tracer, bromide, into an anoxic zone directly below a former sewage-effluent disposal bed where Fe and sulfide concentrations were below detection and the DO was less than 5 uM. An injection with negligible ammonium, a nitrate concentration of 22 uM, and DO of approximately 260 uM was maintained at approximately 15 L/hr for a period of 75 days. An array of multi-level samplers (MLS), placed at distances ranging from 1 to 7 m down-gradient from the injection well, was sampled prior to and throughout the 75-day injection, and during a 25-day period after the injection. Water samples from the MLS were analyzed for DO and a variety of aqueous constituents. The DO decreased from approximately 260 uM to 210 uM over 7 m of transport, indicating the presence of rate-limited oxygen consumption. An increase in nitrate from 22 to approximately 36 uM indicated the presence of rate-limited ammonium oxidation. However, this ammonium oxidation was not sufficient to account for all of the DO consumption. Further characterization of these processes was accomplished by use of PHREEQC, a one-dimensional, geochemical reactive transport model. The 1D model is based on an ion association model for aqueous speciation. Surface complexation reactions were used to define the speciation for surface-complexed species, including ammonium and major cations. Kinetic reactions were defined for oxidation of ammonium and aerobic respiration of sorbed organic carbon. The initial chemical condition was specified as an equilibrium between a background solution, determined by using field data, and the surface sites, while flow was specified with constant flux boundary conditions on the basis of a steady-state injection. The model was calibrated by adjusting equilibrium constants and matching simulations to breakthrough curves observed in the tracer test at several distances downstream of the injection along the plume centerline. Modeling of breakthrough curves at different MLS ports suggested that aquifer heterogeneity and variability in the injection affected the geochemical reactions to some extent. Model simulations indicated that consideration of both aerobic respiration and ammonium oxidation was necessary to account for the observed oxygen consumption. This result, which was consistent with bacteria and dissolved carbon data, demonstrates that aerobic respiration and ammonium oxidation are important processes to consider when modeling the aerobic restoration of anaerobic, sewage-contaminated aquifers.

B31F-06 1135h INVITED

Multi-Component Reactive Transport Modeling of Field-Scale Bioremediation: The Schoolcraft Site

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This paper describes three-dimensional multi-component reactive transport modeling for bioremediation of a carbon tetrachloride (CT) contaminated plume at the Schoolcraft site in Western Michigan. The denitrifying bacterium Pseudomonas Stutzeri Strain KC is used to mediate cometabolic reactions that degrade CT to harmless end products. CT contamination at this site occurred due its use in the past as a fumigant in grain silos. The goal of the field bioremediation design was to inoculate a transect perpendicular to the natural gradient flow of a CT plume with microbes that could effectively remediate the CT contamination through a series of pulsed nutrient injections. The final design consisted of fifteen wells spaced one meter apart in which each well can operate either as an injection or an extraction well depending on the event. This design allowed us to operate in a semi-passive mode of operation with only 6 hours of pumping per week. Our modeling approach integrates information from laboratory-scale studies aimed at understanding the relevant rates and processes under controlled conditions with plume-scale modeling in the presence of a high degree of hydraulic control and significant heterogeneity to delineate the important differences in processes/rates as we proceed from the laboratory to the field. We describe the development of a seven component reactive transport model that includes the transport of aqueous and sorbed-phase CT, mobile and immobile bacteria, acetate (electron donor), nitrate (electron acceptor) and tracer (bromide) and show detailed comparisons of observed and simulated concentrations at a number of wells and at different depths. Processes simulated in the model include advection, dispersion, degradation, two-site sorption, microbial attachment, detachment, growth and decay. We describe the influence of several modeling decisions (e.g., effects of dynamic partitioning, bioavailability and sorption) on the predictions of the model. Most parameters in the reactive transport model were fixed based on earlier laboratory experiments and literature values and only a few parameters were changed due to the likelihood of differences between the laboratory and field. The computational model used a non-uniform grid with very fine cells placed around the delivery well gallery to better resolve the gradients. We present the spatial-temporal evolution of the degradation front and the microbial concentration fields and demonstrate how high-resolution numerical models can be used to aid our understanding of complicated field-scale processes.

B31F-07 1150h

Modeling Biogeochemical Reactive Transport in Fractured Granites: Implications for the Performance of a Deep Geological Repository

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Several countries around the world are considering deep repositories in fractured granitic formations for the final disposal of high-level radioactive waste. Evaluating the long term safety of such repositories requires sound conceptual and numerical models which are being developed from data and knowledge gained from in situ experiments carried out at deep underground laboratories such as that of spö in Sweden. One of the key aspects for performance assessment concerns to groundwater redox conditions because: (a) the presence of oxygen will affect to the corrosion of canisters, (b) possible production of hydrogen sulphide from sulphate reduction will also have a negative effect on these metallic containers, and (c) several long-lived radionuclides are much more soluble and mobile under oxidizing conditions. Several projects have been performed at spö to investigate different aspects of the groundwater redox evolution. The vast amount of in situ-generated information has been used in this work to set up coupled hydrobiogeochemical models. Numerical models account for saturated groundwater flow, solute transport by advection, dispersion and molecular diffusion, geochemical reactions involving both the liquid and solid phases, and microbially-catallyzed processes. For the spö site, modelling results provide quantitative support for the following conclusions. (A) At the operational phase of the repository, shallow fresh groundwater could reach the depth of the underground facility. Shallow groundwaters loose dissolved oxygen during the infiltration through soil layers and then, respiration of dissolved organic matter is induced along the flow paths through the reduction of Fe(III)-bearing minerals of the fracture zones. Microbial anaerobic respiration of DOC provides additional reducing capacity at the depth of the tunnel. (B) After repository closure, atmospheric oxygen will remain trapped within the tunnel. Abiotic consumption of this oxygen has been computed to occur in a period of about 1,000 years as a result of diffusion-reaction processes. Coupled biogeochemical mechanisms, such as respiration of dissolved organic matter and aerobic methane oxidation, accelerate the oxygen uptake to less than a month.

B31F-08 1205h

Rare Earth Element - Humic Acid Interaction: Experimental Evidence for Kinetic and Equilibrium Fractionation in Aqueous Systems.

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Dissolved organic matter (DOM) is well known for it's strong binding capacity for trace metals. In order to better predict the role of DOM in the speciation and transport of trace metals in the environment we coupled capillary electrophoresis (CE), a molecular separation technique, to a Sector Field Inductively Coupled Plasma Mass Spectrometer (SF-ICP-MS). The combination of these two techniques allows for the study of non-labile metal speciation in aquatic samples. By separating Rare Earth Element (REE) complexes with EDTA and Humic Acid's (i.e. ligand competition) we have been able to determine conditional equilibrium binding constants (Kc) and kinetic rate constants for all 14 REE's with Humic (HA) and Fulvic Acids (FA) as a function of pH (6-9) and ionic strength (IS, 0.01-0.1 mol/L). Assuming a 1:1 binding mechanism, logKc values for REE-FA varied from 9.0 (La) to 10.5 (Lu) at pH 6, 0.1 mol/L IS, and 11.7 (La) to 14.6 (Lu) at pH 9, 0.1 mol/L IS. LogKc values for REE-HA were 10.6 (La) to 12.2 (Lu) at pH 6, 0.1 mol/L IS and 13.2 (La) to 16.5 (Lu) at pH 9, 0.1 mol/L IS. Slightly higher values for Kc were obtained at 0.01 mol/L IS. The general observations of stronger REE-HA binding compared to REE-FA, and stronger binding with increasing pH and decreasing IS correlate with our current understanding of metal-DOM interactions (1). Both Kc's as well as kinetic rate constants increase with increasing REE mass number (decreasing ionic radius); a reflection of the well-known lanthanide contraction. This is the first comprehensive metal binding dataset between REE and DOM, and the first experimental evidence for differential equilibrium and kinetic binding behavior between REE's and DOM. The 30-1000 fold increase in binding strength of heavy REE's with DOM provides for a an equilibrium fractionation mechanism that may explain features of the global geochemical REE cycle such as fractionation related to weathering, estuarine mixing, and REE scavenging in the deep ocean (2). The experimental dataset has also been interpreted with the Non-Ideal Competitive Adsorption - Donnan (NICA-Donnan (1)) model for HA and FA metal binding, such that REE-HA binding can be predicted as a function of pH and IS. The NICA-Donnan model is a standard object in the novel object oriented chemical speciation code ORCHESTRA (Objects Representing Chemical Speciation and Transport (3)) that we used to explore the possible effects of pH and IS on fractionating the REE's along an estuarine gradient.

(1) Milne, C. J.; Kinniburgh, D. G.; Van Riemsdijk, W. H.; Tipping, E. Environmental Science & Technology 2003, 37, 958-971. (2) Elderfield, H.; Upstillgoddard, R.; Sholkovitz, E. R. Geochimica Et Cosmochimica Acta 1990, 54, 971-991. (3) Meeussen, J. C. L. Environmental Science & Technology 2003, 37, 1175-1182.

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B31G MCC: 3014 Wednesday 1020h

Ecosystem Interactions with Land-use Change II *(joint with H)*

Presiding: **G P Asner,** Carnegie Institution**; R DeFries,** University of Maryland

B31G-01 1020h INVITED

The Conservation Value of Human-Dominated Countryside

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The future of biodiversity and the benefits it supplies society depend largely on the conservation value of human-dominated 'countryside,' the growing fraction of Earth's unbuilt land surface whose ecosystem qualities are strongly influenced by humanity. I will report on the conservation value of tropical countryside for a variety of groups of organisms and ecosystem services. The work is based on species distributions and dynamics; remote sensing, radio telemetry, and GIS; and assessments of the ecosystem functions performed by diverse organisms. While conservation value appears high today in regions under low- and intermediate land-use intensity, the window of opportunity for securing this value is closing rapidly with on-going intensification of land use.

B31G-02 1040h

On the Impact of Historical Land-use Changes on the Summer Climate of a Swiss Region

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In the second half of the 19th century a major civil engineering project was initiated to adjust the lake and river system in the three-lakes region on the Swiss Plateau. The landscape was dramatically modified: the frequently inundated plains were drained and replaced by nowadays intensively used agricultural land. In this study, the impact of these historical (150 years) land-use changes on the climate of a summer month are investigated. The mesoscale dynamical Local Model of the German Weather Service is used with a very high horizontal resolution of 1.5×1.5 km^2, nested in a coarser grid of 7×7 km^2. In order to evaluate the influence of the land-use changes on the mesoscale climate, the same atmospheric data were used for initial and boundary conditions for all one-month long simulations with historical (circa 1850) and present (1997) conditions. For an initial assessment, a case study was conducted over three clear-sky summer days in July 1998 where detailed meteorological data are available. It could be shown that in the area of land-use changes the daily average temperature was 0.25°C cooler for the present land-use conditions. During the day, heterogeneous changes in temperature were observed depending on the type of land-use conversion. In areas where afforestation has taken place, an average warming of more than 1.0°C could be observed. In contrast, deforestation resulted in a cooling of up to 2.0°C. During the night, the average temperature was up to 0.6°C cooler for the present land-use conditions. Due to topographical effects, the nighttime cooling is mainly restricted to low-lying areas on the formerly frequently inundated plains. The diurnal temperature range in the area of land-use changes increased by 0.1–0.3°C. With additional sensitivity experiments, it could be shown that the daytime temperature decrease caused by morphological changes dominated the temperature increase due to changed physiological properties.

B31G-03 1055h

The History of Land-Use Change in the South Florida Ecosystem: Paleoecologic Data as a Guide for Restoration

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The south Florida ecosystem has undergone profound changes during the last century as a result of urbanization, agricultural development, and the construction of a massive water control system - the Central and Southern Florida (C&SF) Project. Created in 1948, the C&SF Project was designed for flood protection and to provide water for people and agricultural development. The extensive network of canals, levees, and water-control structures cover over 18,000 square miles and have completely altered the natural sheet flow of water across the land. Water was, and is, the principal driving force of this unique subtropical ecosystem, a significant portion of which is public land, including Everglades National Park, Biscayne National Park, Big Cypress National Preserve, the Florida Keys National Marine Sanctuary, Dry Tortugas National Park, and six National Wildlife Refuge Complexes. The Comprehensive Everglades Restoration Plan (CERP) has been designed in an effort to restore more natural water delivery to the ecosystem. This plan will cost over 8 billion dollars and take more than 30 years to complete. To successfully implement the CERP, land managers and restoration planners need answers to questions such as what are our restoration targets? What conditions are we restoring the system to? What portion of the changes seen in the 20th century can be attributed to land-use changes and what portion to natural change? What are the impacts on living resources? Paleoecologic and biochemical research is providing the answers to these questions. Analyses of cores from Florida Bay and Biscayne Bay have highlighted the following important findings. (1) Although land-use changes have played a role in determining salinity for Florida Bay as a whole, salinity is more strongly correlated to rainfall than any other single factor. (2) Anthropogenic activity influences the magnitude of salinity variations seen in recent times in Florida Bay, and they probably act on a local basis to influence salinity patterns near areas of canal outflow. (3) Declines in species diversity and increases in dominance of salinity-tolerant species have occurred since the 1980s in several benthic invertebrate groups in different regions of Florida Bay. (4) Increases in abundance and/or density of sub-aquatic vegetation appear to have occurred in the last 50 years, compared to the first half of the 20th century. 5) In central Biscayne Bay salinities have become increasingly marine and increasingly stable over the last century. (6) Southern Biscayne Bay has experienced relatively large swings in salinity over multi-decadal and centennial timescales, but marine influence at the site has increased over the last century. (7) Sub-aquatic vegetation in Biscayne Bay has undergone bay-wide patterns of change over the last 200-500 years but a decline in *Thalassia* appears to have occurred in central Biscayne Bay around the middle of the 20th century. These findings are providing land management agencies with the information they need to plan and prioritize restoration effectively.

URL: http://sofia.usgs.gov/flaecohist/

B31G-04 1110h

Land Use and Stream Ecosystems in the Ozark Highlands, Missouri and Arkansas - Extracting a Weak Signal From Background Noise

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Land use history in the Ozark Highlands of Missouri and Arkansas included widespread timber harvest in the late 19th and early 20th centuries, followed by substantial depopulation that left a mosaic of land dominated by timber harvest, grazing, and other agricultural land uses. There is regional concern that present-day timber harvest and agricultural land-use practices may have detrimental effects on highly valued, biologically unique, and species-rich Ozarks streams. Our synthesis of five recent studies of landscape characteristics and stream ecosystems in the Ozarks documents scale-dependence and geographic complexities of links from land use to stream ecosystems. Over 100 study streams in the combined dataset range 6 - 4,300 km^2 in drainage area and drain rural land ranging 15-100% forested. Fish, aquatic insect, and periphyton communities can be reliably associated with some mesohabitat- and reach-scale measures of habitat and water quality. Biotic communities in some streams also appear linked to drainage-basin land use through controls on nutrient availability. However, physical habitat, thought to be an important factor affecting biotic community structure, is often only weakly linked to drainage-basin land use. We suggest that the weak relationships between drainage-basin land use, physical habitat, and biotic community structure in these streams is due to several interacting factors including: 1) stream morphology and physical habitat responses to land-use change are lagged in time, introducing considerable temporal noise in synoptic datasets; 2) lagged geomorphic responses accentuate and complicate the influence of drainage-basin area on habitat characteristics; 3) spatial variation of geology and physiography is large relative to the magnitude of land-use stress in this rural landscape, resulting in considerable spatial noise; 4) the karst landscape of much of the region tends to produce a bimodal sediment load and flashy hydrology; clay and silt are flushed from these streams whereas chert gravel moves slowly, resulting in land-use induced aggradation by coarse sediment rather than fine; 5) fish species distribution and abundance appear to be affected by drainage network structure as well as historical artifacts.

B31G-05 1125h INVITED

Hydrological Impacts of Land Use Change in the Central Appalachian Mountains, U.S.: A Multi-Scale Analysis

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Quantifying, understanding, and predicting the hydrological impacts of land use changes and land management practices are important objectives of both the academic hydrologist and the civil engineer. Relationships between stormflow response and land use have been most readily observed at small spatial scales (e.g., hillslopes, small experimental watersheds), but have proved difficult to establish in larger basins where (1) high-resolution precipitation data are usually unavailable, (2) land use patterns are often exceedingly complex, and (3) land use changes are essentially uncontrolled. In the Central Appalachian Mountains of the U.S., conversion of forests to mined lands (through devegetation, excavation of overburden and coal deposits, and subsequent reclamation) is the dominant land use change presently occurring. In the Georges Creek basin in western Maryland, for example, the portion of the watershed classified as mined (including active, reclaimed, and abandoned surface mines) increased from 3.8 to 15.5% from 1962 to 1997; modest urbanization of the basin (2.4 to 4.7%) also occurred during this period. In 1999, we initiated a comparative field study to determine if surface coal-mining and subsequent land reclamation practices affect stormflow responses at multiple spatial scales: (1) plot, (2) small watershed, and (3) river basin scales. Results from the plot-scale experiments suggested that soil infiltration capacity is grossly reduced during mining and reclamation, apparently due to loss of forest litter and soil compaction by heavy machinery. At the small watershed (<25 ha) scale, a comparative analysis of a pair of gaged watersheds indicated that conventional methods of surface mining and reclamation can increase peak stormflow, total storm runoff, and storm runoff coefficient by about 250% relative to similar forested watersheds in the same region. Finally, frequency analysis of long-term runoff data from the larger, extensively-mined Georges Creek (area = 127 sq. km.) and predominantly-forested Savage River (area = 188 sq. km.) watersheds in western Maryland was unable to establish a comparable land use effect on stormflow response, due to inherent climatic variability. Such an effect was suggested, however, when high-resolution, gage-adjusted rainfall data generated from NEXRAD (NEXt generation weather RADar; WSR-88D) radars were employed for developing unit hydrographs for specific extreme events. Inadequacies in spatial rainfall estimation thus appear to be a major limiting factor in scaling changes in observed stormflow responses from small experimental watersheds to larger river basins undergoing extensive land use changes. We conclude that land use change effects in gaged river basins can be discerned if flood hydrographs are interpreted using accurate, areal precipitation data.

B31G-06 1145h

The impact of land use change on the energy and water fluxes between atmosphere and tropical vegetation in Central Sulawesi, Indonesia

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The conversion of tropical rain forest to agriculturally used land is a widespread process throughout Indonesia. Besides the effects on the biological diversity and the hydrological functions of a forest, this also has an impact on the turbulent exchange processes between vegetation and atmosphere, the radiative properties of the surface and therefore on atmospheric boundary layer and local climate. Within the framework of the project STORMA "Stability of rain forest margins" (SFB 552, University Goettingen, financed by the German Research Foundation), the energy and water fluxes above one of the major land use types, a Cacao plantation, were investigated using the Eddy-Covariance method. Simultaneously meteorological measurements of the variables wind speed and velocity, temperature, humidity, rainfall, soil heat flux and the components of the radiation budget were performed, in order to complete the energy balance and investigate the dependencies of the turbulent exchange processes on the atmospheric boundary conditions. The measurements are being compared to a SVAT model, providing the heat flux into the vegetation. Energy balance closure is used as a means to check the quality of the measured fluxes. The comparison to measurements above undisturbed rain forest by means of the ratio of sensible to latent heat flux, the Bowen ratio, indicates a significantly different boundary layer regime of the atmosphere above the Cacao.

B31G-07 1200h

Local and Long-Distance Effects of Land Use Change on Nutrient Levels in Streams and Rivers of the Conterminous United States

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Determining the effects of land use change (e.g. urbanization, deforestation) on water quality at large spatial scales has been difficult because water quality measurements in large rivers with heterogeneous basins show the integrated effects of multiple factors. Moreover, the observed effects of land use changes on water quality in small homogeneous stream basins may not be indicative of downstream effects (including effects on such ecologically relevant characteristics as nutrient levels and elemental ratios) because of loss processes occurring during downstream transport in river channels. In this study we used the USGS SPARROW (Spatially-Referenced Regression on Watersheds) models of total nitrogen (TN) and total phosphorus (TP) in streams and rivers of the conterminous US to examine the effects of various aspects of land use change on nutrient concentrations and flux from the pre-development era to the present. The models were calibrated with data from 370 long-term monitoring stations representing a wide range of basin sizes, land use/cover classes, climates, and physiographies. The non-linear formulation for each model includes 20+ statistically estimated parameters relating to land use/cover characteristics and other environmental variables such as temperature, soil conditions, hill slope, and the hydraulic characteristics of 2200 large lakes and reservoirs. Model predictions are available for 62,000 river/stream channel nodes. Model predictions of predevelopment water quality compare favorably with nutrient data from 63 undeveloped (reference) sites. Error statistics are available for predictions at all nodes. Model simulations were chosen to compare the effects of selected aspects of land use change on nutrient levels at large and small basin scales, lacustrine and coastal receiving waters, and among the major US geographic regions.

URL: http://water.usgs.gov/nawqa/sparrow

B31G-08 1215h

Teleconnections Between Tropical Deforestation and Midlatitude Precipitation

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Past studies have indicated that total deforestation of Amazonia would result in an important reduction of the rainfall in that region, but that this process had no significant impact on the global temperature or precipitation and had only local implications. Here, we show that deforestation of tropical regions activates Rossby waves, which affect significantly precipitation at mid-latitudes by 'teleconnections'. In particular, we find that the deforestation of Amazonia and Central Africa severely reduces rainfall in the US Midwest during spring and summer, when water is crucial for agriculture in that region. Deforestation of South-East Asia reduces winter precipitation in the Western US and, consequently, the water storage that is released from snow melting later in the spring.

B32A MCC: Level 1 Wednesday 1330h

Modeling Coupled Biogeochemical Cycles in Natural and Contaminated Systems: Linking Hydrogeological, Microbiological, and Geochemical Processes II Posters *(joint with H, OS)*

Presiding: **J T McGuire,** Texas A&M University**; E Roden,** University of Alabama

B32A-0367 1330h POSTER

Modeling the Response of Terrestrial and Aquatic Ecosystems in the Northeastern U.S. to Changes in Atmospheric Deposition

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As a result of the Clean Air Act, atmospheric deposition of SO42- has declined significantly across the northeastern U.S. The acid-base status of many surface waters across the northeastern U.S. has significantly improved in response to these decreases. The response of soil and surface waters to changes in atmospheric deposition also varies among different subregions due to the different atmospheric deposition rates, soils, land use and other characteristics. In this study, an integrated biogeochemical model (PnET-BGC) was applied to 145 DDRP (Direct/Delayed Response Program) watersheds across the northeastern U.S. to simulate the changes in soil and surface waters in response to changes in atmospheric deposition at the regional scale. Sites of this study span across the Adirondacks, northern Pennsylvania/Catskills, northern New England, southern New England and Maine. The model simulated surface water chemistry was validated against synoptic surveys in 1984 and 2001. Preliminary modeling results indicated that besides the spatial gradients in S deposition, other factors such as wetland retention, seasalt impaction, land use, surficial and bedrock geology affect spatial variability in lake SO42- concentrations. In response to changes in atmospheric deposition, changes in lake SO42- concentrations were affected by amount of changes in S deposition and the ability of watersheds to retain SO42-. For sites in the Adirondacks and southern New England region, model predictions of changes in acid neutralizing capacity were consistent with measured changes.

B32A-0368 1330h POSTER

Iron mobility in acidic and iron rich sediments: From chemical equilibrium to hydrological controls

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Retention of ferrous iron at the interface between ground- and surface water is crucial for the acidity balance of lakes influenced by acid mine drainage. Iron budgets for two sediments with differential groundwater inflow (ca. 1 and 10 L m-2 d-1) were developed studying iron sedimentation, ground- and pore water chemistry, solid phase iron and sulfur chemistry and mineralogy, sulfate and iron turnover, and the corresponding Gibbs free energies of the latter processes. In both areas iron was sedimented as schwertmannite (Fe8O8(OH)x(SO4)y , 8-x = 2y, 1,0<x<1,75) at rates of 5.5-5.9 mmol m-2 d-1 leading to iron(III) enriched sediments (3.9-6.2 mmol g-1 dry weight). Compared to the surface water, the inflowing groundwater had higher pH (4.5 vs. 3), ferrous iron (6-20 mmol L-1 vs. 0.8-2.0 mmol L-1) and sulfate (5-60 mmol L-1 vs. 8-13 mmol L-1) concentrations. The inflow of the groundwater caused a change in sediment pore water chemistry and increased the pH to above 5.5. The pH increase was probably mostly due to decreased transformation rates of schwertmannite to goethite (0.27 mmol m-2 d-1 vs. 5.6 mmol m-2 d-1), also decreasing the production of H+ in the sediment. Compared to the control, in the area with groundwater inflow solid phase iron sulfide (0.011 mmol m-2 d-1vs. 0.0019 mmol m-2 d-1) and carbonate were formed at a higher rate, and more sulfate was reduced in incubation experiments. This finding can be explained by saturation indexes of siderite and sulfate reduction becoming thermodynamically more competitive by about 40 kJ eq-1 compared to iron reduction. However, only a small fraction of the reduced ferrous iron and sulfide was retained in the sediment, emphasizing the importance of reoxidation processes.

B32A-0369 1330h POSTER

Carbonate Dissolution and Precipitation in Coastal Environments

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In order to better understand and quantify mixing-driven mineral precipitation and dissolution in coastal environments, we conducted laboratory experiments designed to investigate dissolution and precipitation of $CaCO_3$ upon mixing between carbonate-saturated fresh- and salt-water solutions under different CO_2 partial pressures, and for different mixing ratios. Mixing of seawater or saline subsurface water with fresh water can be of major importance in the chemical diagenesis of carbonate rocks and sediments. We used both artificial seawater and NaCl solutions of different strengths. Two-dimensional flow cells filled with glass beads and crushed calcium carbonate rock were used, respectively, to measure calcium carbonate precipitation and dissolution. An important feature of these experiments is that the results are shown to agree well with a relatively simple transport theory describing mineral precipitation and dissolution that results from the non-linear dependence of $CaCO_3$ saturation upon electrolyte concentration. The theory demonstrates that the rate of dissolution or precipitation depends linearly on the dispersivity, specific discharge, and curvature (and sign) of the solubility as a function of salinity, but varies as the inverse square of the mixing zone width. The theory is largely scale independent and depends upon field parameters that can be determined. Analysis of data from three field sites (Yucatan peninsula, Bermuda, Mallorca) demonstrates excellent agreement between field observations and theory.

B32A-0370 1330h POSTER

Hydrocarbon Intrusion From Contaminated Seawater Into Coastal Freshwater Aquifers

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We focus on a recently recognized mechanism which suggests the potential for significant intrusion of organic contaminants from polluted seawater to freshwater aquifers. The solubility of organic compounds in water is inversely related to the concentration of dissolved electrolytes and directly related to the activity coefficients. The solubility of organic molecules is therefore assumed to be very low in marine environments, and the possible contamination of coastal aquifers via transfer from sea water has been ignored so far. This is despite the fact that coastal marine environments may be highly contaminated by toxic organic chemicals. In fact, concentrations of organic pollutants may be much higher than expected only from theoretical considerations of solubility. This is because the total concentration of organic contaminants contained in seawater is given not only by the dissolved contaminant concentration, but also by the presence of mechanically-dispersed organic droplets. Our initial work suggests the existence of a "salt pump" mechanism: while migration of organic compounds is due to chemical gradients, it is significantly enhanced by the presence of salt. Results from laboratory experiments demonstrating the intrusion of hydrocarbon mixtures from contaminated saline water into fresh water are presented.