kg m^{-2} yr^{-1}, unsurfaced roads can increase hillslope-scale sediment production rates by up to four orders of magnitude. Sediment production rates from erodible streambanks were estimated to be nearly 13 kg m^{-2} yr^{-1}, while uprooting of trees along stream margins was estimated to deliver 0.17 kg yr^{-1} of sediment per meter of stream length. The St. John Erosion model (STJ-EROS) uses a series of empirical sediment production models and sediment delivery ratios to estimate watershed-scale sediment yields in a GIS-based system. Using this model, the estimated sediment yields for the highly-developed 6.0 km^2 Fish Bay basin was 41 tons km^{-2} yr^{-1}, while the estimated sediment yield for the less-developed 4.3 km^2 Lameshur Bay basin was only 11 tons km^{-2} yr^{-1}. The model simulations suggest that current sediment yields are seven and four times above undisturbed conditions in the Fish Bay and Lameshur Bay basins, respectively. The predicted sediment yields are consistent with measured sediment yields and sedimentation rates in both Fish Bay and Lameshur Bay. In both cases actively used unsurfaced roads were identified as the dominant source of sediment. Cutslopes and streambanks played a secondary role in total sediment yields, while undisturbed hillslopes and treethrow contributed only minimal amounts.

H51F-08 1205h

Use of Water and Chemical Budgets to Quantify Interbasin Groundwater Transfer in a Lowland Rainforest

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Previous water quality data strongly suggested the presence of interbasin groundwater transfer (subsurface seepage beneath topographic boundaries) into lowland rainforest watersheds at our study site in Costa Rica. This hypothesis was tested by using physical hydrologic data and water quality data (major ion concentrations) together to construct water and chemical budgets for two small adjacent watersheds at the site, the Arboleda (50 ha) and Taconazo (26 ha). Water budgets were computed for four consecutive 12-month periods beginning 1 December 1998 and ending 30 November 2002. Major ion budgets were computed for the latter two of these four budget years (12/00-11/01 and 12/01-11/02). Streamflow was continuously measured at a V-notch weir on each watershed, rainfall was measured with tipping bucket gauge in a nearby clearing, the (insignificant) change in water storage each budget year was estimated from the difference in water table elevation between the start and end of the year, and ET was estimated using Li-cor pyranometer data for our budget years and an empirical relationship between annual Priestly-Taylor ET estimates and annual pyranometer-based energy inputs at our site. Chemical data were used to distinguish between two chemically different waters (high-solute "bedrock groundwater" and low-solute "local water") in streamflow and in interbasin groundwater transfer (IGT). The water budgets unambiguously confirm a large IGT into the Arboleda watershed; on average about 15,000 mm of water entered the watershed each year, 5,000 from rainfall and 10,000 from IGT. About 44% of the IGT was bedrock groundwater, and the remainder was low-solute local water, chemically identical to subsurface water derived from rainfall onto the watershed. The Taconazo had little or no IGT (the water budgets and chemical data show no IGT of bedrock groundwater and a small positive IGT of local water that is not clearly distinguishable from zero, given the uncertainties in the budgets). Chemical budgets differed even more greatly than water budgets between the two watersheds, because of the large differences (factors of 13 to 30) in major ion concentrations between bedrock groundwater and local water. Annual Na, K, Mg, Ca, Cl, and SO4 budgets in the Arboleda were dominated by the roughly 4,400 mm of bedrock groundwater IGT (this accounted for about 93% of the inputs of these six ions to the watershed). IGT of local water accounted for about 4% of major ion inputs, and atmospheric deposition less than 3%. Results show the importance of IGT to the hydrologic and geochemical status of lowland rainforest in this area, and suggest the clear need to account for IGT in small watershed studies from which conclusions are to be drawn regarding the hydrogeochemistry of a particular land use or landscape type. IGT may be an important link between distant upland and lowland areas through an interposed groundwater system, and as such should be considered in both practical and research-oriented water resource questions.

H51G MCC: 3020 Friday 1020h

Nitrogen Sources and Cycling in Aquatic Systems II *(joint with B, OS)*

Presiding: **R B Alexander,** U.S. Geological Survey**; E W Boyer,** State University of New York

H51G-01 1025h INVITED

In-stream Processing of N: Implications for Regional N Losses

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In many regions with high N inputs from human activity, large unmeasured N sinks have been inferred by comparing watershed inputs and outputs. One of the most likely N sinks is N uptake or denitrification within or adjacent to the stream channel. Recent research conducted as part of the LINX project helps to quantify some of these sinks and pathways. In 10 headwater streams, 15-NH4 was added at tracer levels and tracked through the various pools and fluxes of the N cycle. Results show that whole-stream enrichments (where N concentration is increased over background concentrations to determine N uptake) underestimate ambient rates of N uptake; that nitrification can be a very large fraction of NH4 uptake; that NH4 removal is related to Q and not biotic characteristics of the stream; and that NO3 uptake is often 10-fold slower than NH4 uptake. Given the very rapid N cycling in headwater streams, N losses in large rivers may be much more closely tied to these headwater processes than previously recognized. This is especially likely in watersheds where non-point source inputs are dominant.

H51G-02 1045h INVITED

Reach-Scale Application of ^{15}N-Enriched Nitrate Tracer for Measuring Denitrification in a Nitrate-Rich Stream

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Denitrification is one of the most important processes removing nitrate from streams and rivers before it is delivered to coastal ecosystems, but denitrification is difficult to quantify at the reach scale. We conducted a reach-scale isotopic tracer test to measure denitrification and other related processes in a nitrate-rich stream in the upper Mississippi River basin in September 2001. Bromide and ^{15}N-enriched nitrate were injected into the stream for 7 hours, yielding plateau concentrations in the stream for a distance of approximately 1 km. Concentrations of bromide were used to determine transport parameters and ground-water inputs. The concentrations and isotopic compositions of nitrate, nitrite, and nitrogen gas were used to determine reach-scale rates of nitrate addition and denitrification. This was done by combining the data in a forward-stepping numerical model that simulated a parcel of water moving through the reach, subject to denitrification, nitrification, ground-water discharge, and air-water gas exchange with changing temperature. The mass fluxes of nitrogen gas were dominated by discharge of denitrified ground water and air-water gas exchange, whereas the flux attributable to denitrification was relatively small. Nevertheless, there was systematic ^{15}N enrichment of the nitrogen gas going downstream indicating denitrification of surface-water nitrate. The reach-averaged rate of denitrification indicated by the isotopic tracer was equivalent to 130 μmol/m^2/hr (as benthic flux), 0.7 μmol/L/hr (as zero-order rate constant), or 0.01/hr (as first-order rate constant). This rate of denitrification should have been sufficient to reduce the nitrate load substantially within the tracer reach; however, the denitrification loss was more than offset by addition of nitrate from a combination of nitrification and discharge of ground-water nitrate. Consequently, there was a net increase in the nitrate load even though denitrification was a major sink for N in the stream. The in-stream nitrate isotopic tracer experiment provided a sensitive direct reach-scale measurement of denitrification in a nitrate-rich stream where other mass balance methods were not definitive because of insufficient sensitivity or offsetting sources and sinks.

H51G-03 1105h

Denitrification in Streams Impacted by Acid Mine Drainage: Effects of Iron, pH, and Potential Electron Donors

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Acid mine drainage (AMD) contaminates between 8,000 and 16,000 km of streams on U.S. Forest Service land in the Western United States and more than 7,000 km of stream in the Eastern U.S. Relatively little is known about nitrogen cycling in these acidic, heavy metal laden streams, however, denitrification can be inhibited under low pH conditions. The objective of this research was to examine AMD sediments for bacteria capable of denitrification. The process of denitrification is known to increase pH, which may be particularly important in acidic environments. Denitrification potential was assessed in AMD sediments from several Colorado AMD impacted streams ranging from pH 2.6 to 4.91, using microcosm incubations with fresh sediments. Added nitrate was immediately reduced to nitrogen gas without any lag period, indicating that denitrification was actively occurring in these environments. Rates varied from 0.33 to 2.52 umoles NO3-N/ g-sediment/ day depending on the site. The pH of the microcosms increased between 0.23 to 1.49 pH units in 5 days, depending on the site. Additional microcosm studies were conducted to examine the effects of iron concentrations (Fe2+ and Fe3+), initial pH conditions, and several potential electron donors. Addition of iron above ambient concentrations seemed to have little effect on denitrification rates, whereas rates increased with increasing initial pH. The addition of carbon and hydrogen stimulated denitrification rates, which in turn increased the rise in pH. These results suggest that not only is denitrification possible in AMD streams, it may also be a useful remediation option, if suitable methods can be found to stimulate activity.

H51G-04 1120h

Tracer Tests and Peeper Samplers Used to Quantify In-Stream Nitrate Fluxes and Removal Rates in an Agricultural Watershed

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The interface between surface water and ground water in riparian zones influences the quality and quantity of waters moving between linked reservoirs. Microbial respiration along this interface, for example, can act as a sink for dissolved nitrate, organic carbon, oxygen, and sulfate. We are investigating the removal of nitrate in a river draining the Pajaro Valley, a coastal, agriculturally-developed watershed that features elevated nitrate levels and groundwater pumping in excess of recharge (overdrafting). During summer base flow (discharge $\sim$ 0.3 m^3/sec), when no significant precipitation has fallen in the valley for 2-3 months, the Pajaro River consistently loses 0.1-0.2 m^3/sec of its discharge to the underlying alluvial aquifer along a 10-km reach east of Watsonville, CA. At the same time, nitrate concentrations (which are typically in excess of the EPA MCL), decrease by $\sim$30% along this reach. An observed a decrease in nitratre/chloride ratios along this reach suggests that biologic uptake (assimilative or dissimilative), not dilution, is primarily responsible for the observed decrease in nitrate concentrations. Sulfate/chloride ratios also decrease, and this along with pore water profiles obtained from streambed (peeper) samplers, suggests that dissimilitary nitrate reduction (denitrification) is primarily responsible for a significant fraction of the observed nitrate decrease. We performed a series of tracer experiments to quantify discharge, storage parameters, travel time, and nitrate

and sulfate removal rates in the river. We used breakthrough curves obtained from subsurface sampling locations in close hydrologic contact with the stream to quantify subsurface nitrate removal rates not limited by diffusion.

H51G-05 1135h

Nitrogen Isotopic Fractionation by In-Stream Populations of Ammonia-Oxidizing Bacteria

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Nitrogen cycling in the upper Illinois River basin is heavily impacted by agriculture and the application of nitrogenous fertilizer. Nitrate concentrations in many of its tributaries in Indiana (e.g. Iroquois River, Sugar Creek) have large seasonal fluctuations, ranging from less than 10 micromolar in the late summer to greater than 650 micromolar in the spring. We have performed a series of experiments to study the impact of this seasonal influx of nitrogen on bacterial populations and corresponding biogeochemistry related to nitrogen cycling in small streams. In this study, microcosms were used to measure nitrogen isotopic fractionation during nitrification by natural communities of water-column bacteria amended with NH_4^+. The in-stream nitrifier communities were also studied using molecular biological techniques to expand a previously observed correspondence between ammonia monooxygenase sequence and isotopic fractionation. The isotope effect (ϵ) for ammonia oxidation (14 permil) in June was calculated from a Rayleigh model based on changes in $\delta^{15}NH_4^+$ during the microcosm incubation. Supporting analyses indicated that NH_4^+ was oxidized primarily to NO_2^-. The evolution of the $\delta^{15}N$ in the $[NO_2^- + NO_3^-]$ pool was also consistent with an ϵ of 14 permil for ammonia oxidation. This value is similar to previous reports of NH_4^+ fractionation in the Chesapeake Bay and for *Nitrosomonas* species cultured from low- NH_4^+ environments, but is significantly different from *Nitrosomonas* species cultured from eutrophic environments. These results introduce a relationship between microbial community structure and isotope fractionation that may be used to better understand nitrogen cycling in streams.

H51G-06 1150h

Estimates of Nitrogen Removal in U.S. Streams and Reservoirs from the SPARROW Watershed Model

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Greater understanding is needed of the biotic and abiotic processes that remove nitrogen (N) from streams and reservoirs to quantify transport to downstream coastal waters where eutrophication is a major concern. Recent studies have improved estimates of N removal rates (e.g., denitrification, biological uptake) over small spatial scales in low-order streams. However, limited knowledge of the factors that explain the large variation in literature removal rates has made it difficult to accurately predict N transport through the range of stream and reservoir sizes that link sources to downstream waters. Spatially referenced watershed models (SPARROW) have been used to statistically estimate long-term mean-annual rates of total nitrogen removal in streams and reservoirs over large spatial scales. These rates are estimated as a function of physical and hydraulic properties (channel depth, water travel time) that influence the contact and exchange of water with benthic sediment. We recently refined our SPARROW model structure with expanded descriptions of climatic, topographic, and other surficial features of terrestrial and aquatic landscapes. We find that the net rates of N removal decline from about 0.3 day-1 of water travel time in streams with depths less than 0.5 meters to negligible quantities in large rivers (greater than 4 meters). These rates are generally consistent with those of earlier regional and national SPARROW models and with measured rates from the literature (adjusted for water travel time) over the reported range of stream depths. A settling velocity of approximately 8 meters year-1 is estimated for lakes and reservoirs and agrees well with literature rates for lakes where denitrification is the predominant removal process. We applied these removal rates within the SPARROW stream and reservoir network to estimate the regional-scale N transport and delivery to U.S. coastal waters.

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

H51G-07 1205h

The impact of changing land use practices and climate variability on nitrate export by the Mississippi River

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The increased use of nitrogen fertilizer in the Mississippi River Basin since the 1950s has been blamed for declining water quality, the degradation of aquatic ecosystems and the growth of a seasonal hypoxic zone in the Gulf of Mexico. In this study, we use the IBIS terrestrial and agro-ecosystem model and the HYDRA aquatic transport model to examine how agricultural practices and climate variability influenced terrestrial and aquatic nitrogen cycling across the Mississippi Basin and the export of nitrate to the Gulf. The modeling system accurately depicts the observed trends and interannual variability in nitrate export by the Mississippi River ($r^2 > 0.8$), and several of the major tributaries, between 1960 and 1994. The challenge of simulating nitrate export from the western sub-basins highlights the key role of nitrogen retention processes like denitrification. The simulations demonstrate that three factors led to the doubling of nitrate export by the Mississippi River since 1960: (1) an increase in fertilizer application rates, particularly on corn; (2) the expansion of soybean cultivation; and (3) an increase in runoff across the basin. By the early 1990s, crops alone may have accounted for almost 90% of the nitrate leached to the river system, despite representing only 20% of the watershed area. The majority of the nitrate exported to the Gulf now appears to originate from several "hot spots", including a stretch of the Corn Belt' across Iowa, Illinois and Indiana. The relative contribution of such heavily fertilized lands is even greater during wet periods, due to high leaching losses and relatively low in-stream nitrogen retention. These findings demonstrate that the effort to reduce the flux of agriculturally-derived nitrogen to the Gulf of Mexico could be further complicated by increasing variability in climate.

H51H MCC: 3024 Friday 1020h

Interactions Between Fluids and Fractures III *(joint with T, V, NG, MR)*

Presiding: **L C Murdoch,** Clemson University**; L Germanovich,** Georgia Institute of Technology

H51H-01 1020h

Complex Dispersion in Simple Fractured Media

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Complex dispersion can develop in simple networks of fractured media. Numerical studies, involving modeling flow and particle transport through networks, were conducted to understand complex dispersion in the context of more variable networks and to evaluate the scaling between dispersion and characteristics of the network. Simulation trials examined how changes to the orientation of the overall network, fracture aperture, fracture connectivity, and fracture length influenced mass transport. The grid orientation effect inherently gives rise to the complex, non-Fickian dispersion. Spreading caused by variability in aperture and connectivity produces the more familiar, elliptical pattern of spreading. In the various model trials, we created situations where either or both of these spreading mechanisms could dominate. When both grid orientation and heterogeneity effects were comparable, particle swarms took on a curious hybrid shape reflecting the outcome of two different spreading mechanisms. With sufficient heterogeneity, the grid-orientation effect was swamped and disappeared.

H51H-02 1035h

Investigation of Matrix Diffusion in Deep Hot-Dry-Rock Reservoirs Using Single-Well Injection-Withdrawal Tracer Tests

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The dimensioning of geothermal energy usage from deep hot-dry-rock reservoirs requires knowledge of the effective heat exchange surface between liquid and solid phases. Tracer tests are an appropriate technique for the investigation of this surface since matrix diffusion and hence tracer transport is a function of the effective contact area. However, investigations within such reservoirs are difficult: Usually only one borehole is available due to economic restrictions, high temperature stimulates tracer decay, and matrix diffusion is masked by hydrodynamic dispersion within the advective pore space due to heterogeneity. To overcome these difficulties, an experimental concept was developed. It is based upon the synchronous application of several non-retarding tracers with different diffusion coefficients. Using the single-well injection-withdrawal (SWIW) technique, the effect of hydrodynamic dispersion is partially reversed, while the effect of molecular matrix diffusion is enhanced. Hence the differences between the tracer breakthrough curves are due to different matrix diffusion. Knowing the diffusion coefficients of the individual tracers, an effective contact surface between liquid and solid phases can be estimated. Since each tracer is subjected to the same advection and dispersion, the formation heterogeneity is of minor importance and the different transport behavior can be attributed to the molecular diffusion only. The tracers under investigation are sulfonated naphthaleneformaldehyde condensates (SNFC) and the corresponding monomeres. These compounds are available in various chain lengths, spanning a range of aqueous diffusion coefficients. Modern HPLC methods enable their analysis down to a ìg/l level. Since SNFC are environmentally benign, they could be recently applied within the unsaturated soil zone, in a shallow aquifer as multitracer mixture, and in geothermal systems. The experimental approach and first results are presented.

H51H-03 1050h

The role of Peclet number on the alteration of variable aperture fractures by dissolution: A comparison of physical experiments with computational simulations

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