at least one week. The equilibrated solutions were then filtered and analyzed for concentrations of YREE and Ba (ICP-MS), chloride and sulfate (ion chromatography), and pH (glass electrode). A simple model was used to determine the stability constants from these measurements.
Averaged results from four experiments, two with and two without added sulfate, have standard deviations of 0.03 log units or less. Within this precision, the pattern of stability constants is not flat, as has been assumed, but has a very distinct shape. The pattern is nearly flat from La to Gd, possibly with a slight maximum at Eu. From Gd to Lu it shows a gradual and almost linear decrease, with the stability constant of Lu being more than 0.2 log units below that of La. The stability constant of Y is close to that of Er. Our pattern is in broad agreement with several careful earlier studies that have been largely ignored in the recent literature. Comparison with the substantial body of existing work also indicates that our stability constants are well within the published range for individual YREE. This revised pattern may have significant consequences for the interpretation of YREE patterns in high-sulfate environments such as runoff from mine tailings and certain groundwaters.

B72B-0771 1330h POSTER

Surface Complexation Modelling in Metal-Mineral-Bacteria Systems

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The reactive surfaces of bacteria and minerals can determine the fate, transport, and bioavailability of aqueous heavy metal cations. Geochemical models are instrumental in accurately accounting for the partitioning of the metals between mineral surfaces and bacteria cell walls. Previous research has shown that surface complexation modelling (SCM) is accurate in two-component systems (metal:mineral and metal:bacteria); however, the ability of SCMs to account for metal distribution in mixed metal-mineral-bacteria systems has not been tested. In this study, we measure aqueous Cd distributions in water-bacteria-mineral systems, and compare these observations with predicted distributions based on a surface complexation modelling approach.

We measured Cd adsorption in 2- and 3-component batch adsorption experiments. In the 2-component experiments, we measured the extent of adsorption of 10 ppm aqueous Cd onto either a bacterial or hydrous ferric oxide sorbent. The metal:bacteria experiments contained 1 g/L (wet wt.) of B. subtilis, and were conducted as a function of pH; the metal:mineral experiments were conducted as a function of both pH and HFO content. Two types of 3-component Cd adsorption experiments were also conducted in which both mineral powder and bacteria were present as sorbents: 1) one in which the HFO was physically but not chemically isolated from the system using sealed dialysis tubing, and 2) others where the HFO, Cd and B. subtilis were all in physical contact. The dialysis tubing approach enabled the direct determination of the concentration of Cd on each sorbing surface, after separation and acidification of each sorbent.

The experiments indicate that both bacteria and mineral surfaces can dominate adsorption in the system, depending on pH and bacteria:mineral ratio. The stability constants, determined using the data from the 2-component systems, along with those for other surface and aqueous species in the systems, were used with FITEQL to independently predict the amount of adsorption and the partitioning of the Cd in the bacteria-metal-mineral systems. Results from these comparisons suggest that surface complexation modelling is a viable resource for predicting metal partitioning in multi-sorbent geologic systems.

B72B-0772 1330h POSTER

Reaction Kinetics of Alanine Solutions at Elevated Temperatures

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The reaction kinetics of α-alanine under non-enzymatic, aqueous hydrothermal conditions has been the subject of few experimental studies. Varying conclusions on the alanine system have been reached, with some observing breakdown by pathways such as decarboxylation, and others observing polymerization and cyclization reactions (e.g. Abelson et al.(1957), Berhardt et al.(1984), Kawamura et al.(2001), Li et al.(2002), Vallentyne et al.(1964)). We have been able to observe the reaction kinetics of alanine **in situ** at temperature and pressure with a special gold-lined spectrophotometric cell which is also itself the reaction vessel. The identities of the reaction products were further confirmed using ion chromatography (Dionex AminoPAC). A postulated reaction scheme involving reversible polymerization and irreversible breakdown pathways will be presented and its dependence on temperature and other factors will be discussed, with an aim to reconciling conflicting data in the literature. Rate constants for this scheme, derived mathematically from the experimental data using a factor analysis-based method, will be presented up to 185 °C and 20 bar.

URL: http://www.geochem.ethz.ch

B72B-0773 1330h POSTER

Laboratory, Field, and Modeling Studies of Aerobic Cometabolism of CAHs by Butane-Utilizing Microorganisms

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The ability of butane-utilizing microorganisms to aerobically cometabolize a mixture of chlorinated aliphatic hydrocarbons (CAHs) in laboratory microcosms and in an in-situ field demonstration was modeled using parameter values measured in laboratory experiments. The butane grown culture was inoculated into soil and groundwater microcosms and exposed to butane with several repeated additions of 1,1,1-trichloroethane (TCA), 1,1-dichloroethylene (1,1-DCE), and 1,1-dichloroethane (1,1-DCA) at aqueous concentrations of 200 μg/L, 100 μg/L, and 200 μg/L, respectively. The utilization of butane and the transformation of the CAH mixture in the batch microcosms were simulated using differential equations accounting for Michaelis-Menten kinetics with cell growth and decay, substrate utilization, transformation product toxicity, and substrate inhibition of CAH transformation. Both competitive inhibition kinetics and mixed inhibition kinetics, determined in prior laboratory studies, were included in the model construct. The equations were solved simultaneously using fourth-order Runge-Kutta numerical integration. The batch microcosm experimental results were simulated well with parameter values determined independently in culture kinetic studies, with some minor adjustments. Having adequately defined the parameter values from laboratory studies, the biotransformation model was combined with 1-D advective-dispersive transport to simulate the results of in-situ bioremediation tests conducted at the Moffett Field Test Facility in CA. The butane-utilizing culture was injected into a 7 m subsurface test site and exposed to alternating pulses of oxygen and butane, along with TCA (150 μg/L), 1,1-DCE (50 μg/L) and 1,1-DCA (150 μg/L). The model simulated well the transient transformation of the CAHs in response to different butane and oxygen pulse cycles and injection concentrations. Model simulations correlated well with field results and indicated that better remediation performance was achieved when more butane and oxygen were injected in the field test plot with short pulse cycles. 1,1-DCE was the most effectively transformed, followed by 1,1-DCA, and TCA, consistent with model predictions. The model simulations also indicated that as time proceeded, indigenous microorganisms were likely responsible for the effective transformation of 1,1-DCE and limited transformation of 1,1-DCA and TCA. This was consistent with PCR based molecular analysis of the microbial population that was stimulated.

B72C MCC: 132 Sunday 1330h

Water, Energy, and Carbon Exchange in Forest Systems II *(joint with A, H, GC)*

Presiding: **B Law,** Oregon State University**; P Thornton,** National Center for Atmospheric Research**; D Baldocchi,** University of California, Berkeley

B72C-01 1330h INVITED

Controls on the seasonal cycle of NEE: Inferring temperature dependence of photosynthesis in evergreen needleleaf forests using eddy covariance data

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An earlier study showed that simulations of coupled energy, water, carbon, and nitrogen cycles across a broad climate gradient in evergreen needleleaf forests were able to capture between-site variability in leaf area and annual and seasonal variability in evapotranspiration within and across sites, but that the simulated seasonal cycle of net ecosystem exchange of carbon (NEE) compared poorly to observations. In this study we show that this model bias is associated with the choice of Rubisco enzyme kinetic parameters. Optimization to minimize the model bias in seasonal cycle of NEE at each site results in a range of kinetic parameters across the climate gradient. We present results relating the optimized parameters to site climate. We also demonstrate the influence of model bias in the seasonal cycle of NEE on model estimates of NEE at annual and longer time scales.

B72C-02 1345h

A New Model for Scaling from Leaf Lifespan to Conifer Forest Structure and Function

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Generic relationships between the lifespan, physiology and biochemistry of leaves have recently been quantified for the first time in contrasting biomes and functional groups. These relationships have important consequences for ecosystem biogeochemical cycles, and therefore offer the potential for simulating large-scale forest properties on the basis of leaf lifespan. We have used the scaling mechanisms involved to develop the University of Sheffield Conifer Model (USCM), a tool for simulating conifer carbon, nitrogen, and water fluxes using data on leaf lifespan, climate and soils as inputs. Simulations of net primary production and partitioning, leaf area index, evapotranspiration, nitrogen uptake and land surface energy partitioning show close agreement with observations from sites across a wide climatic gradient. This indicates the generic utility of our model for modern forests, and adequate representation of the key processes involved in forest function. The new development of a technique for estimating leaf lifespan from the anatomical properties of fossil woods provides a secure basis for extrapolating model simulations to conifer forests of the geological past. Future simulations with our model will therefore examine conifer forest feedbacks on paleoclimate during warm intervals in the Mesozoic and early Tertiary.

B72C-03 1400h

Large Eddy Simulation of Coupled Water and Carbon Exchange and Transport Through and Above Forest Canopies

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There are outstanding questions surrounding the measurement and modeling of carbon and water fluxes over complex landscapes. Typically, forest fluxes are measured with the eddy covariance technique from a single tower. A unique study over a loblolly pine stand in the Duke Forest yielded high frequency velocity, temperature, water vapor and carbon dioxide fluxes from a network of six instrumented towers, simultaneously. In this talk we explore the canopy-atmosphere dynamics active during this experiment through the use of a Large Eddy Simulation (LES) code. The LES includes a numerical representation of the plant canopy structure, a biophysical process sub-model, and mixes the sources and sinks through the boundary layer with a filtered form of the Navier-Stokes equations. Through this combination of a spatially distributed dataset and a 3D model of canopy flows and processes we investigate the relative influences of canopy structure and meteorological forcing on observed and modeled fluxes. This work has implications for our understanding of the effects of canopy turbulence on eddy covariance flux measurements.

B72C-04 1415h INVITED

Two-Dimensional Airflow within Canopies on Hilly Terrain: Implications for Flux Monitoring, Inverse Models, and Data Assimilation

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Topography influences almost all aspects of forest-atmosphere carbon exchange, yet only a limited number of studies have investigated the role of topography on the structure of turbulence within vegetation and its ultimate effect on photosynthesis and turbulent fluxes. Here, we limit our attention to the interplay between radiative transfer, flow dynamics, and ecophysiological controls on CO2 sources and sinks within a canopy situated on an idealized two-dimensional sinusoidal ridge. In particular, we address how topography alters the forest-atmosphere CO2 exchange rate when compared to uniform flat terrain. Towards this end, a first order closure model that accounts for the flow dynamics, radiative transfer, and the nonlinear ecophysiology within the canopy volume is proposed. The model shows that the horizontally averaged and vertically integrated photosynthesis departs from its flat terrain value by a factor comparable in magnitude to the mean hill-slope. In contrast, as we traverse the hill, Fc, the surface-normal eddy flux of CO2 above the canopy, departs from its flat terrain counterpart by factors as large as 3 while its horizontally averaged value differs from that on flat terrain by 100%. The difference between Fc and the integrated biological sources and sinks (Sc) is supplied by horizontal and vertical advection terms that are individually much larger than the Sc we wish to measure. By demonstrating that the variations in advection and Fc across the hill are relatively independent of the source-sink distribution of CO2 in the canopy, we show that we can correct systematically for advection using standard techniques of data assimilation and inverse modelling.

B72C-05 1430h

Using Flux Measurements Over Forests to Improve Climate Predictions by the GISS GCM

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A physiologically-based canopy photosynthesis and stomatal conductance model is described and included in the Goddard Institute for Space Studies (GISS) GCM modelE land surface scheme. The model is parameterized and tested using energy, moisture, and carbon flux data collected using the eddy covariance technique over conifer, deciduous broadleaf, and evergreen tropical forest types. Canopy conductance is assumed to depend on canopy photosynthesis, vapor pressure deficit (vpd), and soil moisture. Photosynthesis is predicted from leaf biochemistry. Predicted transpiration and photosynthesis are particularly sensitive to the amount of photosynthetic machinery and the assumed dependence of the leaf surface carbon dioxide gradient on vpd and soil moisture - parameterizations specified directly from the observations.

Predicted climate is significantly improved compared to previous simulations with the GCM, especially surface temperature and precipitation over the Amazon region, south-eastern United States, and the Sahel. Mean seasonal temperatures are improved by over 2 degree C and precipitation by 50 per cent in some regions. Soil moisture is greatly increased in many regions where it was previously too low - especially the Americas, southern and eastern Africa, the Sahel, and central Eurasia. The response of canopy conductance to vpd plays a major role in these improvements. Land surface annual gross primary productivity, the driver of the biotic terrestrial carbon cycle, is predicted to vary 76-84 Gt[C] between years, about two thirds the mean annual value inferred from observations. This difference is due to remaining problems with precipitation over South America, Africa, and southern Asia.

B72C-06 1445h

Is the size of the Carbon Sink caused by "Woody Encroachment" of U.S. Grasslands overestimated? One DGVM calculates an answer.

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The DGVM MC1 includes a modified version of the biogeochemistry model CENTURY that simulates soil processes and also simulates wild fires occurrence and effects. MC1 simulated all the locations in the conterminous U.S. that had switched from a period of dominance by grasses (at least 30 years) to a period of dominance by woody vegetation during the historical period (1895-1993) using VEMAP transient climate as input. The model simulated the size of the carbon pools in live plant biomass and in the soil under the different vegetation types. Simulations show decreased soil organic carbon with increased vegetation biomass as woody vegetation replaces grass vegetation. At high precipitation sites, the decrease in soil carbon associated with the conversion to woody vegetation is greater than at low precipitation sites, agreeing with Jackson et al. (2002). The negative relationship between annual average precipitation and simulated changes in soil carbon mimics that found by Jackson et al. (2002). Biomass consumed by wildfires during the grassland phase was compared to that consumed during the shrubland phase. Even though there was an increase in aboveground carbon associated with the conversion to woody vegetation, total biomass consumed by wildfires was 35 percent lower during the shrubland phase. In conclusion, potential carbon storage in live plant biomass increases when shrublands invade the grasslands as trees can store more carbon and are less likely to be consumed by wildfires. However the soil carbon sequestration potential decreases in those sites. In our study, MC1 simulates a decrease in total system carbon storage as the decrease in soil carbon exceeds the increase in vegetation carbon when woody vegetation invade the grasslands.

B72D MCC: 132 Sunday 1520h

Interactions of Permafrost With Climatic, Hydrologic, and Ecosystems Processes I *(joint with C, H, GC)*

Presiding: **W C Oechel,** San Diego State University**; J Brown,** U.S. Permafrost Association

B72D-01 1520h INVITED

Impacts of Changing Permafrost Extent on Vegetation Transitions on the Seward Peninsula, Alaska

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Permafrost is an important control over the distribution of major vegetation types in the low arctic, and temporal changes in permafrost extent may thus be tightly coupled to changes in plant community distribution. For example, spruce trees have become more widespread during the 20th century on the Seward Peninsula, but in permafrost-affected areas with low topographic relief spruce have invaded tundra only where permafrost has thawed. Two hypotheses may explain the apparent dependence of treeline advance on permafrost. First, increased soil temperature associated with thawing permafrost may enhance spruce success. Second, degradation of permafrost may increase soil drainage in areas with low topographic relief, and thus create more favorable conditions for spruce. We investigated these hypotheses at a thaw pond complex on the Seward Peninsula, comparing the relationships between soil properties (thaw depth, surface and subsurface soil moisture) and woody plant communities in three sites: within the partially drained basin of the thaw pond, along the thaw pond banks and on the flat tundra surface surrounding the thaw pond.

White spruce (*Picea glauca*) occurred primarily on or within 10 m of the top of pond banks. Spruce have established there continuously since at least 1820, and are present in groves with densities > 1500 trees/ha. Since 1960, spruce have successfully established at lower densities (1,000 trees/ha) in tundra sites within 10 m of the top of the banks. We found no spruce > 20 m from the banks. Live spruce occur within the pond basin only on palsas, but several dead spruce were found in the basin itself. Shrub community structure also varied significantly among sites. Two relatively large-stature shrubs,*Betula nana* and *Salix* sp., were more abundant on banks than in other sites, and the height of the shrub canopy was > 50% greater on banks than in other sites. Late summer thaw depth did not differ significantly among the three site types, but soil moisture was highest in the pond basin, intermediate on the tundra sites, and lowest on the banks. These data thus confirm previous findings that in tundra areas with low topographic relief spruce establishment occurs only in close proximity with thawing permafrost, and suggest that improved soil drainage is the most likely explanation for that relationship.

Permafrost melting may therefore promote the growth and establishment of spruce in certain tundra landscapes by providing new, well-drained microhabitats in which trees are able to establish in relatively high densities. Changes in microtopography that accompany permafrost degradation may thus lead to an expansion of forest-tundra and tall shrub-tundra vegetation into areas currently occupied by low shrub tundra or tussock tundra. Conversely, forest-tundra vegetation may be unlikely to establish in this type of landscape in the absence of permafrost degradation. This potential dependence of vegetation change on permafrost melting in areas with low topographic relief may cause vegetation in these areas to show a nonlinear response to climate warming, and thus has important implications for our understanding of likely trajectories of vegetation change in the low arctic.

B72D-02 1540h

Vegetation-Soil-Active Layer Relationships Along a Low-Arctic Bioclimate Gradient, Alaska

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Northern Alaska has three of five Arctic bioclimate subzones, which are representative of the circumpolar Low Arctic. This portion of the Arctic has more or less continuous tundra plant cover and well-developed moss canopies. We examined the biomass and remotely sensed spectral properties of the vegetation canopy, active-layer thickness, and the soil properties at 21 sites on the Arctic Slope and Seward Peninsula of Alaska. The sites were grouped into three bioclimate subzones according the summer warmth at the sites. The summer warmth index (SWI) is the sum of