

by the litterfall of the two dominant canopy trees. The leaf mineral content was determined for 15 of the dominant species. The highest contents were found for Ca, Mg, K, Na and Si. Calculated annual fluxes of these elements were respectively 81 kg/ha; 24 kg/ha; 16 kg/ha; 11 kg/ha and 6 kg/ha, and are highly dependent on the productivity of the two dominant tree species.

B42A-0129 1330h POSTER

Development and Application of a Carbon Sequestration Model in Forest Ecosystem in Taiwan

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IPCC tables were used to estimate the carbon emission or removal of land-use change and forestry sector of Taiwan in 1990-2000, and transfer to net carbon dioxide. Its about 2,000Gg, and C sequestration increases over the years. There are 3 problems to deal with when calculate the sink and source of CO₂ in the sector of forestry and land-use. The first is the lack of updated annual data of changed area of forest types and communities gotten from forest inventory in the period of 10-20 years. Second, there is a requirement of compromised land classification system of all kinds of forest types, and a complete growth and yield model system for annual increment volume counting. Finally, the study of soil carbon circulation is still unclear.

The Holdridge Life Zone Classification Model and Forest Gap Model are used to approach the vulnerability and adaptation assessment of the impacts of climate change on forest vegetation. To adapt the models, we gathered meteorological data from 26 Climate observation stations and 816 precipitation stations; in addition, land-use maps made from interpolating 32,720 aerial photos and 4,002 plots ground surveys 40mX40m DEM are also used in our spatial analysis. Trend and Kriging spatial analysis models of GIS are used to interpolate the grid-surface information from point data of precipitation and average temperature. The two primary parameters of Holdridge life zone classification model are bio-temperature and annual average precipitation. Using this model, we then classify Taiwan Life Zone into rain forest, moist forest and wet forest ecoregions and 10 sub-ecoregions. The forest types, species compositions of the 10 sub-ecoregions are obtained from overlapping the ecoregions map and land-use map by using Arcview GIS. The environmental changes of Taiwan were simulated by using Holdridge life zone classification model as doubly increasing CO₂ density and incrementing temperature from 1°C, 2°C and 4°C scenarios.

Forest Gap model were applied to estimate the growth of China-fir and Japan-fir plantation in Taiwan annually. We integrated and analyzed the data of climate, forest growth and land use for developing the diminish strategy of greenhouse gas emission and increasing sink carrying capacity in forest and land-use sector in the future.

URL: <http://fm4sem.nchu.tw>

B42A-0130 1330h POSTER

Momentum Transfer by a Mountain Meadow Canopy: a Simulation Analysis

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Using a mountain meadow as a case study it is the objective of the present paper to test Massmans (1997) model of momentum transfer by vegetation and several parameterisation options for the required within-canopy variation of the phytoelement drag (Cd) and sheltering (Pm) coefficient. A constant ratio between Cd and Pm is found to overestimate and underestimate non-dimensional wind speed in the upper and lower canopy, respectively. A simple parameterisation of Cd/Pm as a function of plant area density is developed, using values optimised by least squares regression between measured and predicted within-canopy wind speeds. In a further step, a separate parameterisation of Cd and Pm is developed: Cd is simulated to decrease exponentially with increasing cumulative plant area index; Pm is modelled as a saturation-type function of plant area density. A validation with independently measured data indicates, that both parameterisations work reliably for simulating wind speed in the investigated meadow. Model predictions of the normalised zero-plane displacement height and the momentum roughness length fall only partly within the range of values given in literature, which may though be explained by the accumulation of plant matter close

to the soil surface specific for the investigated canopies. The seasonal course of the normalised zero plane displacement height and the momentum roughness length are discussed in terms of seasonal variation of the amount and density of plant matter.

Massman W.J. (1997) An analytical one-dimensional model of momentum transfer by vegetation of arbitrary structure. *Boundary-Layer Meteorology* 83, 407-421.

B42A-0131 1330h POSTER

Multidecadal Variability of the Climate, the Biosphere and the Carbon Cycle in a Coupled Atmosphere-Biosphere Model, CCM3-IBIS.

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We analyze a 400-year run of the coupled atmosphere, vegetation and soil model CCM3-IBIS to detect different modes of variability in the climate, vegetation and carbon cycle. IBIS (Foley et al., 1996; Kucharik et al., 2000) is a dynamic vegetation model that describes the physical, physiological and ecological processes occurring in vegetation and soils in a coherent and mechanistic way. The model includes land-surface physics, canopy physiology, plant phenology, vegetation dynamics and competition, and carbon cycling. We coupled IBIS to the NCAR CCM3 at a T31 resolution (3.75 x 3.75). We ran a 400-year equilibrium simulation of the 'present day' climate imposing a constant atmospheric CO₂ concentration of 350 ppm and fixed sea-surface temperatures. Modeled values of NPP, biomass and leaf area index, total soil carbon, standing litter, and total soil CO₂ flux compare favorably with field measurements and with results from other vegetation models driven with observed climatology.

A spectral analysis shows that the total continental precipitation, the net primary productivity and the heterotrophic respiration present slow modes of variation with timescales of roughly 3, 8, and 25 years. Because CCM3-IBIS operates with fixed sea-surface temperatures, this detected variability can only be attributed to changes in vegetation structure and functioning. Semi-desertic regions contribute the most to the 25-year mode.

This study shows that feedbacks between vegetation dynamics and the atmosphere alone can produce internal variability at decadal scale.

B42A-0132 1330h POSTER

Decreased Carbon Storage in the Ocean as a Biogeochemical Consequence of Sequestration on Land

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We describe a previously uncharacterized mechanism mediated by the transport of dust through the atmosphere, in which land use is linked with biological productivity in the open ocean. As a simple corollary to the influential "iron hypothesis", any reduction in the present-day levels of dust supply to the ocean can be expected to produce an additional limitation of marine productivity. Recognizing that historical changes in land use have given rise to globally important sources of dust, it logically follows that should such changes be partly reversed or ameliorated, the availability of mineral dust for deflation by wind action will be reduced, and with it, marine productivity. Just such a reduction in dust supply might arise with any future enactment of carbon sequestration activities involving reduced disturbance and increased stabilization of soils, as allowed under the Kyoto Protocol.

We employ a numerical model of the ocean-atmosphere carbon cycle incorporating explicit iron biogeochemistry to demonstrate that the effectiveness of carbon removal from the atmosphere via certain sequestration measures on land will be diminished by a reduction in the quantity of carbon taken up by the ocean.

B42B MC: Hall D Thursday 1330h

Assessing Bioremediation II (joint with H)

Presiding: J P McKinley, Pacific Northwest National Laboratory; F S Colwell, Idaho National Engineering and Environmental Laboratory

B42B-0133 1330h POSTER

Chemical Evidence for Uranium Bioreduction at Shiprock, New Mexico

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The Department of Energy Uranium Mill Tailings (UMTRA) site at Shiprock, New Mexico includes a mill tailings disposal cell on a mesa overlooking the floodplain of the San Juan River. A plume of contaminated groundwater extends across the floodplain to the river. Although organisms that can reduce uranyl have been identified at the site, the extent of intrinsic reduction is difficult to assess. Uranyl concentrations vary due to mixing between three components: the contaminant plume, river water, and water from a flowing well of deep origin. Chloride and ³H were used to construct a three-component mixing model for floodplain groundwaters. The fraction of each component at each sampling point was used to estimate the uranyl concentration expected from dilution of the plume source by the other components. A much lower concentration than expected was taken to indicate bioreduction. Experimentation indicated that uranyl would only be bioreduced where nitrate was first completely removed; the model results showed evidence for uranyl reduction only where nitrate had been markedly and significantly removed, also by bioreduction. Low nitrate concentrations in these zones may have resulted from nitrate reduction mixing with nitrate-bearing water.

B42B-0134 1330h POSTER

Partial Transformation Products as Indicators of Microbial Hydrocarbon Degradation in Soils

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Monitored natural decay (intrinsic bioremediation), a cost-effective method for remediating contaminated property, is widely applied to fuel contaminated sites. If an intrinsic bioremediation approach could be supported for the clean up of polynuclear aromatic hydrocarbon (PAH) contaminated properties, millions of dollars in clean-up costs could potential be saved, especially in transfers of industrial properties that will continue to be used for industrial purposes. Proving intrinsic biodegradation of polynuclear aromatic hydrocarbons (PAHs) is problematic. Slow PAH biodegradation rates in contaminated soils mean that oxygen mass transfer rates into the soil exceeds bacterial oxygen demand. Likewise carbon dioxide production during degradation is sufficiently slow that carbon dioxide will not accumulate in the soil gas to levels exceeding background, uncontaminated soils. Therefore, oxygen depletion and carbon dioxide accumulation, typical indicators of intrinsic remediation activity at fuel contaminated sites, are of little use in demonstrating intrinsic PAH remediation. Additionally, direct measurement of PAH loss over time is of limited use in the absence of extensive historical records, especially at sites that are still emitting PAHs as part of their operations. PAH loss rates may be in the order of 10% per year, whereas combined sampling and analytical error can be greater than 50%. It is our hypothesis that PAH degradation products, such as aromatic carboxylic acids and

dihydrodiols, will be present in soils where biodegradation is occurring and absent in soils that are biologically inactive. We have developed methods for the extraction of PAH biodegradation products from soils and the analysis of these metabolites by both gas chromatography and high performance liquid chromatography. We have tested our hypothesis against soils undergoing both active and passive bioremediation. Our results indicate that PAH degradation products are detectable in many soils and that the presence of metabolites is correlated with PAH degradation.

B42B-0135 1330h POSTER

Process Modeling of Flow, Transport, and Biodegradation in Landfill Bioreactors

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The need to control gas and leachate production and minimize refuse volume has motivated laboratory experiments and model development for design and assessment of bioremediation treatment processes. In parallel with landfill bioreactor laboratory experiments, we have developed T2LBM, a module for the TOUGH2 multiphase flow and transport simulator that implements a Landfill Bioreactor Model. T2LBM provides simulation capability for the processes of aerobic or anaerobic biodegradation of municipal solid waste and the associated three-dimensional flow and transport of gas, liquid, and heat through the refuse mass. T2LBM considers the components water, acetic acid, carbon dioxide, methane, oxygen, and nitrogen in aqueous and gas phases, with partitioning specified by temperature-dependent Henry's coefficients. T2LBM incorporates a Monod kinetic rate law for the exothermic biodegradation of acetic acid in the aqueous phase by either aerobic or anaerobic microbes as controlled by the local oxygen concentration. Methane and carbon dioxide generation due to biodegradation with corresponding thermal effects are modeled. Acetic acid is considered a proxy for all biodegradable substrates in the refuse. Aerobic and anaerobic microbes are assumed to be immobile and not limited by nutrients in their growth. Although a simplification of complex landfill processes, T2LBM shows reasonable agreement to published laboratory experiments of biodegradation and gas production depending on the choice of numerous input parameters. Simulations of the landfill bioreactor laboratory experiments show that the mechanistic approach of T2LBM can be used to model bioremediation assessment indicators such as oxygen consumption associated with respiration tests.

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B42B-0136 1330h POSTER

Mesoscale Laboratory Models of the Biodegradation of Municipal Landfill Materials

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Stabilization of municipal landfills is a critical issue involving land reuse, leachate treatment, and odor control. In an effort to increase landfill stabilization rates and decrease leachate treatment costs, municipal landfills can be operated as active aerobic or anaerobic bioreactors. Rates of settling and biodegradation were compared in three different treatments of municipal landfill materials in laboratory-scale bioreactors. Each of the three fifty-five-gallon clear acrylic tanks was fitted with pressure transducers, thermistors, neutron probe access tubes, a leachate recirculation system, gas vents, and air injection ports. The treatments applied to the tanks were (a) aerobic (air injection with leachate recirculation and venting from the top), (b) anaerobic (leachate recirculation with passive venting from the top), and (c) a control tank (passive venting from the top and no leachate recirculation). All tanks

contained a 10-cm-thick layer of pea gravel at the bottom, overlain by a mixture of fresh waste materials on the order of 5-10 cm in size to an initial height of 0.55 m. Concentrations of O₂, CO₂ and CH₄ were measured at the gas vent, and leachate was collected at the bottom drain. The water saturation in the aerobic and anaerobic tanks averaged 17% and the control tank averaged 1%. Relative degradation rates between the tanks were monitored by CO₂ and CH₄ production rates and O₂ respiration rates. Respiration tests on the aerobic tank show a decrease in oxygen consumption rates from 1.3 mol/day at 20 days to 0.1 mol/day at 300 days, indicating usable organics are being depleted. The anaerobic tank produced measurable methane after 300 days that increased to 41% by volume after 370 days. Over the test period, the aerobic tank settled 30%, the anaerobic tank 18.5%, and the control tank 11.1%. The concentrations of metals, nitrate, phosphate, and total organic carbon in the aerobic tank leachate are an order of magnitude lower than in the anaerobic tank leachate.

This work was supported by Laboratory Directed Research and Development Funds at Lawrence Berkeley National Laboratory under Department of Energy Contract No. DE-AC03-76SF00098.

B42B-0137 1330h POSTER

Factors Controlling Concentration of Metals in the Leachate from Aerobic and Anaerobic Laboratory Landfill Bioreactors

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Costs and environmental issues associated with operating municipal landfills have motivated laboratory experiments investigating methods to increase biodegradation and decrease fugitive emissions of both liquid and gas. Rates of settling, biodegradation, and emissions were measured in three large laboratory-scale bioreactors filled with 30 kg of typical municipal waste. The bioreactors (200-L clear acrylic tanks) were instrumented to monitor pressure, temperature, moisture, humidity, gas composition, and leachate composition. Three treatments were applied: 1) aerobic (air injection with water addition and recirculation), 2) anaerobic (no air injection, water addition and recirculation), and 3) a control tank (no air or water injection). Preliminary studies showed measurable concentrations of Fe, Ba, Cu, Al, Mn, Ni, and Zn in the leachate. To investigate this further, bi-weekly leachate samples were, and were analyzed for dissolved Fe, Ba, Cu, Al, Mn, Ni, Zn, NO₃⁻, NO₂⁻, NH₄⁺, PO₄³⁻, SO₄²⁻, Cl⁻, F⁻, Na⁺, Ca²⁺, total organic acid, Eh and pH. The aerobic tank leachate had metals concentrations that were an order of magnitude lower than the leachate from the anaerobic tank. Possible explanations include the existence of fewer organic-metal complexes due to the decrease in the dissolved organic matter in the leachate for the aerobic treatment, or the higher pH and redox potential in the aerobic treatment. A sensitivity analysis was performed using MINTEQA2, a U.S. EPA geochemical speciation model that reports on metal speciation based on water composition parameters, for a combination of actual and estimated data. Initial results suggest that the presence of certain organic acids dramatically increases the metal-organic complexation, consistent with observations of greater metal concentrations in the anaerobic treatment leachate.

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URL: <http://www-esd.lbl.gov/CEB/index.html>

B42B-0138 1330h POSTER

Diversity of Pristine Methanotrophic Communities in a Basalt Aquifer: Implications for Natural Attenuation of TCE

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Natural attenuation of a large trichloroethylene (TCE) plume within the Oxid Snake River Plain Aquifer (SRPA) appears to be occurring by aerobic co-metabolism. Methanotrophs are some of the key TCE degraders known to inhabit the aquifer. To better understand the role methanotrophs may have in TCE degradation and the relationship of methanotrophs to dissolved methane concentrations, groundwater collected from wells in the SRPA was analyzed for geochemical properties and methanotroph diversity. Microorganisms removed from groundwater by filtration were used as inocula for enrichments or were frozen and subsequently extracted for DNA. Primers that target Type I and Type II methanotroph 16S rDNA or genes that code for soluble (mmoX) and particulate (pmoA) methane monooxygenase subunits were used to characterize the indigenous methanotrophs via PCR, cloning, and sequencing. Groundwater had dissolved methane concentrations that ranged from 1 to >1000 nM. Analysis of sequencing results suggest that the group Methylocystaceae is a predominant Type II methanotroph in each sample. Methanotrophs can be detected and enriched from groundwater containing even low methane concentrations. Analysis of gene sequences provides assessments of methanotroph abundance and diversity with respect to the aquifer methane concentrations, imparting greater insight into the genetic potential of the microbial community capable of degrading TCE. This research will continue to focus on the evaluation of natural attenuation by methanotrophs.

B42B-0139 1330h POSTER

Soil Contamination by a Former Railroad Shop in Mexico: Proposed Handling and Remediation

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The study deals with an area of 589,062 m² occupied by a national railroad shop located in Aguascalientes, a city in the central part of Mexico. Since 1903, the city became a transcendental railway center in the country and a transportation route toward the United States. Main activities were maintenance and repair of railroads cars, supply of fuel, and foundry of metallic pieces. The place was contaminated for 100 years, up to the recent sale of that company. The workshop area, now surrounded by populated urban areas, is abandoned.

This study presents an evaluation of a previous survey of soil contamination in the different areas of the workshop. Based on our evaluation, we are proposing an optimal handling and remediation of the area. The survey referred 19 shallow boreholes (0-12 meters). Cores and chemical samples were analyzed. We defined the most relevant characteristic and contaminants of the soil samples. In terms of health risk analysis, we conclude that the most important contaminants are hydrocarbons and heavy metals. The following areas present the most significant health risk: the fuel supply zone, the oil petroleum or tar (called in Mexico "chapopote") lagoon, the painting area and the dump of axes and wheels.

B42B-0140 1330h POSTER

Assessing the Feasibility of In-Situ Aerobic Cometabolism of Chlorinated Solvents by a Single-Well Push-Pull and Natural Gradient Drift Tests in McClellan AFB, CA

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A single-well push-pull test has been developed to evaluate in-situ aerobic cometabolic treatment of chlorinated aliphatic hydrocarbons (CAHs), such as trichloroethylene (TCE) and cis-1,2-dichloroethylene (c-DCE). A series of single-well natural gradient drift and push-pull tests were conducted in two monitoring wells at the McClellan Air Force Base, CA, where aquifer is contaminated mainly with c-DCE and TCE.

Transport characteristics of dissolved solutes [bromide (tracer), propane (growth substrate), ethylene, propylene (nontoxic surrogates to probe for CAH transformation activity), DO and nitrate (nutrient)] were evaluated in push-pull transport tests by injecting 200-L of groundwater containing the solutes into the

aquifer (Push), providing a rest period of 18 hours (Reaction), and then extracting 400-L of the test solution/groundwater mixtures (Pull). Mass balances showed over 95% of the injected bromide was recovered, and the recoveries of the other solutes were comparable with bromide. The dispersion of all the solutes was similar indicating sorption or other partitioning processes were minimal. These results indicate that bromide could be used as a conservative tracer for biological activity tests and that little loss of the dissolved gaseous substrates occurred prior to biostimulation of the aquifer.

A series of biostimulation tests were performed by injecting 500 L-groundwater containing propane (6 mg/L), DO (25 mg/L), nitrate (9 mg/L as N) and bromide (100 mg/L) into the aquifer. Temporal groundwater samples were obtained from the injection well under natural gradient drift conditions. With repeating biostimulation tests the rates of both propane and DO utilization were increased significantly. The results demonstrated that the progress of biostimulation could be assessed by injecting and monitoring under natural gradient drift conditions.

Successive push-pull activity tests were performed after biostimulation was achieved using the same procedures as the transport tests. Propane utilization, DO consumption, and ethylene and propylene cometabolism were well demonstrated in successive push-pull tests. The stimulated propane-utilizers cometabolized ethylene and propylene to produce ethylene oxide and propylene oxide, cometabolic by-products. Zero-order rates were estimated and ranked from the highest to the lowest as follows: propane > ethylene > propylene.

Previous microcosm laboratory tests showed c-DCE was cometabolized more rapidly than TCE. Thus, if CAH cometabolism is occurring, the concentration ratios of c-DCE/TCE should reflect this rate difference. A greater decrease in the ratio was observed during the propane activity tests than during the ethylene and propylene activity tests, as expected since propane was rapidly removed and served as an energy source to enhance cometabolism, while ethylene and propylene likely inhibited cometabolism. The result indicates that c-DCE cometabolism was likely occurring.

B42B-0141 1330h POSTER

Activity-Dependent Enzymatic Assay for the Detection of Toluene-Oxidizing Bacteria Capable of Trichloroethylene Degradation

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Toluene-oxidizing bacteria produce enzymes that cometabolically degrade trichloroethylene (TCE). These inducible enzymes are produced only in the presence of certain aromatic substrates such as toluene or phenol. Recent laboratory studies have utilized analog chemical substrates to identify production of bacterial enzymes capable of degrading trichloroethylene. These analog substrates produce chromogenic and/or fluorescent products when biotransformed by the enzymes of interest. In this study, 3-hydroxyphenylacetylene (3-HPA) was identified as an activity-dependent enzymatic probe for the detection of three of the four known toluene oxygenase enzymes capable of TCE degradation. Laboratory studies were conducted using pure cultures of *Burkholderia cepacia* G4, *Burkholderia pickettii* PKO1, and *Pseudomonas putida* F1. Cell cultures grown on lactate (non-enzyme inducing) or lactate and toluene (inducing) were trapped on black polycarbonate filters, exposed to 3-HPA, and examined for fluorescence using an epifluorescent microscope. Additionally, *B. cepacia* G4 cells were grown under the same conditions, but in the presence of mineral and basalt specimens to allow for bacterial attachment. The specimens were then exposed to 3-HPA and examined under an epifluorescent microscope. Our results demonstrate that cells induced for the production of oxygenase enzymes, both unattached and attached, are able to transform 3-HPA to a fluorescent product, although cells attached to geologic materials, such as basalt, take substantially longer to transform the probe. Cells grown under non-inducing conditions do not transform the probe, regardless of their attachment status. Additionally, well water samples taken from a TCE-contaminated aquifer were successfully assayed using the 3-HPA enzymatic probe. The development of this enzyme activity-dependent enzymatic assay provides a fast and reliable method to assess the potential for TCE and aromatic contaminant bioremediation.

B42B-0142 1330h POSTER

Biogeochemical Processes Contributing to Nickel Dynamics Within a Mine Tailings Impacted Lake

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Nickel mining in the Sudbury area in Ontario, Canada has been pursued since the late 1920's by Falconbridge and INCO. Large tailings deposits have therefore been generated and require remediation. At the Onaping mine site, Moose Lake is used as the treatment pond for tailings. The drainage released has had a profound effect on Moose Lake's geochemistry, rendering it highly acidic (pH below 3.5), metal impacted, and chemically stratified. These conditions removed higher trophic levels, thus making microbial processes dominant. Since Moose Lake discharges into the Onaping River system, waters from its upper basin need to be treated. Presently, chemical treatment is performed, however this procedure is not useful for long-term remediation. Rather, an effective remediation strategy for Moose Lake requires an understanding of metal transport through, and cycling within, its water column and particularly of the role that microbial processes play in influencing metal fate. Since the prevailing geochemical conditions and processes occurring within this lake are not well characterized, our aims are to: determine metal concentrations through the water column; identify potential solid phases retaining metals; and to identify biogeochemical processes controlling the dynamics of their partitioning. Initial samples were collected from June - Sept. 2001 for water column metals (particulate (above 0.45 µm), colloidal (0.2-0.45 µm) and dissolved (lower than 0.2µm), iron (Fe³⁺ and Fe²⁺) sulfate and sulfide, microbial community structure and physico-chemical parameters (pH, temperature, O₂, redox, conductivity). Results indicate that the water column is chemically stratified at a depth of 3.5 m (25 m max. depth). Water column pH is less than 3.5 and shows low to anoxic conditions below the chemocline. Metal analyses indicate high dissolved nickel concentrations (700 µM). A depth related decrease of Ni levels was observed near the sediment-water interface, probably due to solid partitioning in the lower depths. High concentrations of hydrogen sulfide and ferrous iron were also detected at this depth, likely indicating sulfate and iron reduction. Metal analyses in the colloidal and particulate phases are ongoing and will be presented. Samples collected throughout the water column by slide samplers reveal two distinct zones rich in microbial cells; one at the chemocline (3.5-4m); and the second coinciding with the zone of sulfate and iron reduction near the sediment-water interface. Observations of DAPI-stained cells have shown morphologically distinct samples from these two zones. Cells from the chemocline zone also displayed a characteristic green pigmentation, which combined to a peak in oxygen observed at the same depth, suggests photosynthetic properties. Cells from the sediment-water interface were coated with black (sulfidic) particles. The taxonomic makeup of these assemblages is currently analyzed by molecular techniques (FISH). Early analyses show that two microbially distinct and active zones occur in this acidified system. Dissimilar processes are likely occurring in these geochemically differing zones with potentially distinct impacts for metal cycling and ultimate fate. Diurnal differences in metabolic activities may influence dynamic processes particularly at the chemocline where photosynthesis occurs. These populations might differently affect metal cycling by their biomineralization capacities or by sorption through microbial-mineral complexes. Results of ongoing analyses will be presented in the context of the long-term goal of this project, aimed at untangling the role of these distinct microbial consortia on metal cycling within Moose Lake.

B42B-0143 1330h POSTER

Denitrification in a Petroleum-Contaminated Aquifer: In-Situ Assessment Using Push-Pull Tests Combined With Acetylene Inhibition and ¹⁵N-Techniques

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Microbial denitrification is an important process during in-situ bioremediation in many petroleum hydrocarbon (PHC)-contaminated aquifers. Field-scale

quantification of denitrification is commonly based on measured consumption of nitrate, e.g., using geochemical data obtained from monitoring wells or data obtained from single-well, push-pull tests (PPTs). The objective of this study was to investigate in more detail the fate of nitrate in-situ during denitrification. We performed three PPTs in a monitoring well of a PHC-contaminated aquifer in Erlen, Switzerland. Injected anoxic test solutions contained bromide as conservative tracer, and nitrate in PPT1, ¹⁵N-nitrate in PPT2, and ¹⁵N-nitrate/acetylene in PPT3. During PPT extraction phases, we measured concentrations of bromide, nitrate, nitrite, nitrous oxide, dinitrogen and ammonium, and determined stable nitrogen isotope ratios in nitrous oxide, dinitrogen, and ammonium. We computed first order rate coefficients of nitrate consumption for PPT1-3, ¹⁵N-dinitrogen production (PPT2-3), and ¹⁵N-nitrous oxide production (PPT3). Similar rate coefficients for nitrate consumption (0.39 ± 0.06 1/d to 0.43 ± 0.07 1/d) were obtained in all PPTs. However, ¹⁵N-dinitrogen production in PPT2 and the sum of ¹⁵N-dinitrogen and ¹⁵N-nitrous oxide production in PPT3 accounted for only ~50% of the observed nitrate consumption in those tests. Moreover, while we detected traces of ¹⁵N-ammonium during PPT2, dissimilatory nitrate reduction to ammonium did not appear to be a relevant process at this site. As a consequence, we were unable to close the mass balance on nitrate based on the measured parameters, which may indicate that nitrate consumption by reductive assimilation (not directly assayed in our study) played an important role during our tests. Furthermore, production of ¹⁵N-dinitrogen in the presence of acetylene during PPT3 provided evidence that some nitrate (or nitrite) was chemically reduced. Our results suggest that denitrification rates determined from nitrate consumption alone may overestimate the contribution of this process to PHC-degradation in contaminated aquifers.

B42B-0144 1330h POSTER

Demonstration of In situ Anaerobic Transformation of Toluene and Xylene Using Single-Well Push-Pull Tests and Deuterated BTEX Surrogates

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Obtaining unambiguous evidence of in-situ transformation of benzene, toluene, ethylbenzene and xylene (BTEX) in the subsurface is a difficult task. Recently, benzylsuccinic acid and its methyl analogues were shown to be unequivocal degradation products of anaerobic toluene and xylene biodegradation. Conducting tracer tests at BTEX-contaminated field sites is problematic because background contaminant concentrations potentially interfere with the interpretation of field test data. To avoid the time and cost associated with removing background contaminants, alternative approaches are needed. Deuterated analogs of toluene and xylene are well-suited for use in field tracer tests because they are inexpensive and can be distinguished analytically from background toluene and xylene. In this study, single-well push-pull tests, in which deuterated toluene and xylene were injected, were performed to assess the in-situ anaerobic biotransformation of toluene and xylene in BTEX-contaminated wells.

A total of 4 single-well push-pull tests were conducted at BTEX-contaminated field sites near Portland, OR and Kansas City, KS. Test solutions consisting of 100 mg/L bromide, 250 mg/L nitrate, 0.4 to 2.5 mg/L toluene-d₈, and 0.4 to 1.0 mg/L o-xylene-d₁₀ were injected at a rate of 0.5 L/min. During the extraction phase, samples were taken daily to biweekly for up to 30 days. Samples for volatile organic analytes were collected in 40-mL volatile organic analysis (VOA) vials without headspace. Samples for BSA and methyl-BSA were collected in 1 L glass bottles and preserved with 5% (w/w) formalin. Samples were shipped on ice and stored at 4 C until analysis.

Unambiguous evidence of toluene and xylene biotransformation was obtained with the in-situ formation of BSA and methyl-BSA. The concentrations of BSA ranged from below the detection limit (0.2 µg/L) to 1.5 µg/L. The concentrations of methyl-BSA ranged from below detection to the quantitation limit (0.7 µg/L). The highest BSA concentrations detected corresponded to 0.1 - 0.2 mol% of the injected deuterated toluene. Zero-order degradation rates for deuterated toluene, estimated as the rates of BSA formation, were 0.0004 to

0.001 day⁻¹. Because methyl-BSA concentrations did not exceed the quantitation limit, the rate of xylene degradation could not be calculated. The formation of BSA and methyl-BSA was coupled with the utilization of nitrate, presumably due to denitrification. Transformation of toluene and xylene to BSA and methyl-BSA, respectively, was observed for wells characterized by low concentrations of toluene and xylene relative to total BTEX. To the best of our knowledge, this is the first report to document the use of deuterated BTEX surrogates in field-tracer experiments.

B42B-0145 1330h POSTER

Fumarate as a Probe and Stimulant for In Situ Reductive Dechlorination of Trichloroethene

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There is evidence that fumarate and trichloroethene (TCE) undergo reduction reactions under similar redox conditions and that microbial strains capable of utilizing both TCE and fumarate as electron acceptors exist. Thus, we propose that fumarate can be used in reactive-tracer tests in TCE-contaminated groundwater to (a) determine if favorable conditions for TCE reduction are present and/or (b) stimulate growth of fumarate/TCE-utilizing microorganisms as a means of increasing TCE bioremediation rates. Five separate series of single-well push-pull tests were conducted in wells with different background contaminant and biogeochemical profiles at a TCE-contaminated site. In test series I and V, in situ reduction rates for injected trichlorofluoroethene (TCFE), a TCE-surrogate, were determined. In test series II, III, and IV, in situ reduction rates for injected fumarate were determined. TCFE reduction rates varied between wells in test series I but were consistent with expected results based on background TCE reduction product profiles. In test series II, fumarate reduction occurred in those wells where TCFE had been reduced and not in those where TCFE had been reduced slowly or not at all, indicating that fumarate may be used to determine if TCE-reducing conditions are present. In test series III and IV, fumarate reduction occurred in several of the wells in which it had not occurred in test series II. In addition, fumarate reduction rates increased in those wells where reduction had occurred in series II, indicating that fumarate additions stimulated the growth of fumarate-reducing microorganisms. TCFE reduction rates were higher in test series V than in test series I, indicating that fumarate additions led to increased TCE reduction rates. These findings are significant since there is a need for methods that (a) probe for TCE reducing conditions and (b) increase TCE bioremediation rates.

B42B-0146 1330h POSTER

Comparison of Microcosm Tests and a Field Demonstration of Cometabolic Air Sparging With Propane for the Bioremediation of Trichloroethylene and cis-Dichloroethylene

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Cometabolic air sparging (CAS) is an innovative form of conventional air sparging, and is designed to degrade or remove chlorinated aliphatic hydrocarbon

compounds (CAHs) in groundwater and to potentially treat these contaminants in the vadose zone. A CAS demonstration was conducted at McClellan AFB, California, for removal of chloroethenes (TCE, cis-DCE) from groundwater using propane as the cometabolic substrate. In support of this field demonstration both groundwater and vadose zone microcosm studies were performed. The microcosms were created with groundwater and aquifer materials from the demonstration site. Concentrations of compounds in the microcosms were created to mimic conditions where the demonstration was performed. The microcosms were used to test the potential of the propane-utilizers to transform the CAHs of interest, and determine their nutrient requirements while transforming these compounds.

Results from the first season of field-testing showed propane-utilizers could be effectively stimulated in the saturated zone with repeated intermediate sparging of propane and air. The lag time for effective propane utilization to be observed in the field was about 30 to 40 days, while in laboratory microcosms the lag period was about 12 days. Consistent with the field tests the groundwater microcosms showed cis-DCE was more rapidly transformed than TCE. Microcosm tests also indicated that propane inhibited the transformation of cis-DCE and TCE, and as observed in the field, most of the transformation of these compounds occurred after propane was reduced to low concentrations. In the field demonstration propane utilization rates and rates of CAH removal slowed after three to four months of repeated propane additions, which coincided with the depletion of nitrogen (as nitrate) in the treatment zone. Similar results were obtained with repeated additions of propane to the microcosms. In the field test ammonia was added to the propane/air mixture to provide a bioavailable nitrogen source. This resulted in enhanced rates of propane utilization and CAH transformation in the saturated zone. Microcosm results also showed ammonia was effective in enhancing propane utilization and CAH transformation rates, and the transformations caused a toxic effect that significantly increased the propane-utilizers requirements for nitrogen. A 2 to 4-fold increase in nitrogen consumption was observed when CAHs were transformed.

Propane utilization was observed to be much slower in the vadose zone of the field demonstration, compared to the saturated zone, and very limited CAH transformation was observed. Propane utilization rates in the vadose zone microcosms were an order of magnitude lower than what was observed in the saturated microcosms. Bioavailable nitrogen was required to maintain propane utilization rates. Higher CAH concentrations were found to inhibit the stimulation of the propane-utilizers under these conditions. Thus the vadose microcosms yielded results that were consistent with the field demonstration.

B42B-0147 1330h POSTER

Development of a Conceptual Model for Monitored Natural Attenuation of Methyl t-Butyl Ether

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Monitored natural attenuation (MNA) has become a common remediation strategy for groundwater contamination. This strategy has extended to MTBE despite the fact that its higher solubility, higher mobility, and slower degradation rate compared to other gasoline constituents could make demonstrating natural attenuation more difficult for this compound.

Given the increasing focus on natural attenuation by mass removing processes such as biodegradation, we must be able to separate the magnitude of attenuation attributable to degradation from that resulting from dilution, dispersion, or sorption. In order to determine field attenuation rates, and specifically biodegradation rates, the plume structure must be well understood. Furthermore, geochemical footprints must be identified and properly interpreted. The sampling network must be appropriate to provide representative data and that data must be properly analyzed to make a defensible demonstration. Existing field studies of MTBE attenuation rates have left unanswered questions about the role of source dissolution behavior, the usefulness of geochemical data, and the adequacy of traditional monitoring network designs.

The research presented here incorporates a controlled large-scale dissolution experiment, a natural gradient tracer test, and numerical simulations to address these questions. The dissolution study captures the source behavior from the moment of the initial spill. The tracer study demonstrates that significant complexity can arise in the dissolved plume structure despite relatively simple hydrogeology. The modeling illustrates the potential errors contributed by sampling network design. The combination represents an unprecedented approach to dissecting monitored natural attenuation in order to understand where the greatest challenges to MNA for MTBE lie. This work eval-

uates how increasing complexity in the source function, hydrogeology or attenuation processes translates into uncertainty in the natural attenuation demonstration. Furthermore, it quantifies the error attributable to sampling network design. The result is a conceptual model for MNA of MTBE that can be used to improve existing protocols.

B42C MC: Hall D Thursday 1330h

Synthetic Analyses of Large-Scale Ecological Processes I

Presiding: C Potter, NASA-Ames

Research Center; G Hurtt, University of New Hampshire; J Foley, University of Wisconsin; J Coughlan, NASA Ames Research Center

B42C-0148 1330h POSTER

Modeling Lidar Waveforms Using a Radiative Transfer Model

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In the past, obtaining reliable measurements of key forest canopy metrics has been difficult, even after the development of remote sensing technology. Fortunately, next-generation lidar systems are proving to be useful tools for deriving critical canopy measurements, such as height, structure and biomass. These studies have all focused on comparisons between basic lidar-derived and field-sampled measurements. The results of these studies have shown that lidar remote sensing instruments can successfully measure forest canopy characteristics. However, physically-based remote sensing models are necessary to more fully understand and interpret the interactions of the laser energy with the forest canopy. In this study the Geometric Optical and Radiative Transfer (GORT) model is used to model lidar waveforms. GORT is capable of modeling lidar returns from canopies with clumped multiple layers and multiple species. For this study, GORT was used to model waveforms over the Sierra National Forest in California. Field data input into GORT are a representative sample of the different vegetation types found in the forest. The modeled waveforms are then validated against actual lidar data collected by the Laser Vegetation Imaging Sensor (LVIS) which mapped the area in October 1999. By modeling lidar waveforms based on the physical principles of radiative transfer, GORT fills a missing link between the remotely sensed and actual canopy structure. The results of this study will also aid in future large-scale land surface mapping by developing a link between lidar and other remote sensing data.

B42C-0149 1330h POSTER

Forest Disturbance Monitoring Using Multi-satellite Data

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The forests in Northeastern China have been undergoing dramatic changes during the last several decades due to forest fire, insect infestation, massive logging, agricultural conversion, and afforestation. These changes affect the climate, the ecosystem, the economy and living heritage in the region and the carbon balance. For example, a forest fire, which burned from 6 May to 2 June 1987, destroyed nearly one million ha of forest in Northeastern China. Following the fire,