top of the timber supports to form a perimeter berm. The liner was secured to the rail supports with nails and staples.

To allow moisture and water to infiltrate and excess water to drain away from the soil, the pad was oriented to allow run-off water to collect in the lowest corner. Continuous monitoring of the run-off collection was not feasible due to remoteness of the location, therefore, two RainDrain™ filters (a carbon passive system designed to trap hydrocarbons while allowing water to pass and be released outside the berm) were installed through the berm liner at the lowest corner of the pad.

In late June 2012, PHC-impacted soils were excavated from the vicinity of well centre and transported to the phytoremediation pad, constructed only 15 m east of well centre to minimize soil transport distances as heli-portable equipment and wet ground conditions slowed the movement of large volumes of soil. The impacted soils were directly loaded into the pad. The excavation was advanced to the top of the permafrost (approximately 1.6 m below ground level) over an area of approximately 105 $m^2$ (11.1 m x 9.5 m). An estimated volume of 170 $m^3$ of PHC-impacted soil was removed from the source area. On completion of the excavation work, a wire-mesh panel fence was erected around the open excavation to prevent access by resident or transitory wildlife. The excavation remained open to return the native soils back to the original location upon successful remediation.

Once the impacted soil had been stockpiled on the pad, the soil was spread to achieve a maximum thickness of 50 cm. The soil thickness of up to 50 cm was designed to allow for optimum conditions for root penetration to the bottom of the impacted soils therefore decreasing the duration of remediation. During this procedure, large woody debris and rocks were removed from the soil.

The soil was mechanically rototilled to break down the soil to smaller conglomerates and substrates to improve the physical structure of the soil, and create voids for airflow (soil aeration), water movement, greater treatment penetration/contact and increase soil exposure to sunlight for photo-oxidation.

Soil Amendments, Fertilization and Forage Species

Biochar (or charcoal) a carbon rich by-product of pyrolysis, was added to select grids to determine if a soil enhancing amendment would have a positive impact on soil fertility and stability in an otherwise inhospitable growing medium. Biochar is a solid material obtained from the carbonization of biomass, such as plants. Biochar has a large number of micropores and a high surface area that enhances the habitat for micro-biota and their propagation (Maraseni 2010), thus making it attractive for PGPR colonization in the rhizosphere. This product was also selected since laboratory research and field applications have demonstrated that it can improve plant yields by increasing soil fertility; stabilizing soil structures; and reducing nutrient leaching, soil acidity, irrigation and fertilizer requirements (Maraseni 2010). Biochar is also considered carbon negative, that is, it can be retained in soil long-term, and can sequester $CO_2$, nitrous oxide ($N_2O$) and methane ($CH_4$) emissions from soils, thus further reducing greenhouse gas emissions (Maraseni 2010).

The fertilizer selected initially for use at the well site was a commercially available 18-24-12 since it provided a balanced mixture of nitrogen, phosphorus and potassium and the soil nutrient conditions were unknown. It has been demonstrated (through field application) that its use encourages plant establishment and promotes early root development and growth.

The forage species used were non-invasive, annual species that are hydrocarbon tolerant (helpful with the short growing season imposed by northern climates). The blend consisted of equal portions of annual ryegrass (*Lolium multiflorum)*, slender wheatgrass (*Elymus trachycaulus)*, creeping red fescue (*Festuca rubra)* and Canada wild ryegrass (*Elymus canadensis)*.

As the secondary goal was to demonstrate PGPR as a commercially viable and available product for reclamation and remediation, the impacted soil on the pad was divided into the following four sections:

- *Section 1*: to assess the effectiveness of PGPR on hydrocarbon degradation.
- *Section 2*: to assess the effectiveness of PGPR on hydrocarbon degradation and to determine if the addition of biochar would enhance the performance of PGPR and hydrocarbon degradation.
- *Section 3*: to assess if the addition of biochar leads to enhanced hydrocarbon degradation.
- *Section 4*: to be used as a control, to assess if no treatment has an effect on hydrocarbon degradation.

Plant Growth-promoting Rhizobacteria (PGPR) Species and Application

A commercially available PGPR product called BioBoost™, a non-pathogenic, non-genetically modified bacterium containing *Delftia acidovorans,* is being used for the project. It was selected, as it was the product of study for the partnership research company and it is one of several PGPR products that are currently being researched for commercial application for soil remediation projects. Laboratory and small scale field trials completed on canola crops have demonstrated that the application of BioBoost™ has led to a 5% increase in plant yields and associated biomass production in the rhizosphere and has a known ability to biodegrade hydrocarbons (BrettYoung 2012).

Following seed germination, BioBoost™ was applied using a backpack sprayer to the soils pre-treated with fertilizer and biochar (in Sections 2 and 3). Early seed germination and root development was required to provide a surface upon which the BioBoost™ could locate, attach and accumulate.

**FIRST YEAR RESULTS**

The phytoremediation pad was divided into a 12 point grid to ensure the same locations for samples could be maintained for comparison. In July 2012, 12 soil samples were collected SP01 to SP12 (Figure 1) to establish baseline hydrocarbon conditions. In October 2012, 12 samples were collected from SP01 to SP12 (Figure 1) to assess the performance and effectiveness of the phytoremediation over the first season.

Under the Canadian Council of Ministers of the Environment (CCME) environmental quality guidelines (EQG) there are four generic land use classifications (CCME 2006). Considering the remote location of the well site, and the applicable exposure receptors, the residential/parkland land use was selected for Tier 1 EQG as the initial remedial endpoint. This land use was selected over the more stringent agricultural land use due to the low future potential that the well site would be utilized for livestock tendering or crop production (CCME 2006).

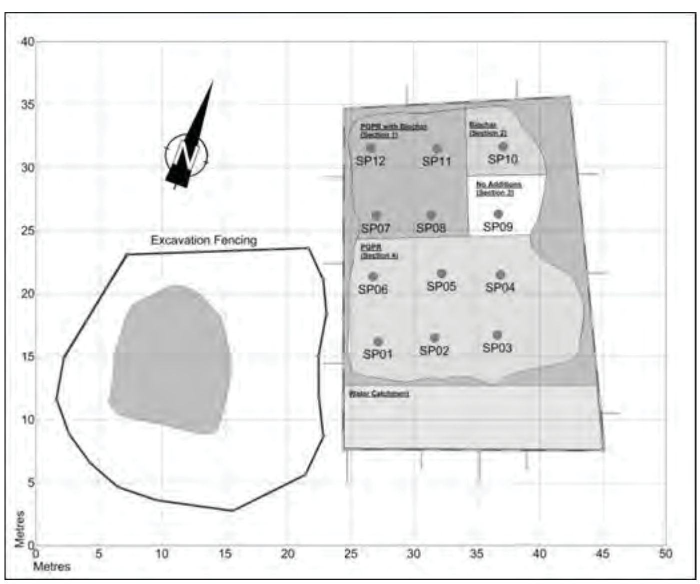


*Figure 1. Excavation and Phytoremediation Pad Layout*

Benzene, Toluene, Ethylbenzene, Xylenes (BTEX)

BTEX constituents that were reported above the EQGs in July had fallen below the EQGs in October at the same sampling points, with the exception of toluene in SP01 where the laboratory detection limit required adjustment above EQG due to moisture content. This suggests that the soils at these locations were remediated, likely by volatilization. Light end hydrocarbons with high vapour pressures have an increased tendency to be readily diffused from the soil matrix to the atmosphere. Volatilization was likely facilitated by soil movement and aeration from rototilling, or by the influence of the four treatment scenarios.

F2 ($C_{10}$-$C_{16}$) Petroleum Hydrocarbons

F2 PHCs were reported above the EQGs in SP01 to SP12 in July and, and with exception of SP11, in October, 2012. Although F2 PHC concentrations remained above the EQGs in October, there was a marked reduction in F2 PHC concentrations in SP01 to SP09. In SP11 this reduction led to a drop in F2 PHC concentrations to below the EQGs. The decrease in F2 PHCs for SP01 to SP09 ranged from 57% in SP07 to 95% in SP06 (Figure 2). Average F2 PHCs percentage reduction was approximately 75% over the 3 month remediation period. The reduction in F2 PHC concentrations is likely the result of a combination of factors, including some volatilization resulting from the movement and rototilling of the soil, soil homogenization, influences from the four treatment scenarios and phytoremediation.

The only exceptions to the downward trend in F2 PHC concentrations were in observed SP10 and SP12 which reported a 56% and 107% increase, respectively (Figure 2). It is possible that this variation reflects the natural heterogeneity of the soil between sampling events or the sample contains a higher abundance of biogenic organic compounds that may have biased the analytical results.

In terms of variations in the rate and effectiveness of phytoremediation associated with the four treatment sections, it appears that varying the treatment conditions had little effect on remediation performance. Consistent reductions of similar magnitude in F2 PHCs were recorded across the pad even in *Section 3* (SP09) which acted as the control location. At this stage in the remedial program, a similar pattern of reduction in the control (SP09) and the other three treatment sections suggest that physical handing, homogenizing and exposing the soil microorganism to the atmosphere (oxygen) for the three month period following preparation alone may have had more of an influence on F2 PHC reductions rather than the application of the various treatments. If the effects of the treatments are to be realized it is expected that the control will remain stable and the F2 PHC concentrations at the other treatment scenarios should decline.

With the addition of PGPR to SP12 in *Section 1* it is anticipated that F2 PHC concentrations should decline at this sampling location. For SP10, located in *Section 2* with biochar and the documented improvements to soil fertility, structure and acidity, there should be future F2 PHC reductions, albeit to a lesser rate and degree than those sections treated with PGPR (*Sections 1* and *4*).

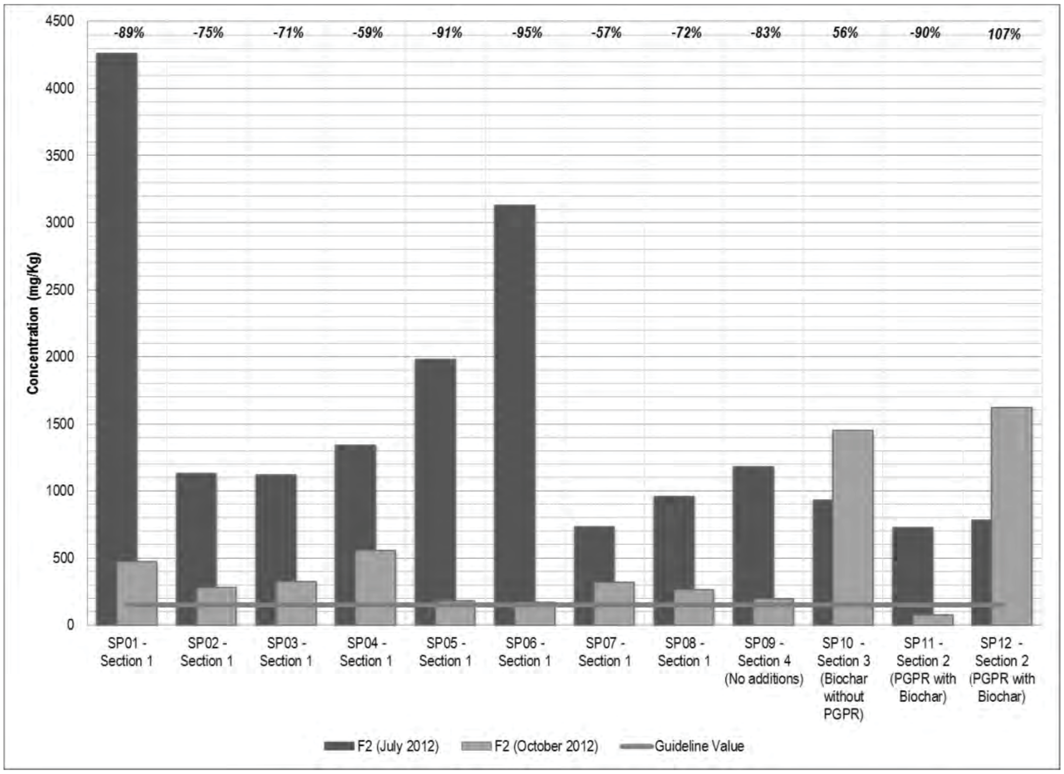


*Figure 2. A comparison of F2 (C10 – C16) soil concentrations between July 2012 and October 2012*

<u>F3 ($C_{16}$-$C_{34}$) Petroleum Hydrocarbons</u>

F3 PHC was reported above the EQGs in SP01 to SP04 in July 2012. Noticeably the F3 PHC concentrations increased between the July and October sampling events in SP02 and SP04 to SP12, with new exceedances of EQGs in SP05, SP08 and SP12. This percentage increase in F3 PHCs at these locations ranged from 1% in SP06 to 296% in SP12 (Figure 3). The average F3 PHC increases were about 83% over the 3 month remediation period.

Although the increase in F3 PHC concentrations may be attributed to the natural soil heterogeneity between sampling events, (a common issue in heavier end hydrocarbons which tend not to homogenize as well as lighter end hydrocarbons), it is more likely that the F3 increase is a result of biogenic interference between sampling events. The CCME method for F3 PHC analysis reports a single concentration for carbon bonds $C_{16}$-$C_{34}$. The reported concentration includes any type of carbon compound with 16 to 34 carbon bonds which can include both biogenic (e.g., plant alkanes, sterols, fatty acids and waxes) and petrogenic (e.g. aromatics, olefins and asphaltenes) compounds.

Previous site assessment findings have indicated that the soils being remediated are peaty and high in organic matter content (which is typical of the soils in the region). Further, with the use of PGPR and application of fertilizers and biochar there will likely be a greater abundance of biomass and plant material (biogenic) in the rhizosphere which will provide an advantage to the degradation of petrogenic compounds in the soil. However, it is hypothesized that due to the high amount of biogenic compounds in the soil, the biogenic compounds are creating a false positive result when analyzed for F3 PHCs.

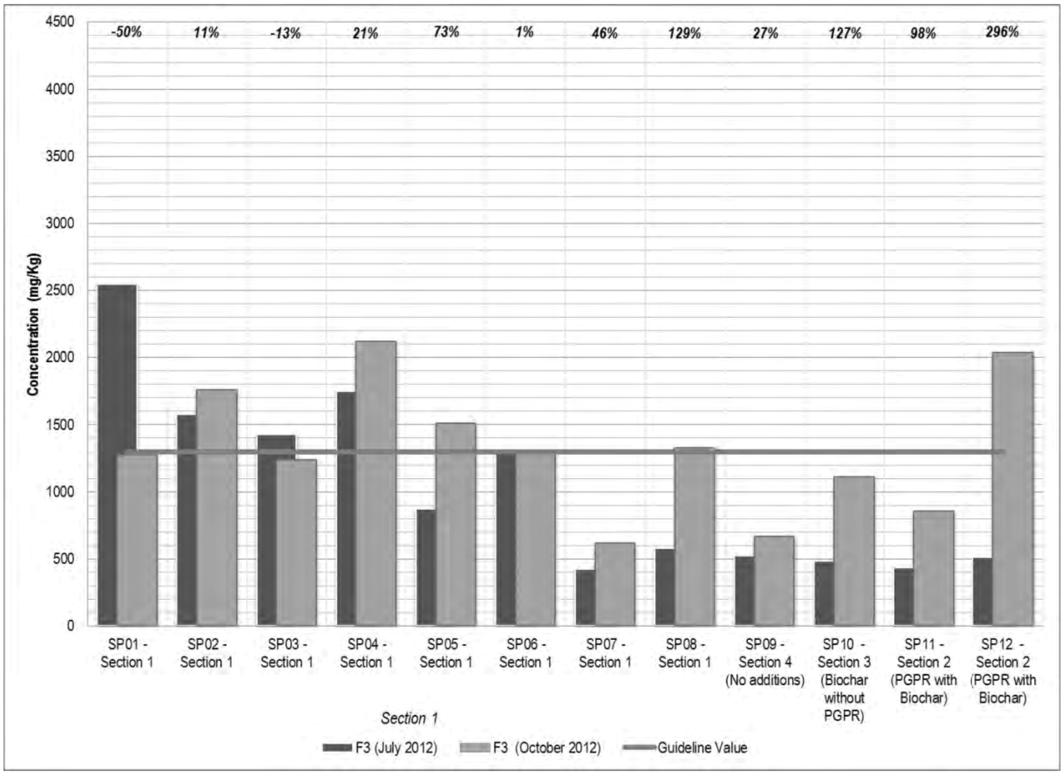


*Figure 3. A comparison of F3 (C16 – C32) soil concentrations between July 2012 and October 2012*

Supporting this theory is that biogenic content would have been lower at baseline conditions in July 2012, then with the addition of PGPR, fertilizer and biochar, there would have been a proliferation of microbial activity and biomass production in the soil which would have resulted in an increase in F3 PHCs in the October 2012 sampling event. This increase between sampling events is evident in the analytical data. Moreover, when looking at the locations where biochar was applied, the percentage increases in these sections (*Sections 1* and *2*), was higher than in sections that did not receive the biochar amendment (*Section 3* and *4*).

Since heavier end hydrocarbons are more complex (they have more carbon chains and structures than light end hydrocarbons) it is likely that the F3 PHC fractions will take longer to degrade (for their concentrations to decline). Also, unlike the lighter end hydrocarbons, F3 PHC have a lower vapour pressure and are less likely to volatilize so are less likely to respond to degradation through physical handing and will require microbial breakdown induced by the phytoremediation process. The only exceptions to the increasing trend in F3 PHCs were in SP01 and SP03 (*Section 1)* which reported a 50% and 13% decrease, respectively, in F3 PHC concentrations (Figure 2). It is possible that this reduction is a reflection of soil heterogeneity between sampling events, but may also reflect the effects of phytoremediation.

In terms of variations in the rate and effectiveness of phytoremediation associated with the four treatment sections, it appears that, with the possible exception of two sample points in *Section 4,* varying the treatment conditions had little effect on remediation performance between the four scenarios. Consistent increases of similar magnitude in F3 PHC were recorded across the pad.

At this stage in the remedial program, a similar pattern of increase in the control (SP09) and the other three treatment sections suggest that physical handling, homogenizing, treatments and exposing the soil microorganism to the atmosphere (oxygen) has had little to no positive effects on F3 PHC reductions. If the effects of the treatments are to be realized it is expected that the control will remain stable and the F3 PHC concentrations in the other treatment scenarios should decline varying.

With respect to the F3 PHC reductions in SP01 and SP03 in *Section 1*, although this may be heterogeneity between sample events it may also reflect the application of PGPR in this section. As mentioned above as the control sample in SP09 received no treatment and had an increase in F3 PHC concentrations compared to SP01 and SP03 (*Section 1*) which did receive treatment and registered a F3 PHC reduction, it could be that the addition of PGPR in *Section 1* is the factor at play in reducing F3 PHC concentrations at these two sample points.

**CONCLUSIONS**

In the implementation of the phytoremediation program at the well site, there were reductions from baseline BTEX and F2 PHC concentrations (above the EQGs in sample points in July, 2012), which were reported below the EQGs at the end of the first remediation season. The exception to this pattern was for F2 PHCs in SP10 and SP12 which reported an increase above the EQGs at the end of the first remedial season in October 2012. For F3 PHCs, with the exception of SP01 and SP03, all F3 PHC concentrations (above the EQGs at baseline) increased in concentration at the end of the first remediation season. For both F2 and F3 PHCs, there did not appear to be any overall significant variations in the effectiveness of the remediation between the four treatment sections. After the first season no improvements were directly attributed to the PGPR; however, it is assumed that degradation will be more evident in subsequent years.

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# Overcoming Northern Challenges

Proceedings of the 2013 Northern Latitudes Mining Reclamation Workshop and

38th Annual Meeting of the Canadian Land Reclamation Association

Whitehorse, Yukon September 9 – 12, 2013

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Northern Latitudes Mining Reclamation Workshop

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## NORTHERN LATITUDES MINING RECLAMATION WORKSHOP

The Northern Latitudes Mining Reclamation Workshop is an international workshop on mining, land and urban reclamation and restoration methods. The objective of the workshop is to share information and experiences among governments, industry, consultants, Alaska Natives, northern First Nations and Inuit groups which undertake reclamation and restoration projects, or are involved in land management in the north or in comparable environments.

The first Workshop was held in Whitehorse, Yukon Territory, Canada in 2001 and it has been held every two years since, alternating between Canada and Alaska. The primary sponsors of the Workshop include the Yukon Geological Survey, Indian and Northern Affairs Canada, Natural Resources Canada, US Department of the Interior Bureau of Land Management, and the State of Alaska Department of Natural Resources.

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The CLRA/ACRSD is a non-profit organization incorporated in Canada with corresponding members throughout North America and other countries. The main objectives of CLRA/ACRSD are:

- To further knowledge and encourage investigation of problems and solutions in land reclamation.
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- To incorporate the advances from research and practical experience into land reclamation planning and practice.
- To collect information relating to land reclamation and publish periodicals, books and leaflets which the Association may think desirable.
- To encourage education in the field of land reclamation.
- To provide awards for noteworthy achievements in the field of land reclamation.

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