

cave deposits associated with microbial mats, and meteoric waters from the Island of Kauai, Hawaii has enabled differentiation between microbial and abiotic mineralization. Kauai cave and surface waters are dominated by calcium, magnesium, silica and bicarbonate, as is common for non-hydrothermal basaltic terranes. Strontium isotope and Ca/Sr ratios in the waters and carbonate minerals indicate that a majority of cations are derived from the basalt. These cations were likely leached during downward percolation of the meteoric water through the host basalt above the caves. The carbon isotope composition of dissolved inorganic carbon (DIC) suggests its derivation from carbon dioxide originating in soil profiles above the caves. The oxygen and hydrogen isotope ratios and chemical compositions of the water indicate that evaporation is not a significant process controlling its composition in the caves. However, evaporation of drops and thin films of water on cave surfaces and within microbial mats likely leads to the precipitation of some Ca-carbonates and magnesite. This behaviour is also suggested by the positive co-variance in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of some of the carbonates. The magnesite is considered to be a late-stage evaporative precipitate and has the highest $\delta^{18}\text{O}$ values of all carbonates in the caves. Extremely elevated $\delta^{13}\text{C}$ values (up to $+8.2\text{‰}$) in some Ca-carbonates relative to that of DIC is best explained by microbial photosynthesis, namely by cyanobacteria, in the microbial mats. The preferential uptake of $\delta^{12}\text{C}$ by these photosynthetic microorganisms is recorded in low $\delta^{13}\text{C}$ values of organic matter in mats and mineralised microbialites. The resulting enrichment in ^{13}C of dissolved inorganic carbon within the mats is recorded in elevated $\delta^{13}\text{C}$ values of the Ca-carbonates.

B43B-04 1415h

Migration and Rearing Histories of Chinook Salmon (*Oncorhynchus tshawytscha*) Determined by Ion Microprobe Sr Isotope and Sr/Ca Transects of Otoliths

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With the goal of monitoring fish habitat during the first year of life, we used the Stanford-USGS SHRIMP RG ion microprobe to determine $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Ca ratios in $25 \times 35 \mu\text{m}$ areas along radial transects of otoliths from juvenile Chinook salmon (*Oncorhynchus tshawytscha*) native to four watersheds of markedly different geology. Otoliths from ocean-type Chinook salmon from the Skagit River estuary, Washington, have pre-hatch regions with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (~ 0.709) suggesting a marine signature inherited maternally, extensive freshwater growth zones with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios similar that of the Skagit River (~ 0.705), and marine-like $^{87}\text{Sr}/^{86}\text{Sr}$ ratios near edges. Otoliths from stream-type Chinook salmon from three watersheds in central Idaho have pre-hatch $^{87}\text{Sr}/^{86}\text{Sr}$ ratios > 0.711 , indicating that a maternal marine Sr isotopic signature is not preserved after the $\sim 1000\text{-}1400$ km migration from the Pacific Ocean. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the outer portions of these otoliths are similar to those of their respective streams ($\sim 0.708\text{-}0.722$). For the Skagit juveniles, freshwater growth is marked by a small decrease in otolith Sr/Ca ratio, with an increase in Sr/Ca corresponding to the observed increase in $^{87}\text{Sr}/^{86}\text{Sr}$ with migration into salt water. Otoliths from the Idaho fish have similar Sr/Ca radial variation patterns that appear to record seasonal fluctuation in ambient water Sr/Ca ratio documented by our water analyses and USGS NASQAN time series data. The ability of the ion microprobe to measure both $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Ca ratios of otolith aragonite at high spatial resolution *in situ* provides a new dimension in studies of fish rearing and migration.

B43B-05 1430h

Evidence of Iron Isotope Exchange at the Ferrihydrite Surface

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Ferrihydrite is the primary iron phase to precipitate from aqueous Fe(III) solutions, and is a precursor to diagenetically produced minerals such as hematite and goethite. Isotopic exchange between aqueous Fe and the ferrihydrite surface could impact measured iron isotope compositions in a variety of settings where ferrihydrite might react with ambient aqueous iron as it aggregates, accumulates, or is diagenetically altered. We chose a manufactured 3-nm sized ferrihydrite for these experiments with a large surface area available for exchange ($\sim 500\text{m}^2/\text{g}$), so this study likely represents an end member case in terms of isotopic exchange. Natural ferrihydrites are generally larger aggregate particles with substantially less surface area ($< 150\text{m}^2/\text{g}$), which may reduce the bulk effects of isotopic exchange. However, even small amounts of isotopic exchange could dramatically affect isotopic compositions of aqueous iron. We have successfully demonstrated that iron isotope exchange occurs between iron oxyhydroxide (ferrihydrite) and aqueous ferric iron using a ^{57}Fe tracer approach. Our results show that $\sim 25\%$ iron isotope exchange occurs after ten days, with no further exchange evident over the duration of the study ($25\text{pm}5\%$ exchange from 10-80 days). The nanoparticulate (3nm) ferrihydrite used in this study has $\sim 30\%$ of its Fe atoms at the surface. We suggest that our ^{57}Fe isotope exchange data reflect the complete exchange of available surface Fe atoms after the first ten days and that further diffusional exchange is not detected over the duration of this experiment. This study highlights the usefulness of using enriched isotope tracers to investigate the rate of exchange between aqueous iron atoms and those at the ferrihydrite surface under equilibrium conditions, and is a critical first step toward better interpreting iron isotope variations measured in natural settings. The demonstration of iron isotope exchange in this study emphasizes that ferric precipitates should not be regarded as isotopically unreactive and their potential impact on the iron isotope compositions of ambient fluids cannot necessarily be ignored. It seems unlikely, however, that the isotopic compositions of the solid ferrihydrite will be strongly affected during diagenesis. Further investigation into the extent of surface exchange on ferrihydrites of various particle sizes is necessary to better characterize the iron isotope variations measured in natural systems. Changes in environmental conditions such as temperature and pH should also affect the reactivity of iron at the ferrihydrite surface, and require further experimental work. It remains unknown if the isotopic exchange properties of the nanoparticles used in this study may be scaled to larger crystals.

B43B-06 1445h

Analyses of Storm Events in an Adirondack Watershed: a Combined Approach Using Stable Isotopes of Sulfate and Nitrate, Chemistry and Hydrology

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The Archer Creek catchment which is the major inlet to Arbutus Lake at the Huntington Forest in the Adirondack Mountains of New York has been the focus of intensive investigations on hydrological and biogeochemical interactions. We used hydrologic information, solute chemistry and isotopic composition of nitrate ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) and sulfate ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) to evaluate how four summer/early autumn storms affected surface water chemistry after a summer of unusually dry conditions in 2002. Precipitation amounts varied among the storms (Storm 1-Sept. 14-18, 19 mm; Storm 2-Sept. 21-24, 33 mm; Storm 3-Sept. 27-29, 43 mm; Storm 4-Oct. 16-21, 68 mm). With the four storms there was an increase in water yield from 2 to 14%. The first storms resulted in relatively small changes in water chemistry. With progressive storms the changes in water chemistry became more marked with particularly major changes in C_b (sum of base cations), sulfate, nitrate, DOC and pH. The marked changes in chemistry were also reflected in changes in the isotopic composition of sulfate and nitrate. The results indicate that

especially for storms 3 and 4 that there was an important solute source most likely attributable to wetlands. The contributions of wetlands was evident due to the large increases in DOC during the storm and evidence of changes in S wetland constituents from both chemical and isotopic information. Although these late summer and fall storms do not play a major role in the overall annual mass balances of solutes for this watershed, these events have distinctive chemistry including depressed pH that have important consequences to watershed processes and the linkage of these processes to climate change.

B44A CC: 524 A Thursday 1530h

Issues of Scale in Catchment Hydrobiogeochemistry (joint with H)

Presiding: A L James, McGill University; J B Shanley, U.S. Geological Survey

B44A-01 1530h INVITED

Scale effects on catchment runoff timing, flow source, and groundwater-streamflow relations

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The effects of catchment size and landscape organization on runoff generation are poorly understood. Little research has integrated hillslope and riparian investigations across catchments of different sizes to decipher first-order controls on runoff generation. We investigated the role of catchment sizes on riparian and hillslope dynamics based on hydrometric and tracer data observed at five scales ranging from trenced hillslope sections (55-285 m²) to a 280-ha catchment at Maimai, on the West Coast of the South Island, New Zealand. The highly organized landscape is comprised of similar headwater catchments, regular geology, steep highly dissected topography, relatively consistent soil depths, and topographically controlled shallow throughflow. We found a strong correlation between riparian zone groundwater levels and runoff in the headwaters, whereas the water tables in the valley bottom of the larger catchments were uncorrelated to runoff. While there was no clear relationship between catchment size and new-water contribution to runoff, lag times of tracer responses increased systematically with catchment size. During wetter antecedent conditions or during larger events (> 30 mm under dry antecedent conditions) hillslope and valley bottom floodplains did contribute to event runoff directly. We found that runoff was generated mainly in headwater riparian zones. We propose that analysis of landscape scale organization, the distribution of dominant landscape features, and associated dominant runoff processes provide a structure for understanding runoff generation and solute transport, especially as catchment scale changes from headwaters to the meso-scale.

URL: <http://landresources.montana.edu/watershed/Publications.htm>

B44A-02 1550h INVITED

Scales, Dominant Processes and Simplified Modeling in Catchment Hydrobiogeochemistry

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Effective and efficient management of our water resources and water-related environment depends largely on our knowledge of relevant processes (e.g. hydrologic, biologic, and chemical) that occur in our catchments.

These relevant processes are defined primarily by the problem of interest and the spatial and temporal scales considered, and their influences are determined by their individual as well as combined effects. The purpose of this talk is to discuss these aspects from the viewpoint of catchment hydrobiogeochemistry. Following on recent studies, the importance of identifying the "dominant" processes aimed at "model simplification" is highlighted. In view of the difficulties (e.g. lack of technological and human resources) in measuring "all the relevant data" of interest, a simple procedure to identify the number of dominant processes using only a single available time series representing a catchment system is reviewed. The concept behind this procedure and its practical relevance, in terms of catchment complexity and nonlinear interactions among the processes, is explained. One possible way to integrate this procedure with (field) "expert advice" and (conventional) "parameter sensitivity analysis" is also presented for further simplification of the catchment modeling procedure. The potential of these ideas for the formation of a global "catchment (hydrobiogeochemistry) classification system" is finally discussed.

B44A-03 1610h INVITED

Scaling Stream Flow Response to Forest Disturbance: the SID Project

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We do not have a good understanding of the hydrologic implications of forest harvesting in Ontario, either for current or alternative management approaches. Attempts to address these implications face a three-fold problem: data on hydrologic response to forest disturbance in Ontario are lacking; most studies of these responses have been in regions with forest cover and hydrologic conditions that differ from the Ontario context; and these studies have generally been conducted at relatively small scales (<1 km²). It is generally assumed that hydrologic changes induced by forest disturbance should diminish with increasing scale due to the buffering capacity of large drainage basins. Recent modeling exercises and reanalysis of paired-basin results call this widespread applicability of this assumption into question, with important implications for assessing the cumulative impacts of forest disturbance on basin stream flow. The SID (Scalable Indicators of Disturbance) project combines stream flow monitoring across basin scales with the RHESys modeling framework to identify forest disturbance impacts on stream flow characteristics in Ontario's major forest ecozones. As a precursor to identifying stream flow response to forest disturbance, we are examining the relative control of basin geology, topography, typology and topology on stream flow characteristics under undisturbed conditions. This will assist in identifying the dominant hydrologic processes controlling basin stream flow that must be incorporated into the RHESys model framework in order to emulate forest disturbance and its hydrologic impacts. We present preliminary results on stream flow characteristics in a low-relief boreal forest landscape, and explore how the dominant processes influencing these characteristics change with basin scale in this landscape under both reference and disturbance conditions.

B44A-04 1630h

Examining Runoff Generation Across Scale: A Test of Mixing Models

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As water moves through the landscape, it transports biogeochemical nutrients and contaminants to the stream channel. The physical processes that deliver water to the stream channel vary in both space and time. As a result, modelling of runoff generation and nutrient budgets remains a challenge. Mixing models are used to help define different sources or end-members of water (e.g. groundwater and soil waters) that mix together to make up stream water. The application of mixing models has focused on the analysis of runoff from headwater basins. However, as water moves downstream, changes in stream chemistry will indicate if the relative importance of end-member contributions changes with location. Furthermore, the geochemical definition of end-members could potentially vary with location. In this research we apply a mixing model to stream discharge taken from a series of forested basins at Mont Saint-Hilaire, Quebec to evaluate both the changing importance of end-member contributions and the validity of their geochemical definitions across scale. In this study, a mixing-model is created from analysis of stream water chemistry collected from the largest basin (1.5 km²) located furthest downstream. The model is then applied to 8 additional locations located upstream that represent progressively smaller basin areas. For each basin, we test if the same mixing-model can reproduce the observed stream chemistry. The number of contributing end-members is estimated by the mixing-model analysis but their physical interpretation relies on independent field sampling of groundwater and soil waters. This study provides a cross-basin application of end-member-mixing-analysis. The results will be used in a cross-basin analysis of runoff generation.

B44A-05 1645h

Analysis of Soil Moisture Patterns in Forested and Suburban Catchments Using High-Resolution Photogrammetric and LIDAR Digital Elevation Datasets

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Field observations of near-surface soil moisture, collected over several seasons in a watershed in suburban Maryland, are compared to values of the topographic index generated using digital elevation models at a range of resolutions and data sources. A companion set of observations, DEMs and topographic index values are presented for a nearby forested catchment. The degree to which topographic index values are an effective model of near-surface soil moisture conditions varies in the two environments: The urbanizing environment requires topographic index values from a DEM with a much finer grid cell resolution to function effectively, and the relationship is stronger in wetter conditions. In the forested environment, the DEM resolution required is considerably lower, and the relationship is strong under all moisture conditions. These results provide some insights into the length scales of near-surface hydrologic processes in the urbanizing environment, and the resolution of terrain data required to model those processes.

B51A CC: 220 C-E Friday 0830h

Isotopes in Biogeochemistry Posters

Presiding: M E Uhle, University of Tennessee; E Hobbie, University of New Hampshire

B51A-01 0830h POSTER

Nutritional associations among fauna at hydrocarbon seep communities in the Gulf of Mexico

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The Gulf of Mexico supports dense aggregations of megafauna associated with hydrocarbon seeps on the Louisiana Slope. The visually dominant megafauna at the seeps, mussels and tubeworms, derive their nutrition from symbiotic relationships with sulfide or methane oxidizing bacteria. The structure of the tubeworm aggregations provide biogenic habitat for numerous other species of heterotrophic animals. Carbon, nitrogen and sulfur stable isotope analyses of heterotrophic fauna collected with tubeworm aggregations in the Green Canyon Lease area (GC 185) indicate that most of these species derive the bulk of their nutrition from chemoautotrophic sources. The isotope analyses also indicates that although two species may be deriving significant nutritional input from the bivalves, none of the species analyzed are feeding directly on the tubeworms. Grazing gastropods and deposit feeding sipunculids were used to estimate the isotopic value of the free-living chemoautotrophic bacteria associated with the tubeworms (d13C -32 to -20‰/‰; d15N 0 to 7‰/‰; d34S -14 to -1‰/‰). The use of tissue d34S analyses in conjunction with tissue d13C and d15N led to several insights into the trophic biology of the communities that would not have been evident from tissue stable C and N analyses alone.

B51A-02 0830h POSTER

Iron Isotope Fractionation During Paleoproterozoic Lateritization of the Hekpoort Basalt in Gaborone, Botswana

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Beukes *et al.* (2002) [*Geology* 30, 491-494] reported the discovery of a lateritic weathering profile developed on the ~2.2 Ga Hekpoort basalt in Gaborone, Botswana. In the lateritic paleosol, Fe is depleted in the lower pallid zone and enriched in the upper laterite and mottled zones. We have investigated the Fe mobility during laterite formation by analyzing bulk-rock Fe isotope ratios of selected drillcore samples. The studied