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Flooding of northern landscapes for the creation of hydroelectric and drinking water reservoirs results in elevated emissions of greenhouse gases and methylmercury in fish. Dissolved organic matter (DOM) is an integral component of both carbon and mercury cycling. At the Experimental Lakes Area in NW Ontario, three reservoirs were created by flooding boreal forests of differing carbon stocks with water from a nearby oligotrophic lake in the FLUDEX experiment. In the reservoirs, DOM concentrations continued to be elevated in all 5 years of flooding. DOM was the dominant form of nitrogen loss and comparable to dissolved inorganic carbon (DIC) release from all reservoirs as a result of flooding. Magnitude of DOM release did not mimic the order of carbon stores and is consistent with laboratory experiments. Changes in the quality of DOM generated throughout the experiment were followed by $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$ and C/N ratios, spectral absorbance, and organic alkalinity. Sources of DOM and processes affecting the fate of DOM were followed in each year of flooding by determining the $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$ and C/N ratios of vegetation, soils and periphyton, leaching experiments of flooded and unflooded soils, and constructing DOC, DON and DIC. $^{13}\text{C}/^{12}\text{C}$ budgets for each reservoir in conjunction with DIC- $^{13}\text{C}/^{12}\text{C}$ budgets.

B43A-07 1330h POSTER

Relationship Between Land Use and the Amount and Reactivity of Dissolved Organic Carbon Exported from Coastal Watersheds

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Changes in the amount and biological reactivity of organic C, N, and P were investigated in coastal watersheds along a gradient of land use. Concentrations of inorganic N and P declined from suburbanized and agricultural headwaters to urbanized reaches further downstream. In contrast, concentrations of organic C, N, and P increased along the river network. At the outflow, organic N and organic P comprised 53% and 71% of the total N and P exported to Chesapeake Bay. The biological reactivity of organic C, N, and P varied with land use and season. Across sites and seasons, 0-41% of organic carbon, 0-41% of organic nitrogen, and 0-58% of organic P were biologically available over a time scale of 3 days. The bioavailability of organic carbon typically increased from forested and agricultural headwaters to larger suburban and urban drainages. Activities of esterase and endopeptidase enzymes by stream microbes also followed similar spatial patterns suggesting that both the bioavailability and chemical composition of organic matter were changing en route to the ocean. Measurements of bacterial production and respiration efficiency suggested that growth and metabolism of microbes in urban streams were less limited by organic matter quality and the availability of inorganic nutrients as compared to forested streams. Substantial quantities of bioavailable DOC, DON, and DOP accumulated along flow paths while concentrations of inorganic nutrients declined. The potential role of agricultural, suburban, and urban streams as transformers of inorganic nutrients to reactive organic fractions may need to be considered when predicting changes in oxygen demand and the total export of bioavailable C, N, and P to coastal environments.

B43A-08 1330h POSTER

Dissolved Nitrogen Dynamics and Dissolved Organic Carbon Biogeochemistry in an Ombrotrophic Bog

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As an extension of an ongoing study on carbon cycling and sequestration, Mer Bleue bog near Ottawa, Ontario was studied for dissolved nitrogen dynamics. Since nitrogen is an important nutrient for plant growth, the retention and export by the bog could reflect the impact of nitrogen deposition on bog productivity and carbon sequestration. Dissolved inorganic and organic nitrogen (DIN, DON) and dissolved organic carbon (DOC) inputs, export, and groundwater concentrations were measured over the 2003 field season (from May 21 to November 18, 2003). Nitrogen inputs were found to be entering the bog dissolved in precipitation in very small concentrations, ranging from 0 to 6 mg/L, and were dominated by NH_4^+ . Export DON and DOC concentrations followed similar patterns, increasing with a decrease in outflow discharge with drier bog conditions throughout the season. Rough budget estimates for DOC, DON and DIN for the 2003 field season are roughly 0.034, 0.101, and 2.861 g · m⁻² · t⁻¹, respectively. The bog was also characterized for groundwater concentrations of DIN, DON, and DOC in the saturated and unsaturated zones of the bog. The general patterns of concentrations show dominance of NH_4^+ deeper in the saturated zone, and DON dominating in the unsaturated, biologically active zone. Although deposited nitrogen is dominated by inorganic forms, the internal processing of nitrogen results in DON export correlated to DOC. The results provide greater insight as to the influence and importance of dissolved nitrogen on carbon retention and sequestration.

B43B CC: 524 A Thursday 1330h

Isotopes in Biogeochemistry: Sediments and Records of Environments

Presiding: S Macko, University of Virginia; M E Uhle, University of Tennessee

B43B-01 1330h

Assessing the Distribution and Sources of Organic Matter in a Coastal Marine Environment Using Compound Specific Carbon Isotopic Analysis of Sedimentary Lipids: Evidence from the Hauraki Gulf, New Zealand

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The Hauraki Gulf, on the northeast coast of the North Island of New Zealand, is highly productive, supporting a large local fishing industry. River runoff to the Gulf is local and limited in volume, whereas the Gulf has prevailing currents and quasi-annual upwelling events that deliver open ocean waters and nutrients to the shelf and are believed to drive the high productivity in the area. Organic matter in coastal and shelf sediments are commonly derived from both allochthonous and autochthonous sources. Bulk chemical characterization of sedimentary organic matter alone cannot conclusively differentiate marine and terrestrial organic matter. Molecular level analysis, however, can yield detailed information on source of organic matter input as chain length and carbon number of marine and terrestrial derived lipids is source specific. The presence of C₂₇, C₂₉ and C₃₂ n-alkanes and C₂₄, C₂₆ and C₂₈ n-alkanoic acids are indicative of input from higher-plant waxes, whereas short chain C₁₂, C₁₄ and C₁₆ n-alkanoic acids are dominant components of algal-derived lipids. Compound specific isotope analysis further pinpoints sources because carbon isotopic values

of marine organic matter are typically enriched in $\delta^{13}\text{C}$ relative to values for C₃ terrestrial plants. We report here on sediment samples recovered from the Hauraki Gulf during the summer of 1999. Samples were collected using a multi-corer from both near-shore and open environments to investigate the sources and distribution of organic matter in the gulf. Results show a mix of sources throughout the gulf and somewhat follow current flows. Nonetheless, the most upcurrent site showed significant terrestrial inputs. Other sites within the gulf, including those located on the shelf, show a mixture of sources. These results indicate that a significant amount of terrestrial organic matter is being transported out onto the narrow shelf of the gulf through small rivers. In contrast, the site most landlocked and furthest down current, showed a strong predominance of marine input. The organic matter at Firth of Thames where relatively high discharges of fresh water enter the gulf, is predominantly derived from algal input and not terrestrial sources as may be expected at the mouth of a river. The dominant n-alkanes are typically short chain (C₁₅, C₁₇, and C₁₉) and the carbon isotope values range between -25 and -30 ‰, typical of marine derived lipids. We interpret the predominance of marine input at this site as due to the influx of nutrients from the surrounding farmland enhancing phytoplankton growth.

B43B-02 1345h

Diagenesis of Organic Matter in a Virginia Salt Marsh: Evaluation Through Compound Specific Isotope Analysis

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Resolving the early diagenetic pathways to preservation of organic matter in a sedimentary sequence is one of the most intriguing challenges in organic geochemistry. What is preserved is usually ascribed to be either the product of retention of refractory materials or "protected" remnants of the destruction of the more labile matter, or more likely, a combination of both processes. A third mechanism, acquisition of newly synthesized material resulting from microbially mediated reactions, is less frequently invoked. In this study, the sources for the preserved organic matter and the sedimentary history of a Spartina marsh sequence on North Hog Island at the Virginia Coast Reserve Long Term Ecological Research (VCR-LTER) site are reported. Through the utilization of both carbon and nitrogen bulk isotopic compositions and compound specific isotopic analyses (CSIA) as well as the distributions of individual fatty acids, the depositional sequences are assessed. The variations in the cores for bulk organic carbon and nitrogen delta 13C and delta 15N typically ranged from -17 to -15 permil and +4 to +10 permil, respectively. The isotopic compositions generally show a trend of increasing in the heavy isotope downcore. These variations can be attributed to microbial utilization of amino acids resulting in bulk isotopic enrichments in deeper layers. Extensive microbial activity was evidenced at depth with increased amounts of odd-chain and branched-chain fatty acids. Overall, there is a decline with increasing depth in the amount of quantifiable fatty acids. Through the CSIA measurements, the original source of the preserved molecular components was observed to be essentially that of the Spartina, with loss of unsaturation deeper in the sequence. At greater depths, newly synthesized, longer-chain, unsaturated fatty acids were observed, possibly resulting from anaerobic pathways. Through mass balance using isotopic compositions of proposed bacterial endmember fatty acids, a significant portion of the preserved material can be shown to be the result of newly synthesized organic matter.

B43B-03 1400h

Formation of Carbonate Minerals in Basaltic sea Caves by Abiotic and Microbial Processes

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A detailed isotopic and geochemical study of carbonate-rich (aragonite, calcite, magnesite) basaltic

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.