CFG6

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Abstracts

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Contents

M1. Keynote Address and Plenary Presentation

Long–term monitoring at McMurdo Station, Antarctica

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In response to national and Antarctic Treaty obligations to monitor the impact of science and logistical operations in Antarctica, the U.S. Antarctic Program (USAP) has initiated a long-term, environmental monitoring program. This presentation summarizes the design of the measurement program, initial results, and lesson learned from monitoring human disturbances at the largest scientific station in Antarctica, McMurdo Station. USAP monitoring efforts are coordinated within a programmatic framework based on the-best-available principles. The goal of the program is to observe and quantify impacts to provide guidance for management decisions. Objectives for the USAP program are to establish the status and trends in station-associated impacts and inform management decisions to minimize or mitigate adverse impacts. The set of variables measured include physical, chemical and biological indicators. Preliminary findings include: 1) physical disturbance on land initially occurred during the first years of the Station's history when establishing a permanent operational base; 2) the most prevalent contaminants detected at the Station are hydrocarbons derived from fuel; 3) surficial soils at the Station contain levels of hydrocarbons that would NOT be expected to elicit acute or chronic biological responses; 4) contaminant metals on the land surface are generally at or near background levels, 5) surficial soils at the Station contain levels of metals that would NOT be expected to elicit biological responses; 6) historical disposal practices in and adjacent to Winter Quarters Bay (WBQ) contaminated bottom sediments; 7) WQB sediments are contaminated with a toxic, complex mixture of PCBs (and PCTs), petroleum hydrocarbons, metals, and debris of various types; 8) the impacted area of WQB appears to be stable and is contained within a small silled basin; 9) organic contaminant compositions are similar to unaltered source materials demonstrating little microbiological degradation despite being released to the environment 30 or 40 years ago; and 10) the stressors in WQB have caused predictable changes in marine benthic community health. This long-term database of observations allows for assessment of program design elements to increase the utility of the information being produced. Major, moderate, and minor recommendations will be discussed. Program enhancements will also be proposed that address specific unanswered questions about environmental quality at the site.

The cost of doing the business of research in the cold

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How we accomplish research in cold regions, and the associated challenges, are changing. Integrated studies and new analytical tools allow greater ability to collect and analyze data, leading to improved understanding of phenomena. Awareness and interest in both natural and anthropogenic climate change are increasing. Concurrently, researchers seek to gain information from new remote locations, requiring novel logistic and operational support. Coupled with these shifts of interest, capabilities and requirements is an overall increase in the cost of doing business. As a result, new strategies to get "more research bang for the buck" are being developed and implemented. This presentation examines these issues from the perspective of the National Science Foundation, the primary US logistics provider for science in the polar environs.

M2. Fundamental Properties of Contaminated Cold Climate Soils (Physical, Chemical, and Biological)

Modification of microstructure in hydrocarbon contaminated freezing soils and permafrost affected sediments

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Freezing of ground has various geotechnical consequences. It is known that when soil is frozen, significant quantities of liquid (unfrozen) water remain. There are translocations of water and ice, and associated reorganization of soil microstructure. The introduction of immiscible hydrocarbon contaminates from diesel fuel, gasoline, and aviation fuel into Cryosols and permafrost affected sediments results in microstructural changes that take place as a function of cryogenic process and as a function of the concentration of the dissolved components of the contaminate. Micromorphological and scanning electron microscope observations revealed evidence of reorganization of silt and clay microfabric with changes in aggregation of particles and interaggregate porosity in Cryosol samples of hydrocarbon contaminated Cryosols. Marked differences in morphology have developed in contaminated Cryosols observed in the active layer compared to those in permafrost-affected sediments. Such changes where observed to cause changes in hydraulic conductivity for a wide range of Cryosols and permafrost-affected sediments.

Partitioning of PCBs between activated charcoal, soil and water in the Canadian Arctic

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Resolution Island, Nunavut is a unique, PCB-contaminated site. This is exemplified by factors such as the scale of contamination, the remoteness of the site, the nature of the bedrock, and the topography of the contaminated area. Most of the contaminated soil at the site has been excavated. The remaining soil that could not be excavated has been disturbed and is currently prone to mobilization during periods of run-off. In order to control the mobilization of this material within the drainage system, permanent barrier systems have been designed and constructed.

Over the years the barrier systems have been modified to correspond with changing site conditions and needs. Initially, particle retention was the primary concern in retaining migrating PCB. As sediment loading decreased over the years due to site closure and re-stabilization, nonwoven geotextile filters were re-introduced into the system to enable retention of highly contaminated fines.

The barrier system is susceptible to changes in temperature. Permeability in a granular filtration system is reduced with the formation of ice lenses and this can increase likelihood of clogging within the system. These ice lenses also reduce the number adsorption sites for PCBs. PCBs desorption from soil onto GAC is dependent on soil conditions such as the soil water ratio. Column and batch tests are currently ongoing to evaluate whether site-specific designed barriers can overcome the challenges posed by temperature, congener planarity effects, secondary mechanisms via uptake of PCBs in water and soil surface charges.

This paper will explore the limitations and advantages in using this type of barrier system to treat PCBs in cold regions.

M3. Freeze-thaw Processes

Effects of freeze-thaw and bio-available water on soil-attached and elutable microorganisms – implications for monitoring

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Soil microbes exist in a dynamic system, especially in surface soils. As our ability to measure enzyme-driven soil processes at greater resolution increases, understanding how soil conditions affect the occurrence and attachment of microbial cells and enzymes becomes more important. Applications include monitoring and bio-inspired sensors. Using elutable fractions, we examined microbial activity, biomass, and community composition in a surface soil subjected to multiple freeze-thaw cycles. Effects on in-situ microbiota were quantified using lipid biomarkers. Relative to soils held at constant temperature, multiple freeze-thaw cycles affected the dominant microbial functional groups that remained attached to soil particles or that eluted with water. Differences were apparent in respiration, total biomass, and community composition. Gram-positive bacteria and fungi, typically associated with complex carbon metabolism and slower growth in soil, accounted for a larger percentage of the soil attached population following freeze-thaw cycling, presumably due to a competitive advantage gained from using carbon substrates released following soil freeze-thaw cycles. In contrast, freeze-thaw cycling had a negative impact on biomarkers for the actinomycetes, which readily eluted from the soil with water. Freeze-thaw treatment did no affect the relative abundance of Gram-negative bacteria. These data indicate that antecedent conditions affect microbially driven processes in surface soils and we suggest that this phenomenon will alter sampling strategies when emerging molecular techniques are used for monitoring.

Orthophosphate fixation of metals at 295 K, 275 K and in the presence of freeze-thaw cycling

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Orthophosphate fixation of metals is poorly constrained in areas with cold and freezing conditions. Here we report a series of experiments that constrain reaction rates and products at 295 K and 275 K, and allow assessment of the stability of the reaction products with freeze-thaw cycling. Reactions incorporating orthophosphate solution, quartz, and oxides or sulfates of Cu, Zn and Pb were examined via repeated XRD scans to examine for changes in crystalline phases over 30 days at both 295 K and 275 K. The materials were then subjected to freeze-thaw cycling from 283 K to 243 K.

We show that at temperatures just above freezing, some reactions are substantially slower and while some sodium salts change phase during freeze-thaw cycling, the metal phosphate salts identified are stable during both freezing and thaw. This has implications for the manner in which metal contaminated materials can be treated with orthophosphate in areas with freezing ground.

Freeze-thaw induced mobilization of gasoline in coarse sands

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Petroleum oils, when discharged in significant quantities in the subsurface by accidental spills or by natural seeps at oil and gas production sites, may act as a source of long-term environmental contamination by slowly but continuously releasing petroleum hydrocarbon compounds to the surrounding aqueous and air phases. The objective of the research was to determine how freezing and freeze-and-thaw conditions, commonly encountered in cold climates, influences the morphology, displacement and migration of petroleum oils in subsurface soils.

Temperature changes that cause freezing and thawing of soil moisture can result in the alteration of the soil meso-pore structure and alter the distribution of immobile oil phases and consequently change rates of mass flux of petroleum hydrocarbons from the spill (source) zone by volatilization, dissolution and biodegradation, which are common natural attenuation mechanisms. Experimental investigations were conducted using coarse sand columns which were uniformly contaminated with gasoline and subjected to freeze-thaw temperature cycles at controlled rates of freezing to -10 C. The effects of freeze-thaw cycles on the extent and volume of oil displacement, pathways of oil mobilization, and changes in oil morphology were assessed quantitatively using X-ray computed tomography (CT) scanning, a non-invasive three-dimensional imaging technique. The medical X-ray CT scanner allowed pore and NAPL volume distribution to be measured in each 0.35 mm X 0.35 mm X 1.0 mm voxel of the packed column and these were determined at 25 C, then after freezing to -10 C, and again after thawing.

Significant mobilization of gasoline was observed from the middle-sections of the column towards the column ends on freezing, and oil volumes changed by up to 150% in certain regions of the column. On thawing, the gasoline showed minimal movement in the column from the distribution attained after freezing. The porosity distribution in the column changed with freezing, but porosity changes were reversible on thawing.

A blob enumeration algorithm was employed to enumerate the number of gasoline blobs, and to determine the blob volumes and specific surface areas in the packed column at the initial state (room temperature) and after the freeze-thaw cycle. It was found that the specific surface area of the gasoline blobs decreased uniformly, and is attributable to the more spherical shape of the blobs after a freeze-thaw cycle and break-up of blobs from multiplets to singlets.

M4. Non-petroleum Organics and Metals

Attenuation of herbicides in a subarctic environment

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Herbicide application has been a common means of controlling undesirable vegetation for many years. Transportation authorities have adopted the use of herbicides to control vegetation along highway rights-of-way to maximize line of sight for driver safety. Much is known about the fate of herbicides in temperate regions, however little is known about the fate of these compounds in cold regions. This purpose of this study is to quantify the attenuation of two common phenoxyalkanoic acid herbicides, triclopyr (3,5,6-trichloro-2-pyridyloxacetic acid) and 2,4-D (2,4-dichlorophenoxy acetic acid), in a subarctic region. Results from two different climatic zones in Alaska indicate that the fraction of each herbicide that is not taken up by susceptible and non-susceptible vegetation is retained to a certain extent in the organic rich surface soils. Loss from this layer is first order during the thawed season. Herbicide is detected in the subsurface as rain events leach the herbicide into the subsurface. No loss of the herbicide is detected through the winter, however during spring thaw an increase in herbicide concentration is measured in the soil. In some cases this increase is substantial. Results from this study will be used to aid Alaska state transportation authorities in developing reasonable means of controlling vegetation along transportation corridors.

Movement of trichloroethylene in a discontinuous permafrost zone

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The objective of this study was to investigate the relationship between the migration pathway of a chlorinated solvent groundwater plume and the surface topography of the discontinuous permafrost table at a site in Fairbanks, Alaska. Thematic maps of the permafrost table elevation, groundwater gradients, and contaminant concentrations were created using ArcGIS and field data from groundwater monitoring wells. The plume concentrations and groundwater gradients were overlain on the permafrost table elevation map to correlate permafrost locations and the spatial distribution of contaminants moving with groundwater. Correlation of the overlay maps established the following trends 1) non-detect concentrations in areas with a high permafrost table elevation, 2) converging and diverging groundwater flow pathlines in response to the permafrost table distribution, 3) channeling of contaminants and water through areas of permafrost, and 4) upward vertical gradients recharging groundwater from the subpermafrost into the suprapermafrost through a discontinuity. The variable distribution of the permafrost table elevations across the site, is affecting the way that groundwater and contaminants move through the aquifer.

Pilot-scale treatment of 1,1,1-TCA with bimetallic nanoscale particle technology under Arctic conditions (Prudhoe Bay, Alaska)

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Bimetallic nanoscale particles (BMP) were applied to a Prudhoe Bay (AK) gravel pad contaminated with 1,1,1-trichloroethane (TCA) in a pilot-scale treatment test. The study was performed in collaboration with the USEPA to evaluate BMP degradation of TCA (a chlorinated solvent) in an arctic environment. The TCA concentrations were variable; mean concentrations in the test plots ranged between 9.42 and 62.8 mg/kg. Two application methods were evaluated in the shallow (2 m depth) pad. In the first test, shallow (0-1.3 m depth) gravel was mechanically mixed with a backhoe while BMP slurry was added. In the second test, BMP slurry was injected into a deeper (1-2 m depth) section of the pad though 16 slotted probes (approximately one probe per 11 m sq.). Direct-drive sampling was performed after a reaction period of three weeks. Analytical results demonstrated that the initial mean TCA concentration in the shallow plot (62.8 mg/kg) was reduced by 90%. Results from the control plot suggested that at least 45% of the loss was related to volatilization during the mixing process; the remaining loss was attributed to dechlorination via BMP. Subsequent tests the following summer (one year later) indicated that additional TCA degradation (5%) occurred in the shallow plot. Results from the deeper test revealed that injection is an unreliable method for BMP application in arctic gravel pads. No evidence of TCA degradation was detected in boreholes placed within 2.1 m of the injection ports. It is speculated that the BMP compound formed a "filter-cake" around each injection port and was not effectively delivered to the gravel substrate.

Ex-situ chemical fixation of heavy metal impacted soil in temperate environments

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Could techniques used in temperate regions for the chemical fixation of heavy metal contaminated soils work effectively in freezing climates? In 2003 Veolia Environmental Services (VES) in conjunction with the Australian Antarctic Division (AAD) used chemical stabilization to treat 1000 tonnes of heavy metal contaminated soil that had been extracted and returned to Australia from Thala Valley, Casey Station, Antarctica.

The ex-situ off site treatment of contaminated soils from remote regions such as Antarctica is extremely costly and logistically challenging. Some contaminated sites cannot be excavated because of risks associated with mobilizing contaminants. Such sites will require other methods of remedial application and one option includes in-situ injection of heavy metal stabilizing agents. This presentation provides information about the technology and an appraisal of the advantages and disadvantages of ex-situ/in-situ remediation for temperate regions. The background will serve to put into perspective the collaborative R & D effort between industry partners (VES and PANalytical), AAD, Melbourne University and Macquarie University to establish whether or not in-situ chemical fixation will be effective in freezing environments.

T1. Cold-adapted Microorganisms and Degradation at Low Temperatures

Microbial activity and abundance of soil microorganisms at a petroleum hydrocarbon contaminated site at Casey Station, East Antarctica

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Petroleum hydrocarbon (PHC) contamination is the most common environmental pollutant in Antarctica, with accidental spills occurring most frequently at research stations located in coastal regions. In 1999, a large diesel spill occurred at Casey Station when approximately 10,000 L leaked from a storage tank. The ecotoxicity of this spill to soil microorganisms was assessed during the austral summer of 2005-2006 (contamination still exceeded 25,000 mg kg^{-1} in some locations) at 32 different locations across the contaminated site at nine sampling periods. The liquid water content and soil temperature was assessed at the time of sampling using time domain reflectometry and thermocouples, respectively. Microbial activity was assessed using the potential activities of substrate-induced respiration, basal respiration, nitrification and denitrification. Community composition of soil microorganisms was observed using phospholipid fatty acid analysis (PFLA) for three of the sampling periods (beginning, middle, and end of summer season). Results from this field experiment indicate that potential nitrification activity, substrate-induced respiration, and basal respiration are sensitive indicators of petroleum hydrocarbon contamination in polar soil. Potential nitrification activity decreased, whereas potential soil respiration increased and potential denitrification activity remained unaffected by an increase in PHC contamination.

Biodegradability analysis of diesel, fish biodiesel, biodiesel blends and synthetic diesel for Arctic soil remediation

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Clayey sand from Interior Alaska was contaminated with diesel, fish biodiesel, biodiesel blends and synthetic diesel fuel (Syntroleum). Samples were incubated in the laboratory at different temperatures (6 and 20° C) and contamination levels (2g and 4g of fuel/kg soil). The research was conducted with the main focus on the following study areas: 1, effect of physical environmental conditions on biodegradability and determination of optimal conditions for degradation, 2, effect of microbial inoculum on biodegradation of different fuel types, 3, microbial growth phase investigation as a function of time, 4, comparison of environmental fate of fish biodiesel blends with conventional (high-sulfur) diesel fuel and 5, investigation of carbon preference for five different fuel types (conventional diesel, diesel heating fuel, Syntroleum, processed fish biodiesel – B100, and biodiesel blend – B20) by conventional (low-sulfur) diesel adapted microbial inoculum.

The respiration rate (CO_2 production) was measured as an indicator of microbial activity and mineralization of contaminants and by analysis for hydrocarbons at the end of the experiment by using Gas Chromatography/Mass Spectrometry. Several volatilization studies were also included since volatilization plays a significant role on the overall carbon mass balance. The analysis investigated the adaptation period (lag times) and different growth phases of the microorganisms to the specific types of fuels under optimal conditions. The study also focused on different microbial culture types already adapted to various hydrocarbon sources as a function of time.

All fuel types are biodegraded, with 20-30% mineralization after 6 weeks. The fastest degradation rate was achieved in Syntroleum and processed fish biodiesel contaminated soils. Raw fish biodiesel did not show any CO_2 production at low temperature during the course the study, most of the hydrocarbon added to the soil was recovered by the gas chromatography. However, at high temperature processed fish biodiesel shows significantly higher degradation rates than raw fish biodiesel. At 6°C the biodiesel blends and diesel fuel shows minimal degradation during a 4 weeks study. Low-sulfur diesel adapted microbes also show preference toward high-sulfur diesel as carbon source compared to low-sulfur diesel, however all other fuel types (Syntroleum, B100, B20) support faster microbial culture growth and are consequently more preferred as an energy source. For most fuel types, respiration rates were higher in samples where mold growth occurred, indicating likely involvement of molds in the fuel biodegradation. Frequent exchange of activated carbon in the headspace reduced fungal growth and CO_2 production.

Lipid biomarkers reflect microbial response to petroleum contamination

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Lipid biomarker analysis has utility in testing the hypothesis that attributes of the extant microbiota can directly reflect the occurrence of contaminant biodegradation. Two past research efforts have demonstrated this utility and are described here. In the first study, a 50-year-old diesel fuel oil contamination plume in upstate New York was examined. A 4.5 m vertical core was obtained and core material was assayed for total petroleum hydrocarbons (TPH) and bacterial membrane phospholipids (PLFA) via a single solvent extraction. Microbial viable biomass and the relative abundance of Gram-negative bacterial PLFA biomarkers were found to be significantly correlated with TPH concentration. The core TPH profile also revealed two distinct areas where the average TPH level of 3,000 μg g^{-1} fell to near detection limits. Both areas were characterized by a three-fold decrease in the hexadecane/pristane ratio, indicating alkane biodegradation, and a distinct PLFA profile that showed a close similarity to the uncontaminated surface soil. By examining the in situ microbial PLFA signatures, we were able to relate specific microbial community attributes to the chemical measure of TPH biodegradation.

In a past field demonstration conducted at 3 locations throughout Alaska, rhizosphere enhanced bioremediation of PAHs was examined. Each field demonstration included vegetation and fertilization as the main factors. Using biomarker-normalized TPH as a monitoring variable, a positive vegetation effect and fertilizer-vegetation interactions were observed. In general, vegetation effects were more pronounced with the more recalcitrant higher molecular weight PAHs. Analysis of in situ microbial community compositions via the PLFA analysis showed clear differences between sites and, within a site differences related to treatment affects. In particular, the vegetation treatment resulted in enhanced fungal biomarkers. This result suggested a relationship between high molecular weight PAH degradation and fungal metabolism.

These two past research efforts demonstrated the utility of the lipid biomarker analysis in identifying microbial community characteristics that were associated with contaminant degradation in a variety of soils. This type and form of information is being gathered for use in enhancing the predictive power of ecological models such as the Army Training and Testing Area Carrying Capacity for munitions model [ATTACC].

T2. Sediments and Ice

Hydrocarbons in Antarctic marine sediments: degradation and ecological effects over 5 years (SRE4)

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For years Antarctica has been considered a clean environment, but as interest in the area has grown, the number of people visiting Antarctica has also grown, giving rise to a waste disposal problem. Diesel fuel and lubricating oils are some of the most common causes of contamination, and the hydrocarbons and heavy metals from these have a major impact. Disposed waste was previously stored in open-air landfill sites close to the stations, which tend to be near shore. Ice-melts occur naturally each year during the annual warming season, resulting in the ground ice, including that in and around the waste disposal sites, melting. The ice-melts aid the mobility of contaminants from the waste site to land and marine sediments, leaving near shore and marine systems at high risk of contamination.

In a previous series of investigations it was noted that sediment contamination had a significant effect on biological communities, and hydrocarbons have a subtle but significant effect on biota too. These investigations gave rise to a long-term field experiment with several areas of study, including the rates of degradation of the different fuels. Marine sediment from near Casey Station was experimentally polluted with the fuels and oils and placed in trays on the seabed near the Station. The work presented here focuses on the degradation of SAB (Special Antarctic Blend) fuel.

During the five years of in situ incubation, six sets of sediment samples were collected. The results showed that some of the SAB fuel components degraded over the five-year period, and that the degradation rate is faster for some hydrocarbons than others. Hydrocarbon degradation has been suggested to be dependant upon the oxygen and water availability in the sediment, the microbial communities present, and temperature. With these factors at an optimum, hydrocarbons degrade preferentially, with the *n*-alkanes degrading rapidly. The results show that degradation results in an obvious UCM (Unresolved Complex Mixture) in the degraded SAB samples after five years. Further work will investigate the link between the more resistant hydrocarbons and the impact on biological communities.

Testing oil spill delineation and mitigation techniques at CRREL

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As the demand and price for oil increases, exploration and development of the oil resources in ice covered water becomes cost effective. With decreasing ice cover in the Arctic, navigation in the Arctic is becoming more of a reality. Both of these trends have the potential to increase the frequency oil spills in ice-covered waters. Conventional oil spill mitigation techniques were developed for open water and their deployment in the presence of ice is very problematic.

CRREL recently supported three important research programs intended to improve spill response in ice-covered waters: developing new technologies to detect oil trapped within and under a solid ice, testing herding agents as a technique to thicken oil for burning and/ or mechanical recovery, and evaluation of modified drum skimmers.

Detection of the oil under and in the ice is the first step in delineating the size of oil spill, which is critical for a quick, effective and focused response. Containment hoops were positioned in the Test Basin prior to freezing the ice. During the freezing process, 45, 90 and 150 L of crude oil were injected under the ice in the three different hoops to encapsulate oil within the ice. Prior to testing the 50 cm thick ice, 45, 90 and 150 L of crude oil was injected under the ice in three more hoops to evaluate oil under the ice. The detection systems evaluated were the Ground Penetrating Radars systems with different frequencies and an ethane sensor. Mechanical skimmers deployed in areas with broken ice are quickly defeated as the pieces of ice block the entrance into the skimmer. An alternative to recovery is in-situ burning, which requires thickening of the oil slick so it can be ignited. The performance of an oil-herding agent was evaluated using different concentrations of oil and ice, with and without waves. The tests provided confidence in the approach, and subsequent testing in a larger area and burning test was conducted. To recover oil under ice requires cutting slots and using mechanical drum skimmers to recover the oil. The ice chips from the cutting operation interfere with operation of the drum skimmer. Also with the oil being cold and viscous, capture efficiency could potentially be enhanced by grooving the drum. Two skimmers with various modified drums were tested with Alaskan crude, hydrocal (a surrogate oil) and diesel fuel from a test tank with and without ice chips. Keller and Clark.

The presentation will summarize mesoscale oil and ice environment created in the CRREL facilities that were the essential first steps in conducting proof-of-concept testing for the oil mitigation techniques.

T2. Posters

Investigating vapor intrusion from a former dry cleaner site in Fairbanks, Alaska

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In downtown Fairbanks, Alaska, historical dry cleaning operations released chlorinated solvents to a wood-stave sewer line, causing subsequent releases to the soil and groundwater through leaks in the line. The groundwater at this site has been investigated extensively since 1997, however until recently the vapors emanating from the subsurface contamination were overlooked. Results from sub-slab soil gas and indoor air samples collected between 2005 and 2007 indicate significant intrusion of tetrachloroethylene (PCE) into several surrounding buildings. The concentrations, however, have been extremely variable from building to building.

Results from this site investigation, beyond just being used to understand and mitigate any risk to building occupants, are also being used to develop guidance on how to evaluate the vapor intrusion pathway in a cold climate. The evaluation of this pathway has multiple complicating factors that must be addressed. There are the technical issues of:

- Accounting for the spatial and temporal variability in soil gas distribution;
- Determining methodologies for consistent, defensible sampling;
- Understanding the influences of different construction and heating techniques, particularly in colder climates; and
- Evaluating the effects of frozen ground on vapor migration.

There are also public and political issues. Sampling for vapor intrusion, just by its nature, is often significantly more intrusive than soil or groundwater investigations. Also the Department lacks the authority to regulate indoor air, a common problem for many of the regulatory agencies in the U.S. Thus, there are no clear national indoor air standards and any chemicals detected in a building must be separated between background and subsurface sources. The few federal, enforceable standards for indoor air that do exist, such as the U.S. Occupational Safety and Health Administration permissible exposure levels, have only a narrow application and are typically many orders of magnitude higher than chronic, risk-based levels.

These issues make vapor intrusion a difficult pathway to investigate and regulate. Through further research on state-lead sites and communication with the scientific community, the Department hopes to develop sound policy for evaluating vapor migration and assessing the risks to human health, specifically addressing any factors that may be specific to Alaska's climate.

Measuring fuel spills for regulation and environmental monitoring using comprehensive two-dimensional gas chromatography

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The Australian Antarctic Division has modified and fine tuned a regular gas chromatograph (GC) to run the more powerful separation technique of comprehensive two-dimensional GC (GCxGC). This is a true multidimensional separation employing Flame Ionisation Detection (FID) for all Diesel Range Organics as shown below.

This instrumentation has been successfully operated in mainstream laboratories and at the Macquarie Island laboratory in the sub-Antarctic. The principal advantage of the GCxGC system is that it separates out all the hydrocarbon pollutants according to both boiling point and polarity. This produces an ordered and readily interpretable chromatogram. The ordered two-dimensional separation is particularly powerful for fuel spill analysis as the different environmentally significant classes (aliphatics, aromatics, PAHs etc) can be readily differentiated and measured. The nature of the ordered separation directly gives data on parameters important to fuel fate modeling (e.g. volatility and water solubility). In addition, the GCxGC separation allows more frequent observation of detector baseline (a major source of TPH error in conventional analysis) and avoids some routine laboratory contamination problems like peaks from silicone rubber components. These factors result in a method that has a lower limit of detection with an enhanced dynamic range. This presentation aims to show how the technique works, how it can be routinely operated in a remote lab and how the data can be used for fuel spill quantization and fuel fate modeling. Implications for regulatory fuel spill assessment, particularly measurement of the environmentally significant aromatic and PAH components will be discussed.

W1. Transport and Interception

Transport of volatile organic compounds through landfill cover systems in cold region environments

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In the Canadian Arctic there are a number of landfills containing soil contaminated with petroleum hydrocarbons such as diesel, which contains volatile organic compounds. Engineered cover systems are employed in landfills and other barrier systems to contain these volatiles, preventing contamination of the surrounding environment. These cover systems often use geosynthetics, including geotextiles, high-density polyethylene (HDPE) and poly-vinyl chloride (PVC) geomembranes. These materials act as a diffusive barrier to contaminants. The mechanisms of transport through these geomembranes and other geosynthetics have been extensively studied. However little work has been done on the effect of exposure to cold climates and freeze-thaw cycles on the performance of these materials.

Permittivity of geotextiles used at Resolution Island, Nunavut indicated that freeze thaw cycles compromise these barrier materials. Permeation tests were carried out on geosynthetic samples taken from field sites in the Canadian Arctic and on samples exposed to simulated cold regions conditions in the laboratory. Results show a reduction in mass transport through the barrier materials at lower temperatures. However the harsh environmental conditions may ultimately compromise the long-term performance of the geosynthetics. The effects of temperature on mass transport of benzene, toluene and xylenes through the barrier materials and the integrity of the liners at lower temperatures will be presented.

Biomonitoring of short range aerial migration of PCBs during site remediation using Arctic plants

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Biomonitors are organisms that provide quantitative information on environmental quality. In this investigation, we use plants as biomonitors of soil contamination at two Arctic sites, both of which were contaminated with polychlorinated biphenyls (PCBs) during the cold war years.

The BAF-3 radar site is located on the summit of Resolution Island, Nunavut, just southeast of Baffin Island. As part of the Distant Early Warning (DEW) Line, it was operational during the 1950's and early 1960's. When BAF-3 was abandoned, approximately 9000 kg of pure PCBs remained on site, 4000 kg of which was removed in 1999. The remaining PCBs were remediated and or disposed of using a variety of techniques between 1999 and 2005. Beginning in 2003, plant samples were collected annually for five years at 12 monitoring locations. During the first three years (2003-2005), there was considerable remediation activity at the site, particularly in 2003 when soil exceeding the Canadian Environmental Protection Act (CEPA) level of 50 μg/g was being excavated. In subsequent years there was reduced activity and minimal soil disturbance.

A similar site, the LAB-2 radar site is located at Saglek, NL, and is operated by the North Warning System Office (NWSO). Historic military activities since the early 1950s resulted in several areas of the site becoming contaminated with PCBs at levels exceeding CEPA. The soil contamination was detected in the early 1990s and remediated from 1997-2004. Beginning in 1997 and continuing to the present, plant samples were collected at LAB-2 initially to assess contaminant uptake into the ecosystem, and later as a monitoring tool.

Soil tissue analysis from plants at both sites indicates that the removal and/or containment of PCB contaminated soils has greatly reduced concentrations of PCBs. Hence, with the completion of the remediation work, a long-term monitoring (LTM) strategy that includes arctic plant tissue analysis may be useful to evaluate the effectiveness of a northern clean-up, monitor the biological recovery on site, as well as serve as an indicator of regional ecosystem recovery.

Assessment of sorbent materials for treatment of hydrocarbon contaminated groundwater in cold regions

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Three different sorbent materials (MYCELX coated sand, granular activated carbon (GAC) and surfactant modified zeolite (SMZ)) were tested for their suitability for capture of soluble hydrocarbons in soil water. These materials were assessed for their potential use in permeable reactive barriers in cold regions. Batch sorption tests at 20^0 C and 4^0 C were performed and the data was fitted to various adsorption isotherms. Ionic strength and pH tests were conducted to determine their impact on hydrocarbon sorption. The results of the surface characterization tests revealed that the quality of MYCELX coating on the sand was highly variable, leading to unreliable adsorption results. GAC proved to be the best sorbent material at high and low temperatures on a mass basis. However, on a surface area basis, SMZ performed better than GAC. The ionic strength and pH had little effect for hydrocarbon sorption onto GAC and SMZ. Both GAC and SMZ exhibited reduced adsorption efficiency at 4^0 C compared to 20^0 C. The extent of the reduced adsorption efficiency varied depending on the hydrocarbon being tested.

W2. Contaminated Site Characterization and Risk Assessment

Control and bioremediation of petroleum hydrocarbon plumes in cold climates

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Petroleum hydrocarbons represent one of the most common contaminants in cold climates. In most cases it is not feasible to undertake site remediation with high-energy technologies due to the high cost of fuel, disruption to the environment and infrastructure and the potential to enhance off-site contaminant migration by excavating when the soil is thawed. Bioremediation is a viable alternative if the limitations of cold temperature, impoverished nutrient status, inadequate soil moisture and poor interaction between contaminants and ameliorants can be overcome. While these limitations are not unique to cold regions, the short summer-window available for remediation, the sensitivity of organisms to contaminants at this time of the year and the strict environmental protection regulations force clean-up efforts to be carefully managed. Current research at the Australian Antarctic Division (AAD) is focused on overcoming these limitations by controlling contaminant migration through the use of permeable reactive barriers (PRB); utilizing controlled release nutrients (CRN) and ion exchange processes to enhance bioremediation and overcoming temperature, oxygen and moisture limitations. Results from the past 3 years for a PRB installed at Casey Station, Antarctica will be presented.

Bioremediation of weathered hydrocarbon soil contamination in the Canadian High Arctic: laboratory and field studies.

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This study investigated the bioremediation of weathered medium- to high-molecular weight petroleum hydrocarbons (PHCs) (mix of diesel and motor oil) found in Quttinirpaaq National Park (QNP), Ellesmere Island, NU, Canada. Few studies have examined bioremediation of this mixture of contaminants. Research has mainly focused on bioremediation of low- to medium- molecular weight PHC mixtures (e.g. diesel). Climate, contaminant characteristics (e.g. low bioavailability and volatility), and logistical constraints (e.g. site remoteness, lack of local infrastructure) can make the bioremediation of persistent PHCs in the High Arctic challenging.

Landfarming (0.4 m^3 plots), the simplest of bioremediation technologies, was tested at two sites in QNP from July 2005 to July 2007. Field experiments were complemented with laboratory microcosm (~15 g of soil incubated for six weeks) and solid-phase bioreactor (18 kg of soil incubated for one to two years) experiments at ambient temperature. Similar amendments were applied in all experiments: addition of nutrients (nitrogen and phosphorus) and/or a specialized synthetic surfactant. In the laboratory, soils were aerated and moisture was controlled. Field plots received minimal maintenance (i.e. tilling and watering twice each summer during visit to sites). Passive warming by a greenhouse was investigated at one site in QNP.

Significant TPH reduction was observed in all experiments. Up to 86% and 63% TPH reduction was observed in the laboratory and the field, respectively. Field TPH reduction rates were ~ half of laboratory rates. In the laboratory, significant removal of compounds >nC16, believed recalcitrant to bioremediation, occurred in all soils but compounds <nC16 were preferentially removed. In most field treatments, TPH reduction was limited to removal of compounds <nC16. Fertilization significantly enhanced reduction of these compounds as well as removal of nC16-nC34 compounds in one of the two fertilized plots at one site (outside greenhouse). The addition of surfactant alone produced no effect. Removal of compounds >nC34 was not observed in the field. The greenhouse increased average soil temperature by ~2.5°C and extended treatment time by ~2 weeks but did not enhance bioremediation. It produced drier soil and reduced air circulation that likely limited both biodegradation and volatilization, Little volatilization was measured in the laboratory but this abiotic process appeared to have been more important in the field. Leaching was negligible. Findings suggest that biodegradation played an important role in contaminant removal. The weathered contaminants, deemed recalcitrant, were amenable to bioremediation. This technique may be a suitable long-term remediation option in the High Arctic, despite suboptimal conditions.

Effect of snow cover on the persistence of a non-indigenous bacterial spore former and cold adapted microorganism

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By predicting how conditions in and under snow influence both indigenous and non-indigenous microorganisms, it may be possible to develop strategies that alter field conditions to favor a desired microbial population, for example one pre-positioned to biodegrade a soil contaminant. Knowledge of snow–soil–microbial interactions could then lead to the development of remediation strategies that exploit snow as both a delivery system and, possibly, as a nutrient source and or germinant. Using replicated field studies, we applied molecular-based taxonomic methods in characterizing native microbial populations in a local soil with and without snow cover. We then introduced an endospore forming bacterial species, *Bacillus thuringiensis,* to the soil prior to snowfall and to the snow covering following snowfall. We also added a cold tolerant species, *Pseudomonas syringae,* to the snow in selected treatments for comparison. The intent was to determine if the added organisms were capable of survival and if application to snow was more advantageous than directly to soil. During a single winter and into the spring, we periodically sampled the snow–soil interface to characterize the prevailing microbial populations. Data suggested that micro-eukaryotes (fungi or protists) increased significantly under snow and that this increase had a negative impact on the added *Bacillus*. Results also showed that the survival of the *Bacillus* was due more to its remaining as an endospore than to outgrowth, which was an unexpected finding. Bacilli applied to snow did persist, but not as well as when applied to soil. In contrast, the snow-applied Pseudomonad did persist for a brief period following snow melt. Results from the study showed that interplay among trophic levels and release of nutrients or inhibitors in the snow may have been important factors in controlling the fate of the added organisms.

W3. Amendments and Optimization

Landfarming fuel contaminated soils in the Canadian Arctic: mechanisms and optimization

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Landfarming is the preferred method of remediating diesel fuel contaminated soils in temperate climates. During landfarming, hydrocarbon can be lost through volatilization or bioremediation. In cold regions the main scientific concerns are that the kinetics associated with both aeration and bioremediation are adversely affected by temperature. This paper will explore the mechanisms of hydrocarbon loss and the kinetics of the processes involved. For example volatilization requires desorption from the soil, transport to the surface layer and removal from the soil/air interface. Both field and laboratory data will be used to further understanding of these complex processes and how they are affected in Arctic climates. Laboratory studies and further field work have been on-going since 2004 in order to gain greater insight into the factors that affect both remediation processes and to develop strategies to optimize each of them. Many landfarms in cold climates are difficult and expensive to access. An in situ landfarm was established at Resolution Island, Nunavut to determine whether significant remediation will occur in cold climates without tilling. Data from these plots and supporting laboratory data will be compared to more traditional landfarming results. The importance of moisture content, tilling, soil temperatures and the choice of protocols to use for the best results at particular soil temperatures will be discussed for landfarming in the arctic.

Biodegradation response to supplemental oxygen in an anoxic sub-Antarctic soil

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A microcosm experiment utilizing a respirometry system and ^{14}C-labeled hexadecane was conducted to investigate the effects of varying oxygen regimes on hydrocarbon degradation in contaminated soil from sub-Antarctic Macquarie Island. Soil was fertilized with NH_4NO_3 prior to incubation. Measurements were made of oxygen consumed, carbon dioxide produced, and ^{14}C evolution over 14 weeks and residual petroleum hydrocarbons, and soil nitrate and ammonium concentrations were measured at the conclusion of incubation. Target O_2 levels during incubation ranged from 0 to 20.9%. The microbial community structure at the start of the experiment and after 4, 8 and 12 weeks incubation was also explored. The amount of ammonium utilized in the aerobic microcosms was significantly higher than in the anaerobic microcosms, which utilized mainly nitrate, suggesting that hydrocarbon degradation under low oxygen concentrations was coupled to denitrification. Residual hydrocarbon concentrations were lowest in soil incubated with a target O_2 of 10.5% and 20.9%. $^{14}CO_2$ evolution was also slower in the anaerobic than aerobic microcosms although there was no discernable lag-phase in either. The microbial communities in the aerobic microcosms had fewer total bacteria, fewer denitrifying bacteria, and a smaller proportion of microbes had genes for hydrocarbon degradation than those in the anaerobic soils. The microbial community in the soil from Macquarie Island is adapted to ambient low oxygen concentrations, however it possesses the ability to utilize available oxygen and hydrocarbon degradation is favored by O_2 levels of approximately 10% or greater.

Use of controlled release fertilisers in permeable reactive barriers

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A permeable reactive barrier (PRB) was installed at Casey Station, Antarctica during the summer 2005/06 season. This barrier was designed primarily to contain hydrocarbon contaminant migration and to accelerate its biodegradation. An important feature of the barriers design was the use of a controlled release nutrient source within a reactive zone. A variety of materials were trialed including Maxbac and Zeopro (a patented ammonium – zeolite and calcium phosphate material). This presentation details the performance of the nutrient sources within the barrier. It also uses a temperature dependant semi-empirical thermodynamic ion exchange model to assist in its description.

Influence of soil characteristics on efficiency of biopiles bioremediation treatments of diesel-oil contaminated subAntarctic soils.

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Biological treatment has become increasingly popular as a remediation method for soils contaminated with petroleum hydrocarbon. In order to determine the efficiency of on-site bioremediation of diesel contaminated subAntarctic soils, a pilot biopiles study was conducted from January 2006 to December 2007 with two different soils of The Grande Terre (Kerguelen Archipelago, 69° 42'E - 49° 19'S). Eight boxes were specially equipped with forced ventilation in such a way that cold or warm air was forced in the lower part of the box and soil was added on a geotextile support in the upper part of the box. Eight other boxes were simply secured on the concrete slab and soil was deposited in the bottom of each box. Each group of 8 boxes was divided in 2 sub-groups of 4 boxes receiving in the following order : control soil with nothing added, soil with only diesel fuel added, soil with diesel fuel and fish meal added, and finally soil with diesel fuel, fish meal and Brij surfactant added. From the two groups of 4 boxes without ventilation, one of them was left without any perturbation of the soil. The other two boxes were manually agitated weekly. All biopiles were sampled on a regular basis over a one-year period. All results demonstrate a serious influence of the soil properties on the biostimulation efficiency. However, temperature elevation and fertilizer addition have a significant impact on the microbial assemblages in both mineral and organic soils.

Influence of field temperature fluctuations and seasonal freeze-thaw on petroleum hydrocarbon biodegradation in soils from a contaminated site at Resolution Island, Nunavut, Canada

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This research investigated the biodegradation of petroleum hydrocarbons in contaminated soils from Resolution Island, using 1 m × 0.6 m × 0.35 m soil tanks that served as pilot-scale landfarming reactors. The experiments were conducted in a large cold room at McGill University where the temperature was regulated to match the daily average temperatures, ranging from -5 to 10°C for the summer months at Resolution Island. Parallel experiments were also conducted where instead of the daily average temperatures, a constant representative temperature of 6°C was maintained. Comparison of the petroleum hydrocarbon biodegradation patterns over those two months provided an understanding of how temperature fluctuations in the field, influence biodegradation rates and microbiological populations.

The pilot-scale landfarming experiments involved amending the soils with N and P nutrients (20:20:20 fertilizer) and with $CaCO_3$ for buffering. The soils were periodically tilled and a slow airflow rate was maintained over the soil surface. Untreated control systems were maintained in parallel. The soil tanks were intensely monitored for temperature, soil moisture content, soil gas O_2 and CO_2 concentrations for assessing microbial respiration activity, total petroleum hydrocarbon (TPH) and hydrocarbon fractions by C-chain length, microbial population size and community composition.

In experiments where the soil tanks were subjected to daily average temperatures ranging from 1 to 10°C, representative of July and August, at the site, petroleum hydrocarbon concentrations were reduced by 55% by biodegradation, compared to only 21% in soil tanks which were subjected to a constant temperature of 6°C. Significant biodegradation of semi- (>C10 to C16) and non-volatile fractions (>C16 to C34) were observed, in both systems. The numbers of viable, cold-adapted hydrocarbon-degrading microorganisms increased significantly during biotreatment. A residual TPH level of ~500 mg/Kg was obtained after a 60-day treatment period in the soils subjected to varying daily average temperatures and was attributed largely to the non-volatile hydrocarbon contamination in the fraction of particles with diameters ranging from 0.6 to 2 mm.

Polymerase chain reaction (PCR)- denaturing gradient gel electrophoresis (DGGE) analyses for the extracted soil DNA from the soils before and after biotreatment indicated shifts in microbial community composition. The emergence of a hydrocarbon-degrading community was identified through 16S rRNA gene sequence analyses and included genus such as *Aeromicrobium*, *Alkanindiges*, *Paenibacillus*, *Blastococcus*, *Rhodanobacter*, and *Acidobacteria.*