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Corn stover is a readily source of biomass for cellulosic ethanol production, and may provide additional income for growers. Published research shows that residue removal changes the rate of soil physical, chemical, and biological processes, and in turn, crop growth. Building a sustainable cellulosic ethanol industry based on corn residue requires residue management practices that do not reduce long-term productivity. To develop such systems, impacts of stover removal on the soil and subsequent crops must be quantified. The ARS/DOE Biofuel Project is the cooperative endeavor among scientists from six western Corn Belt US Dept. of Agriculture, Agricultural Research Service (ARS) locations and US Dept. of Energy. The objectives of the project are to determine the influence of stover removal on crop productivity, soil aggregation, quality, carbon content, and seasonal energy balance, and carbon sequestration. When residue is removed soil temperatures fluctuate more and soil water evaporation is greater. Residue removal reduces the amount of soil organic carbon (SOC), but the degree of reduction is highly dependent on degree of tillage, quantity of stover removed, and frequency of stover removal. Of the three cultural factors (stover removal, tillage, and N fertilization) tillage had the greatest effect on amount of corn-derived SOC. No tillage tends to increase the fraction of aggregates in the 2.00 to 0.25 mm size range at all removal rates. Stover harvest reduces corn-derived SOC by 35% compared to retaining stover on the soil averaged over all tillage systems. Corn stover yield has not differed across stover removal treatments in these studies. In the irrigated study, grain yield increased with stover removal. In the rain-fed studies, grain yield has not differed among residue management treatments. Incorporating the biomass ethanol fermentation by-product into a soil with low SOC showed a positive relationship between the amount of lignin added and the subsequent humic acid concentration and aggregate stability. These and future outcomes from this effort will provide DOE and the developing biomass ethanol industry knowledge and guidelines on the environmental and crop productivity consequences of large-scale collection of corn stover.

B51B-06 0915h

Monitoring Soil Carbon Inputs and Changes with Crop Type and Management Practice Using Pyrolysis-Molecular Beam Mass Spectrometry

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With the increasing need to produce more renewable bioenergy products comes the need to assess the impacts of these agricultural cropping practices on soil carbon inputs and changes. In addition, the anticipated increased use of short rotation woody crops for biomass and bioenergy programs requires that we improve our understanding of the effects of management on soil quality and soil organic matter. We have developed an atmospheric pressure rapid pyrolysis technique that can analyze up to 150 samples per day with direct sampling molecular beam mass spectrometry (py-MBMS). The advantage of this technique is that complex biomaterials can be rapidly pyrolyzed and subsequent fragment condensation reduced which provides molecular data for both light and heavy pyrolysis products. Because of the chemical richness of the resultant mass spectra, we use multivariate statistical analysis techniques to provide efficient pattern recognition and identify major pyrolysis products. These products can then be used to characterize soil organic matter content and composition. Preliminary results from 0-5 cm soils cores taken from soils that were cropped with either continuous till or no till sorghum or soybeans show that we can easily distinguish between till and no till regardless of crop type. Analysis of depth increments of forest soils that experienced a chronosequence of wind disturbances showed that we could distinguish depth, location, and recent and older soil organic matter species of the soil cores with this technique. Analysis of well-characterized CRP (Conservation Reserve Program) soils again allowed us to distinguish depth and location and to accurately predict soil microbial biomass contents. We will present these results and discuss their implications for quantitatively assessing the impacts of bioenergy cropping on soil organic matter.

B51B-07 0930h

The Impact of Elevated CO2 on Soil C and N Cycling as Revealed by Decomposition of 15N-13C Labelled Residues in a Pasture Soil Exposed to FACE Conditions for 9 Years.

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The effect of prolonged elevated atmospheric CO2 on soil C and N cycling remains a widely debated topic. Elevated atmospheric CO2 may alter decomposition rates through changes in plant residue quality and through its impact on soil microbial activity. This study examines whether plant residues produced under elevated CO2 decompose differently than residues produced under ambient CO2. Moreover, a long-term experiment offered a unique opportunity to evaluate assumptions about C-cycling under elevated CO2 made in coupled climate-SOM models. Trifolium repens and Lolium perenne residues, produced under elevated and ambient CO2, at two levels of N fertilizer were incubated in soil for 90 days. Soils and residues used for the incubation had been exposed to ambient and elevated CO2 under Free Air Carbon Enrichment (FACE)-conditions and had received 15N-N-fertilizer for 9 years. The rate of decomposition of L. perenne and T. repens residues was unaffected by elevated atmospheric CO2 and rate of N fertilization; soil respiration and recovery of 15N in the soils was independent whether the residues were grown under ambient or elevated CO2. Any changes in litter C:N ratio due to elevated CO2, did not affect residue decomposition. If under prolonged elevated CO2 changes in soil microbial dynamics had occurred, it was not reflected in the rate of residue decomposition. Only respiration of L. perenne soil, following low N fertilization was enhanced after exposure to elevated CO2, irrespective of the addition of ambient or elevated residues. This increase in respiration was not reflected in an increase in the microbial biomass of the L. perenne soil. The contribution of old and newly sequestered C to soil respiration, as revealed by the 13C-CO2 signature, reflected the turnover times of SOM-C pools as described by multi-pool SOM models. The results appear not to confirm the assumption of a negative feedback induced in the C-cycle by elevated CO2 used in coupled climate-SOM models following an increase in elevated CO2. Moreover, this study showed no evidence for a positive feedback in the C-cycle following additional N fertilization.

B51B-08 0945h

Factors Influencing Changes in Soil Carbon Following Afforestation of Pastures With *Pinus radiata* in New Zealand

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Since 1992, afforestation with *Pinus radiata* D.Don in New Zealand has led to the establishment of over 500,000 ha of new plantation forests, about 85% of which are on grazed pastures. These forests accumulate carbon (C) in vegetation rapidly, storing on average about 230 Mg C ha^{-1} during a 30-year rotation. Although mineral soil C levels can decline following afforestation, the consequences of afforestation on mineral soil C pools are poorly understood. Our observations at several sites throughout New Zealand suggest that afforestation decreases soil C and N cycling rates, increases soil C:N ratios, and lowers soil temperatures. Using the G'DAY ecosystem model, we investigated the interactions between N cycling processes and soil C storage at a site where soil C content had not changed following afforestation. Our simulations, in contrast, showed an increase in soil C following afforestation, primarily as a result of increased above-ground inputs and soil C:N ratio. We concluded that G'DAY overestimated C inputs from the forest floor to the mineral soil. We then used the ROTHC soil C model to examine changes in plant C inputs at another site where mineral soil C declined with afforestation. Below-ground forest C inputs were estimated assuming a steady-state relationship between litterfall and soil respiration; these inputs increased linearly between years 6 and 12, after which they remained constant at 1.53 Mg C $ha^{-1}y^{-1}$ until harvest at year 26. Measured changes in soil C (0-20 cm) and estimated below-ground inputs were then used to estimate above-ground inputs (as a proportion of total litterfall (3.81 Mg C $ha^{-1}y^{-1}$)) to the mineral soil. Our results suggest that 10% of forest floor inputs entered the mineral soil over one rotation. Using these results, and estimates of slash and weed production during/after harvest, we found that mineral-soil C stocks would likely continue to decline during second and third rotations of *P. radiata*; the magnitude of this decline depended in part on slash inputs to the soil. How afforestation changes mineral-soil C could depend on previous pasture management; soil C losses could be higher when afforestation occurs on highly productive pastures. While slash inputs after harvest help minimize soil C losses, they do not compensate for the ecosystem changes in C inputs viz. primarily below-ground under pasture and above-ground under forest.

B51C MCC: Level 2 Friday 0830h

Microbe and Mineral Interactions and the Biogeochemistry of Reduced Sulfur Posters *(joint with A, H, OS, P, V)*

Presiding: **B Twining,** Environment School, Yale University**; J R Scott,** Idaho National Engineering and Environmental Laboratory

B51C-0966 0830h POSTER

Application of Flow Field Flow Fractionation-ICP-MS for the Study of Uranium Binding in Cell Suspensions of Shewanella oneidensis

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Field flow fractionation (FFF) is an aqueous size-based separation technique applicable to the separation of biomolecules, colloids, and bacteria. When interfaced on-line with ICP-MS detection, elemental data can be collected concurrently. In this study we employed hyperlayer- FFF methodology to separate cells of Shewanella oneidensis strain MR-1 from exopolymers present in washed cell suspensions. The cell suspension was injected into a thin channel through which a carrier solution (10mM NH_4Cl) is continuously pumped. A field is applied perpendicular to the direction of channel flow forcing the cells and other particles against an accumulation wall; in this case we used flow (Fl) FFF, where the perpendicular force is another fluid flow, known as the cross flow, pumped across two porous frits on either side of the channel. The cells experience hydrodynamic lift forces moving them from the accumulation wall into faster flowing zones within the laminar channel flow. Because these lift forces depend on particle diameter, size separation takes place as the cells flow down the channel. With a channel flow of 4 $ml.min^{-1}$ and a cross flow of 0.4 ml. min^{-1} the cells eluted with a retention time of 5.2 minutes corresponding to an approximate equivalent spherical cell diameter of 1-2 m based on calibration of the hyperlayer method with sized polystyrene beads. Cell suspensions were spiked with increasing concentrations of U to establish an adsorption isotherm and with fixed U concentrations at varying pH to establish a pH sorption isotherm. Elution of cells was detected by UV absorbance and the eluant exiting the UV detector was interfaced on-line to ICP-MS to detect U. A linear sorption isotherm was determined for U solution concentrations from 0.2 - 16 M. The pH sorption isotherm showed maximum U sorption to S. oneidensis occurs at pH 5, in agreement with other batch sorption studies. A relatively large molecular compound, presumably a cell exudate, since the cells were determined to remain intact with microscopy, was identified by FFF (soluble constituents are not retained in hyperlayer FFF and thus elute in the void volume). This cell exudate complexed U and at higher pH the exudate appeared to have a greater affinity for U than the cell surface. Thus Fl-FFF interfaced with ICP-MS detection appears to be a powerful analytical technique for metal sorption studies with bacteria; analysis can be carried out on very small sample volumes (typical injection volume is 25 L) and additional speciation information can be gained because soluble organic constituents of the cell suspension also elute from the FFF channel and are resolved from the cells. Other possible applications of Fl-FFF include competitive metal binding studies in mixed bacteria suspensions and mixed mineral-bacteria suspensions.

B51C-0967 0830h POSTER

Probing the Microbe-Mineral Interface: Towards A Quantitative Treatment of Mineral-Surface Processes in the Context of Microbial Attachment

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One of the major challenges of geomicrobiology is to resolve the precise manner by which microbial activity influences mineral-surface reactions. While a prerequisite for biological activity at a surface is substrate recognition and attachment, probing the nature of this biological-geological interface is inherently difficult. Accordingly, direct quantification of microbially-mediated dissolution rates are often complicated by an inability to discern relative contributions from direct microbe-mineral surface interactions (biofilm formation) and changes in the solution environment resulting from biological activity. A noninvasive imaging technique is needed that can both detect the microbe at the surface and quantify any resulting changes in mineral-surface topography, while maintaining both a high spatial resolution and a large field of view. Vertical scanning interferometry (VSI) meets these requirements and enables the measurement of both local dissolution (etch pits) and "global" dissolution rates (surface normal retreat). The novel application of VSI to the study of geomicrobiological problems yields capabilities that are complementary to scanning probe microscopy (SPM) methods in providing quantitative insight into microbial-mineral interactions as well as to the relationship between surface microtopography and biofilm formation. Recently, these coupled techniques have elucidated the mechanistic role of Shewanella oneidensis MR-1 in determining the dissolution rates of carbonate minerals. Our results show that Shewanella surface colonization can either block mineral dissolution through attachment to high-energy sites on the surface or enhance dissolution as a byproduct of irreversible attachment. The relative contribution from these processes to the overall dissolution rate varies with the background abiotic dissolution rate of the mineral. This and other studies by our group are beginning to demonstrate that VSI and SPM are well-suited to provide the critical measurements needed to build quantitative and predictive models of microbial surface recognition and their associated effect on mineral-surface processes.

B51C-0968 0830h POSTER

Microbial Diversity Associated With Geochemical Changes in a Deep Subsurface Aquifer

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The microbial diversity of a 1.83km deep, thermophilic, fluid-filled subterranean fracture was monitored over a three and a half month period and correlated to observed changes in the geochemistry of the system. Three water samples were analyzed using 16S rDNA molecular techniques for microbial diversity, isotopic and geochemical composition. Gibbs' free energy of microbial redox reactions predicted that at in situ conditions sulfate reduction, methanogenesis and acetogenesis should be dominant metabolic pathways utilized by microbes, whereas Fe(III)-reduction should only have been favorable in the last sample. Noble gas isotopic data yielded a subsurface residence time of ~10-100 Myr. and the non-meteoric δD vs. δ^{18}O values were indicative of water-rock alteration at $<100^{o}$C. δ^{34}S of sulfide and sulfate differed by $15^{o}/_{oo}$, consistent with fractionation by sulfate reducing bacteria. H_2 concentrations declined with time, which in conjunction with the δ^{34}S data, suggested that hydrogenotrophic sulfate reducing bacteria dominate the community. This was compatible with 16S rDNA analysis, which yielded clones similar to *Desulfotomaculum* and *Desulfofustis* species appearing in the three 16S libraries. δ^{13}C and δD values of CH_4 and light hydrocarbons indicated methanogenic CH_4 was mixing with abiogenically formed CH_4. This is consistent with the presence of Archaeal 16S sequences similar to *Methanosaeta* and *Methanosarcina* species. The temporal increase in acetate concentration could be attributed to clone types similar to known acetogenic bacteria such as *Moorella glycerini*, which were present in the last sample. Clones similar to known Fe(III)-reducing bacteria such as *Geovibrio* species were observed in the first and last samples.

B51C-0969 0830h POSTER

Microbiology and Geochemistry of Acidic Cave Biofilms in the Frasassi Caves, Italy

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Acidic (pH 2-4) and extremely acidic (pH 0-1) biofilms in sulfidic regions of the Frasassi cave system are relatively simple, chemoautotrophic microbial communities. As such, they serve as model systems to test relationships between microbial diversity and physical and geochemical factors. Both biofilm types are isolated from surface sources of C and N and are ultimately powered by oxidation of H_2S present in the cave atmosphere. pH 2-4 biofilms consist of cells in close association with sub-um to sub-mm mineral grains (primarily $CaSO_4$) coating cave walls. Direct counts of cells stained with 4',6-diamidino-2-phenylindole, hydrochloride (DAPI) yield a biomass estimate of 7.5 x 10^6 to 1.3 x 10^7 cells per cm^3. The great majority of these cells are either dormant (contain few ribosomes) or cells which do not hybridize with either bacteria- or archaea-specific oligonucleotide probes. Sparse clusters of short rod and coccus-shaped cells hybridized with a bacteria-specific Fluorescent In Situ Hybridization (FISH) probe. Polymerase Chain Reaction (PCR) amplification of 16S rDNA was successful with bacteria-specific primers as well as with several sets of archaeal-specific primers, suggesting that some of the "dormant" cells are archaea. Extremely acidic biofilms (snottites) drip from macroscopic (1-2 cm length), reddish $CaSO_4$ crystals on the cave walls. DAPI-staining and FISH revealed abundant bacterial rods, bacterial filaments, and fungi in the snottites. Future work will characterize the acidic cave wall biofilms, as well as neutral-pH cave stream biofilms, using 16S rDNA clone libraries in order to determine whether pH is an important factor controlling microbial diversity.

B51C-0970 0830h POSTER

The Biosignatures of Controlled Bbiomineralization of Pyrite From Fe^{2+} and H_2S by Thiomonas sp.

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A novel strain of Thiomonas called strain 51 was recently isolated from a subsurface sulphide-rich aquifer. Under defined culture conditions this strain is capable of forming a variety of minerals such as elemental sulfur, mackinawite, troilite, cubic FeS greigite and pyrite. Previous studies suggested that the formation of these minerals is a case of biologically controlled biomineralization. Strain 51 is uniquely capable of using the formation of iron sulphides, including pyrite, from ferrous iron (Fe^{2+}) and hydrogen sulphide (H_2S) as a source of energy. This type of biomineralization is used in a variety of models of early life and is relevant for life on Earth. Neither the mechanism used by strain 51 to produce iron sulphides, nor the resulting biosignatures have yet been elucidated. We performed a microanalytical study by using transmission electron microscopy (TEM) with energy dispersive X-ray spectroscopy (EDS) to study the ultrastructural distribution of these deposits in relation to the cells as a means of obtaining insights into the mechanism of this type of biomineralization. The formation of iron sulfides by strain 51 appears to be a stepwise process. Prior to forming pyrite, cells produce elemental sulphur (S^{o}) and an Fe-rich precipitate outside the cells, and accumulate considerable amounts of iron in the periplasmic space and in the cytoplasm close to the membrane, in complexes with phosphate, silicate and sulphide. During subsequent steps iron monosulphide minerals are formed such as cubic FeS, mackinawite, and greigite. Pyritization is a late step and appears as nanometer-sized microcrystallites in the periplasmic space and submicron sized microcrystallites outside the cells. The arrangements of these crystals may be important biosignatures in micropaleontology.

B51C-0971 0830h POSTER

Hydrophillic Thiols in the Porewaters of Coastal Marine Sediments

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Porewater profiles of thiolic compounds have been determined at a strongly reducing site in Boston Harbor, Massachusetts. Derivatization with monobromobimane followed by reverse phase high performance liquid chromatography and fluorescence detection have been used to detect at least six thiols in the porewaters. Maximum individual thiol concentrations of up to 10 μM (glutathione equivalents) were either coincident with the sulfide maximum or showed an increase with depth. The profiles of at least two thiols indicate a flux to the overlying water. Samples from a benthic chamber have detected glutathione and several of the unidentified thiols in the oxygenated water overlying these sediments. Silver, copper, and lead porewater profiles have also been determined so that the importance of the metal-RS complexation in porewaters can be considered.

B51C-0972 0830h POSTER

Determination of Mercury Complexation in Seawater by Competitive Ligand Equilibration Using Thiosalicylic Acid

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The measurement of quantitative information, such as the concentration and binding strengths, of organic ligands which complex mercury in natural water is essential for understanding the aquatic biogeochemistry of mercury. Organic thiols have been suggested as a binding site for mercury complexation in natural waters based on its high binding constant and experimental observations with soil humic matter. To date, the direct characterization of the complexation between aquatic organic matter and mercury is limited. This work describes a competitive ligand equilibration method, using thiosalicylic acid as a competing ligand, to determine the complexation of mercury by organic ligands in natural water. Two classes of ligands were observed, one hydrophilic and one hydrophobic. The hydrophilic organic ligands had concentrations of 10 - 60 pM and conditional stability constants of $10^{26.4-27.9}$ in coastal and estuarine samples at pH 9.7. Hydrophobic organic ligands with concentrations between 0.5 and 8.0 nM and stability constants of $10^{21.7-24.1}$ were detected in the same samples at pH 7.0 - 7.5. These latter ligands were determined using the natural chloride ion present as a competing ligand. Both results agree with the extractability of natural mercury complexes. The hydrophilic ligand dominates at low pM mercury levels, while the hydrophobic ligand becomes dominant at nM mercury concentrations. The accuracy of the method was tested using a model ligand, diethyldithiocarbamate, yielding a relative error of 6 %. Speciation calculations using Galveston Bay estuarine water show that >99.9 % of the dissolved mercury is organically complexed at salinities <5 ppt. Competition with chloride reduces organic complexation at higher salinities. A linear relationship exists between log K' and the log [L] of the mercury complexing organic ligands, indicating a continuity of binding characteristics over a broad salinity range in natural water.

B51C-0973 0830h POSTER

Microbial influence on sulfur speciation in Lower Kane Cave, WY

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A distinctive microbial community is being studied within Lower Kane Cave (LKC) of the Madison Limestone, near Lovell, WY, where the cave forming process is principally sulfuric acid replacement of limestone with gypsum. The aquatic microbial mat includes a consortium of both S-reducing and S-oxidizing bacterial communities, which cycle sulfur along the reach of the cave stream. Multiple techniques are being employed to characterize the speciation and distribution of sulfur within LKC in order to identify the individual metabolic pathways, and to what degree sulfur chemistry within the cave is controlled by microbial processes. Aqueous sulfide levels were determined immediately in the field using colorimetric methods and volatilization was directly measured by field GC. Dissolved sulfide levels generally decrease with distance from the stream source, ranging from 0.85 to 0.03 ppm. Volatilization increases over the microbial mats however due to local sulfide production by sulfate reducing bacteria. Cave water, sediment and microbial biomass were sampled from the cave and characterized for major element and sulfur chemistry. Laboratory HPLC determination of transient aqueous sulfoxy species was done to characterize intermediate species, and low concentrations of thiosulfate and trace polythionates were detected. Sediment samples were analyzed for total sulfur and operational sulfur fractions, including acid volatile sulfur (AVS), total reducible sulfur, pyrite and elemental S. Elemental analysis was used to determine the distribution of total S within sediment and biomass to identify potential sulfur storage within the system. Total S ranges from 0.35% dry weight in sediment to 51% dry weight in mats. Operational sulfur fractions were isolated using a modified Johnson-Nishita method, and AVS fractions range up to 0.2% (wt/wt). The presence of microbial mats appears to enhance volatilization of sulfur gases by mechanisms as yet unknown. Correlation of S distribution and speciation with the current microbial communities and stream morphology within LKC indicates influences from both biotic and abiotic processes. The results from this study, however, suggest that microbial consumption dominates over abiotic auto-oxidation and volatilization of dissolved sulfides, while the anaerobic community provides an additional source of reduced S.

B51C-0974 0830h POSTER

Formation of Kinetically Inert Copper Compounds in the Presence of Sulfide and Thiols

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Most of the copper in aquatic environments is bound in compounds that determine the bioavailability and toxicity of the copper but remain unidentified. A recent study has shown that a large fraction of the copper in coastal waters is present in compounds that are kinetically inert to ligand exchange with the strong ligand salicylaldoxime (SA) (Kogut and Voelker, 2003). The goal of this study is to determine whether inert copper compounds are formed in seawater in the presence of sulfide and thiols. Laboratory experiments with water from the Sargasso sea with low levels of NOM was used for experiments where copper, sulfide and cysteine were added and allowed to react. Two analytical techniques for determining concentrations of kinetically inert copper compounds were compared: spectrophotometric detection of copper (I)-bathocuproine after reduction of Cu(II) and pre-concentration of the Cu(I)-bathocuproine complex on a C18 -column, and the previously used competing ligand exchange technique using voltammetric detection of copper-salicylaldoxime complexes.

B51C-0975 0830h POSTER

A New Method to Estimate Water Mass Fractions and Remineralization Ratios

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We present a new method of water mass analysis that accounts for the nonlinear relationships in nutrient concentration observations. This method simultaneously solves for the fractions of different water masses and for the Redfield stoichiometry of remineralization at a given location. Performance is compared to the Optimum Multiparameter (OMP) technique using an extensive pseudodata analysis in which the mixing and remineralization of up to four endmembers from a set of 15 major water masses is simulated. The technique also produces confidence intervals that express the uncertainty due to water mass property characterization. Results for the subtropical Indian ocean using data from the WOCE/JGOFS program are presented.

B51C-0976 0830h POSTER

A laboratory study of anaerobic oxidation of methane in the presence of methane hydrate

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In order to mimic and study the process of anaerobic methane oxidation in methane hydrate regions we developed four high-pressure anaerobic bioreactors, designed to incubate environmental sediment samples, and enrich for populations of microbes associated with anaerobic methane oxidation (AMO). We obtained sediment inocula from a bacterial mat at the southern Hydrate Ridge, Cascadia, having cell counts approaching 10^{10} cells/cc. Ultimately, our goal is to produce an enriched culture of these microbes for characterization of the biochemical processes and chemical fluxes involved, as well as the unique adaptations required for, AMO. Molecular phylogenetic information along with results from fluorescent *in situ* hybridization indicate that consortia of Archaea and Bacteria are present which are related to those previously described for marine sediment AMO environments. Using a medium of enriched seawater and sediment in a 3:1 ratio, the system was incubated at 4°C under 43 atm of methane pressure; the temperature and pressure were kept constant. We have followed the reactions for seven months, particularly the vigorous consumption rates of dissolved sulfate and alkalinity production, as well as increases in HS-, and decreases in Ca concentrations. We also monitored the dissolved inorganic C (DIC) δ^{13}C values. The data were reproduced, and indicated that the process is extremely sensitive to changes in methane pressure. The rates of decrease in sulfate and increase in alkalinity concentrations were complimentary and showed considerable linearity with time. When the pressure in the reactor was decreased below the methane hydrate stability field, following the methane hydrate dissociation, sulfate reduction abruptly decreased. When the pressure was restored all the reactions returned to their previous rates. Much of the methane oxidation activity in the reactor is believed to occur in association with the methane hydrate. Upon the completion of one of the experiments, the chamber methane hydrate, liquid phase, and sediment were separated. FISH analyses of the dissociated hydrate fluid indicate a significant presence of Archaea in or on the hydrate. The cell densities in the bioreactor medium liquid phase were 7.2 x 10^7 cells/cc, and with the methane hydrate, 2.8 x 10^8 cells/cc.

B51C-0977 0830h POSTER

Mineralogical Control on Microbial Diversity in a Weathered Granite?

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Mineral transformation reactions and the behaviour of metals in rock and soils are affected not only by physicochemical parameters but also by biological factors, particularly by microbial activity. Microbes inhabit a wide range of niches in surface and subsurface environments, with mineral-microbe interactions being generally poorly understood. The focus of this study is to elucidate the role of microbial activity in the weathering of common silicate minerals in granitic rocks. A site in the Wicklow Mountains (Ireland) has been identified that consists of an outcrop surface of Caledonian (ca. 400 million years old) pegmatitic granite from which large intact crystals of variably weathered muscovite, plagioclase, K-feldspar and quartz were sampled, together with whole-rock granite. Culture-based microbial approaches have been widely used to profile microbial communities, particularly from copiotrophic environments, but it is now well established that for oligotrophic environments such as those that would be expected on weathering faces, perhaps less

than 1% of microbial diversity can be profiled by cultural means. A number of culture-independent molecular based approaches have been developed to profile microbial diversity and community structure. These rely on successfully isolating environmental DNA from a given environment, followed by the use of the polymerase chain reaction (PCR) to amplify the typically small quantities of extracted DNA. Amplified DNA can then be analysed using cloning based approaches as well as community fingerprinting systems such as denaturing gradient gel electrophoresis (DGGE), terminal restriction fragment length polymorphism (TRFLP) and ribosomal intergenic spacer analysis (RISA). Community DNA was extracted and the intergenic spacer region (ITS) between small (16S) and large (23S) bacterial subunit rRNA genes was amplified. RISA fragments were then electrophoresed on a non-denaturing polyacrylamide gel. Banding patterns suggest that the bacterial population in whole rock, which contained approximately 30 separated bands (indicative of the number of bacterial ribotypes), is greater than muscovite (20), K-feldspar (15), and plagioclase feldspar (12) with quartz exhibiting the lowest number (6). These bands were excised from the gel for sequencing, allowing identification of the major populations. An automated approach was also used to assess similarity of bacterial communities present on each sample type, and this allowed for a statistical evaluation of bacterial diversity. Petrographic studies were carried out to assess mineral alteration effects. Scanning electron microscopy (SEM) was used to visualise in-situ bacterial cells.

B51C-0978 0830h POSTER

Volatile Reduced Sulfur Compounds: Detection and Quantification in a Stratified Freshwater Lake

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It is now generally recognized that volatile reduced sulfur compounds (VRSCs), including hydrogen sulfide (H2S), carbon disulfide (CS2), methyl sulfide (MS), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) are significant constituents for atmospheric sulfur. Therefore, they play an important role in large-scale sulfur cycling. To date these compounds have been thoroughly investigated and quantified in open oceans and coastal marine environments. Additionally the export of VRSCs from marine surface waters to the atmosphere may implicate these compounds in global climate regulation. While current literature focuses on the biogeochemistry of VRSCs in marine systems, a comprehensive understanding of the global biogeochemistry of VRSCs necessitates more rigorous studies in freshwater environments. We will present concentration profiles of VRSCs in Linsley Pond, a stratified freshwater lake in Branford, CT. We developed an extremely sensitive methods for VSRCS measurements that relies on a purge-trap system coupled to gas chromatography with a pulsed flame photometric detector (PFPD). Using this method, we sampled Linsley Pond weekly to bimonthly during the initial stages of stratification in the spring and during mixing in the fall. Influence of the oxidation/reduction potential in the aquatic environment on the distribution of VRSCs over the complete water column and possible sources of VRSCs were also investigated.

B51C-0979 0830h POSTER

Lipid Composition of Soil Profiles and Water-Soluble Colloids Collected Within the Atlantic Coastal Plain in South Carolina

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The Atlantic Coastal Plain physiographic unit of the eastern US represents a large land area ranging from Mississippi to New Jersey. Soils widely distributed in this physiographic unit are characterized by highly weathered, deep coarse textured vadose zones, located on mature landscapes. Furthermore, soil types common in the upper coastal plain (UCP) region have strong similarities to soils widely distributed in watersheds of the Amazon Basin. Thus, an understanding of the biogeochemical dynamics controlling carbon fluxes in these systems has significant implications for natural resource management of large land areas and for the potential to enhance C-sequestration in the terrestrial biosphere. We have examined the distributions of lipids in vertical profiles in upland soils within the UCP. Our results showed that biogenic hydrocarbons, fatty acids, and aliphatic alcohols decreased with increasing depth within the soil profiles. However, differences were observed within subgroups of the lipid classes. The concentration of unsaturated fatty acids decreased markedly in the subsoil horizons while cuticular fatty acids increased. This was especially pronounced when considered as a relative proportion of total lipids. The alcohol fraction was dominated by long-chain aliphatic alcohols of cuticular origin which also increased in relative proportion with depth. Additional studies of a selected profile showed that the lipid composition of the colloidal fraction extracted with water from the surface horizon closely resembled the lipid composition of the deeper soil horizon. These results are corroborated by mineralogical analysis of colloids associated with subsoils which suggest they are derived from the surface the horizons and suggest that the colloidal phase plays an important role in controlling the flux of these cuticular lipid components to the deep sandy, E horizon subsoils.

B51C-0980 0830h POSTER

Pyrite Framboids: A Possible Biosignature For the Study of Ancient Sediments

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Framboids are 0.5-100 μm-sized, raspberry-like, spheroidal accumulations of 10-10^9 microcrystallites. These structures are predominantly composed of pyrite (FeS_2), although other minerals such as greigite (Fe_3S_4), magnetite (Fe_3O_4), and limonite ($FeO{\cdot}OH{\cdot}nH_2O$) have also been identified. Modern framboids are present in a variety of natural environments (soils, sediments, microbial mats), and can also be produced artificially in the laboratory. Even though numerous cases of framboids have been cited from the geological record, little is known about their mechanisms of formation, and biogenicity. Understanding the effects of the conditions of formation upon framboid characteristics from modern environments (e.g. size distribution, microtexture, composition, and mineralogy) will allow us to better understand what pyrite framboids can tell us about sediments from the geological record. The purpose of this project was to determine whether pyrite framboids can be used as a biosignature within ancient sediments. Microbial mats rich in pyrite framboids were collected from the Buncar Springs in Mangalia aquifer (Romania). The pyrite framboid rich microbial mats are formed underground at the anaerobic water-gas (90-95% methane, 5-10% CO_2) interface. Neoproterozoic (750-600 Ma) manganese carbonate deposits containing fossilized pyrite framboids were collected from a mine near the city of Ming Lo, Hunan Province, China. Synthetic framboids were made in the laboratory by a modification of the protocol provided by Sweeney and Kaplan (1973). The morphology of framboids formed within modern microbial mats, within ancient sediments, and those synthesized abiotically in the laboratory were compared, and then correlated with their biogenicity. Images were obtained using environmental scanning electron microscopy and the microtextures were analyzed using shape-analysis tools providing information about the overall size distribution of framboids, number of microcrystallites per unit volume, and size distribution of microcrystallites. The results can be used to make inferences about the abiotic genetic conditions and on the origin of framboids from the geological record. Sweeney, R.E., and Kaplan, I.R. (1973). Pyrite Framboid Formation: Laboratory Synthesis and Marine Sediments. Economic Geology, 68, 618-634.

B51C-0981 0830h POSTER

Environmental Influences on Microbial Mat Community Structure and Mineralization.

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Microbial mats consist of complex microbial communities containing of thousands of phylotypes of microorganisms living in close proximity to one another. These communities frequently thrive at the interface between benthic sediment substrate and overlying water. The microbial community draws nutrients from the environment and releases metabolic waste products which may in turn; serve as substrates for other microbial groups, be exchanged with the bulk environment (sediment or water column), or precipitate into mineral phases. Gross environmental changes, such as nutrient availability, irradiance level, hydrodynamic flow regime, temperature or water chemistry can directly affect the balance between these processes, in turn affecting microbial community and mineral distribution. We will present a brief survey of visually observable community distribution responses in natural microbial mats to controlled shifts in ecosystem incubation conditions. A more detailed examination of significant population shifts in three important microbial mat groups; cyanobacteria, sulfate reducing bacteria and methanogens, using a combination of visualization and molecular methods, in response to manipulation of ambient environmental sulfate levels will be presented. Lowering of sulfate to levels inhibiting sulfate reduction yielded an increase in methane production (see B. Bebout et al., session U09), and resulted in production of a discrete mineralizing layer within the mat running below, but parallel to the mat surface. Multiple zone-axes electron diffraction patterns and energy-dispersive X-ray spectroscopy were used to unambiguously identify the phase as aragonite. Implications of this incipient mineral phase as a possible precursor to carbonate mineralization in a previously non-mineralizing microbial mat system will be discussed in the context of interacting effects of the sulfate water chemistry change on community composition and rate process changes within the mat.

B51C-0982 0830h POSTER

Distinct D/H Signatures From Miocene Sediment Water in Clarkia Fossil Bed, Northern Idaho: Implications for Preservation of Ancient Biomolecules

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Water saturated in the Clarkia Miocene lacustrine sediments (15-20 Million years old) at the St. Maries River Valley in northern Idaho holds critical information regarding preservation of exceptional leaf compressions, unaltered ancient biomolecules, and their isotopic signals. To further understand the nature of sediment water, we developed a method to extract these waters from sediments and to characterize their D/H compositions. During an one-year duration, sediment water was periodically obtained from the Horizon 2B and along a vertical profile at the P-33 site, and water

samples from nearby pond, creek, precipitation, a underground aquifer were also collected monthly for comparison. The hydrogen isotope compositions from sediment waters in Horizon 2B are distinct from other environmental waters in the following two ways: (1) They differ from pond, creek, and ground water by up to 36 per mil and from meteorological water by up to 72 per mil. (2) The hydrogen isotope ratios remain stable throughout the year with little fluctuation (within error range). The D/H ratios along the vertical section vary slightly by about 20 per mil. The hydrogen isotope values of sediment water offset D/H ratios determined from different lipid compounds derived from Clarkia sediments by 122-196 per mil. Although the precise age of the sediment water can not be determined, a source other than modern environmental water is highly likely. Further information regarding its mobility and resident time is critical to elucidate the role that these water molecules have played in degradation of abundant labile ancient biomolecules and their isotope signatures preserved in Clarkia fossils and sediments.

B51C-0983 0830h POSTER

Compound Specific Isotope Analysis of Fatty Acids in Southern African Aerosols

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This study, conducted as a part of the Southern African Regional Science Initiative (SAFARI 2000), applied compound specific isotope analysis to describe aerosols at source regions and rural locations. Stable carbon isotopic compositions of individual fatty acids were determined for aerosol samples collected at four sites throughout southern Africa. Mongu, Zambia and Skukuza, South Africa were chosen for their location within intense seasonal Miombo woodland savanna and bushveld savanna biomass burning source regions, respectively. Urban aerosols were collected at Johannesburg, South Africa and rural samples were collected at Sua Pan, Botswana. Fatty acid isotopic compositions varied temporally. Urban aerosols showed significant isotopic enrichment of selected short chain fatty acids ($C < 20$) compared to aerosols produced during biomass combustion. Sua Pan short chain fatty acid signatures were significantly different from the other non-urban sites, which suggests that sources other than biomass combustion products, such as organic eolian material, impact the Sua Pan aerosol profile. However, a high degree of correlation between Sua Pan and Skukuza long chain fatty acid $\delta^{13}C$ values confirm atmospheric linkages between the two areas and that isotopic signatures of combusted fatty acids are unaltered during atmospheric transport highlighting their potential for use as a conservative tracer.

B51D MCC: Level 2 Friday 0830h

Estimating Terrestrial Carbon, Water, and Energy Fluxes From Site to Region III Posters *(joint with A, H)*

Presiding: **J Styles,** Oregon State University**; M Arain,** McMaster University

B51D-0984 0830h POSTER

Advection and Thermotopographic Flows Near A Flux Tower: Coupled or Not?

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Ecosystem-atmosphere exchange of carbon, water, and heat is routinely measured at numerous sites around the world, using the eddy-covariance technique. However, recent research has questioned the interpretation of some of these measurements, particularly at night and in areas of complex terrain. Much of this research has focused on horizontal and vertical advection, resulting from thermotopographically driven horizontal flow divergence (drainage flows). This paper examines horizontal and vertical flow patterns above and below the forest canopy at the Morgan-Monroe State Forest (MMSF) AmeriFlux site in south central Indiana. Mean vertical motions above canopy were investigated using data from a 46 m ridge-top tower. We found a tendency toward downward vertical velocities at night relative to the daytime. Some evidence suggests that this vertical convergence is driven by nocturnal thermotopographic flows. To examine sub-canopy flow through a small gully located near the main tower, a small (8 m) mast was installed. Flow direction in the gully was generally well correlated with the along-gully component of the above-canopy wind, indicating dynamic coupling. However, there were periods when wind in the gully was decoupled from flow aloft and was consistent with thermotopographic flow. Details of thermotopographic flows, in both the leaf-off and vegetative seasons, will be discussed; these include temporal patterns, relationships to likely drivers such as radiation and temperature gradients, and relationships with above canopy vertical velocities. It was found that the three-dimensional flow structure at MMSF is more complex than in non-forested terrain, particularly during the vegetative season. This research supports arguments that the inclusion of simple advection terms in calculations of NEE, based on above-canopy measurements, is not generally applicable. The results suggest a need for further investigation into the flow patterns at MMSF and at other forests in complex terrain. Furthermore, additional study of thermotopographic flows in forested terrain is needed.

B51D-0985 0830h POSTER

Observing Subcanopy CO_2 Advection

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Underestimation of nocturnal CO_2 respiration under calm conditions remains an unsolved problem at many forest flux stations. In this paper, the hypothesis is tested that horizontal mean transport of CO_2, not previously measured, may account for the missing CO_2. A systematic methodology was developed that comprises characterizing the subcanopy motions, determining the appropriate size of the subcanopy network required to make the measurements, developing a method of integrating the measurements in the vertical, and determining the required averaging time. Measurements were performed at the Harvard Forest (Petersham, MA), over 4 years. Subcanopy flows were decoupled from the flows aloft 75% of the time. While stress divergence contributed 38% of the daytime forcing of subcanopy flows, negative buoyancy dominated nocturnal forcing 58% of the time, generating drainage flows 51% of the time. The drainage flow direction was dictated by the length of the slope, not its angle. Pressure gradient forcing across the lee side of the hills was predicted to be significant, but the simple flow reversals expected were not observed. The appropriate horizontal size of the network of wind and CO_2 sensors was shown to be on the order of 100 m, ensuring that sensors were generally observing coherent processes on this scale or larger and thus displaying some correlation. Horizontal transport of CO_2 at Harvard Forest was found to be restricted to the bottom 10 m of the forest. The fraction of the negative buoyancy force in the sum of dynamic driving forces described nights with missing flux problems ("deficit nights") significantly better than the commonly used friction velocity criterion. Including the measured horizontal transport terms did not on average fully account for the observed difference in NEE of 1.2 ± 0.3 μmoles $m^{-2}s^{-1}$ between deficit and non-deficit nights, but decreased the difference to 0.7 ± 0.5 μmoles $m^{-2}s^{-1}$.

B51D-0986 0830h POSTER

Large Uncertainties in Estimating Grassland Carbon Fluxes: Can Net Ecosystem Production Be Inferred?

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Despite interest in estimating ecosystem carbon budgets based on easily collected field data, no previous study to our knowledge has compared various methods of estimating total above- and belowground net primary production (NPP) and net ecosystem production (NEP, the annual carbon accumulated by an ecosystem) from commonly measured biomass and soil surface CO_2 flux data in grasslands. Here we used field data from two grassland restorations and a row-crop agriculture treatment enrolled in the Conservation Reserve Program as a model for an analysis of methodological uncertainty in estimating ecosystem carbon budgets over a short time period. The goal of this study was to investigate how a range of methods for estimating NPP and NEP suggested in the literature might be used to predict ecosystem carbon budgets based on short-term field measurements. We conclude that it is extremely difficult to close the carbon budget of a temperate grassland using flux-based methods that account for plant-derived carbon inputs and soil surface CO_2 losses. Current uncertainties in (1) estimating aboveground NPP, (2) determining belowground NPP, and (3) splitting soil respiration into heterotrophic and autotrophic components strongly affect the magnitude, and even the sign, of NEP. A comparison of these estimates, across a treatment of different plant species mixes and land management, cannot reliably distinguish differences in NEP, nor the absolute sign of the overall carbon budget. These uncertainties likely exist in all grassland carbon budget studies using this approach, so conclusions about whether these systems are truly carbon sinks, or how they should be managed to sequester carbon, must be made with extreme care. Longer-term stocks methods, periodically linked to flux-based measurements of individual processes, may be the only way to close the carbon budget in these systems with any reasonable degree of certainty at the present time.

B51D-0987 0830h POSTER

A global relationship between hetero-/autotrophic respiration and total soil surface CO_2 flux?

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Soil surface CO_2 flux (R_S) is overwhelmingly the product of respiration by roots (autotrophic respiration, R_A) and soil organisms (heterotrophic respiration, R_H), two source fluxes with different carbon sources and temperature dynamics. Many studies have attempted to partition R_S into these two components, with highly variable results. An analysis of all published data reporting annual R_S and the R_A/R_H partitioning, encompassing 54 primarily forested sites, suggests that the heterotrophic and autotrophic source fluxes are each strongly ($R^2 > 0.8$) related to total annual CO_2 flux across a wide range of ecosystems. Study biome, measurement method, mean annual temperature, and leaf habit had no significant effect on these relationships. Because belowground measurements are difficult to perform but measuring annual R_S is straightforward and common, these relationships may provide a useful method with which to estimate the heterotrophic and autotrophic contributions to soil surface CO_2 flux for undisturbed terrestrial ecosystems.

B51D-0988 0830h POSTER

The Joint Influences of Climate, Litter Quality, and Soil Fauna in Regulating above- and Belowground Decomposition: a Pan-Tropical Study

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I report on the results of a collaborative study investigating the joint influences of climate, litter quality, and soil fauna in regulating above- and belowground decomposition in tropical forest ecosystems. We have assembled a network of 15 collaborators working in 22 tropical forests including sites in Hawaii, Central America, South America, India, Madagascar and Papua New Guinea. In general, most lowland tropical forests experience continually warm climates but vary greatly in the amount and seasonal distribution of precipitation. We predicted that tropical dry and wet forests differ in the degree to which decomposition processes are controlled by soil fauna and litter quality. We developed a standardized litter bag protocol that is being implemented by each collaborator at his or her field site. Preliminary results suggest that litter quality,