H11B-0242 0830h POSTER

Interplay Between Hydrodynamic and Biofilm in Stream Flows

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An experimental flume was built in order to investigate the mutual effects on flow parameters in presence of biofilms. Such experimental tool, also, allows to study the effects of the substrate, the possible exchanges between groundwater and surface water, and finaly the nature and the age (quantity) of biofilm. Considering the difficulties encountered on a previous experimental study (Godillot and al., IAHR J., 2001, Vol.39 (3)), due to the nature of the substrate and of the flow, the gravels were replaced by PVC sticks (diameter 10 mm) arranged side by side perpendicularly to side walls of the channel. This should induce a two-dimensional roughness and interpretation of physical measurements would be made easier, mainly concerning turbulent parameters. It has been shown, as previously, that in presence of bioderm, there is significant modifications of the mean flow : a strong acceleration and deceleration respectively near the surface and near the bioderm. Furthermore, modifications of turbulent parameters were observed : turbulent intensities and Reynolds stress are signs of hydrodynamic changes in the benthonic zone. In the beginning and in absence of blowing (flow normal to the substrate at the interface between the substrate and the main stream flow), the shear stress decreases and then starts to increase, due probably to a more important colonization of the sticks and to the appearance of important filaments at the top of the periphytic matrix. In presence of blowing, the periphytic mat has to be inclined to fill more space, but also to clog water entrance causing shear stress to increase. To this date, it seems that the shear stress is linked with the quantity and the nature of the periphytic algae. Data collected on periphytic mats and direct visualization of its growth through pictures and movies will support the interpretation of the physical parameters resulting from this experimental study.

H11B-0243 0830h POSTER

A Reactive Radial Diffusion Model with Multiple Non-Identical Porous Soil Particles

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Diffusive mass transfer in porous media is often analyzed via a conceptual model of the medium involving porous particles of idealized geometry (e.g., spherical, cylindrical) that dictates the mathematical form of the diffusive flux. In most cases the system is represented using a single idealized particle model. We generalize this approach to allow multiple particles of different sizes and chemical properties. A mathematical model has been formulated and solved numerically to determine spatial (among particles) and temporal variations in intra-particle sorbed and aqueous concentrations that exchange mass dynamically with the extra-particle well-mixed aqueous phase. In addition to accommodating multiple particles of different sizes and chemical properties, the model handles (1) reversible intra-particle sorption kinetics, both linear and site-limited, (2) first-order decay both in intra- and extra-particle aqueous volumes, (3) phase partitioning at particle surfaces; and (4) dynamic mass-transfer across particle boundary layers. The numerical formulation involves a particular term, which has not been reported in previous studies, that carries mass-interaction among different particle categories. Applications of the model on several examples illustrate the general behavior. The model is free of stability, convergence, and mass-balance error problems for all applications.

H11B-0244 0830h POSTER

Microbial Oxidation of As(III) to As(V) in the Aquatic Environment: Implications for As Toxicity

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The toxicity of many elements depends strongly on the chemical species present. A good example is As. Arsenic toxicity decreases in the order of As(III), As(V), monomethylarsenic(MMA), dimethylarsenic(DMA), arsenobetaine(AB) and arsenocholine(AC). Accordingly, knowledge of the stability and transformation of As species in natural environments has significant implications for As environmental toxicity and remediation techniques for As contaminated sites such as mines. Experiments were conducted to investigate the toxic effects of As(III) and As(V), and the inter-conversion of the two inorganic As species, under two levels of total dissolved oxygen (DO=1.5 mg/L and 6.5 mg/L). The aquatic organism used was the benthic invertebrate Chironomus tentans. As(III) and As(V) were measured simultaneously in the experimental solutions, using a high performance liquid chromatograph coupled to a hexapole ICP-MS. The latter utilises a collision cell technique that eliminates $^{40}Ar^{35}Cl$ interference on ^{75}As, hence greatly improves the detection limit, precision and accuracy of analysis of As in natural water over conventional ICP-MS. The results show that under the experimental conditions, As(III) was gradually transformed into As(V) during a 48-hour period. The conversion of As(III) to As(V) was concentration dependent: 100% conversion occurred over 48 hours with 0.5 mg/L of As(III), whereas 80% and 0% conversion occurred for 2 mg/L and 8 mg/L, respectively. During the 48-hour period, all physical and chemical parameters of experimental solutions (e.g., pH, Eh and DO) remained constant. Furthermore, there was no difference in the transformation rate between low DO and high DO conditions. These results suggest that oxidation of As(III) to As(V) was not controlled by physical or chemical changes in the solutions, rather it was induced by bacteria. During the experiments, nutrients were continuously added into the solutions to feed the organism, resulting in a bacteria build-up. This conclusion is supported by a 10-day experiment that shows an increase in conversion rate at 48, 96 and 240 hours, due to a presumed increase in bacterial activity.

H11B-0245 0830h POSTER

Major and trace element hydrochemistry in a spring-fed river (Spring River, Arkansas)

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This study assesses the unique hydrology of the Spring River of Arkansas and the consequent variations in the chemistry of the waters. The Spring River supports one of the most diverse fish fauna in the south-central region of the U.S. and is an economic base for this region of Arkansas.

The mouth of the Spring River in northeast Arkansas is located at Mammoth Spring where 34 million liters of water per hour flow out of the spring mouth at a constant temperature of 150 C. The spring water is discharged from a limestone-dolostone aquifer. This slightly alkaline high Ca water "warm" end-member (zone 1) mixes with cooler downstream waters derived primarily from surface run-off. Groundwater discharge into the trunk and tributary stream beds lessens with distance from the spring. The chemistry of the waters, particularly the temperature and major solute chemistry demonstrates simple binary to ternary mixing of water sources. Along the length of the river three distinct temperature zones develop and persist year round. Zone 1 is located close to Mammoth Spring and is characterized by constant year round temperatures of 14-degress to 15-degrees C. Approximately 20 km downstream tributaries intersect the trunk stream creating a mixed zone (zone 2). Approximately 50 km down stream of the mouth the water temperature reaches its lowest average year-round temperature (zone 3).

The major and trace element chemistry of the zones are unique and therefore serve as end-member compositions for mixing models. Of particular interest to this study are the episodically high levels of nitrate in the spring water (20-30 mg/L). There is a seasonally defined trend of nitrate concentrations decreasing with distance from the spring mouth. Superimposed on this trend are recurrent high nitrate levels derived from small tributaries approximately 20-30 km down stream from the spring. Early studies associated the high nitrate levels with effluent from the State and Federal Hatcheries located downstream from the spring mouth however our results do not support the conclusion that these industries are nitrate point sources. Rather there appears to be two discrete nitrate sources, spring water and agricultural run-off into smaller tributaries (ditches). As part of this study we are assessing the feasibility that the nitrate in the spring water is geologic and is derived from the aquifer material.

H11B-0246 0830h POSTER

Groundwater-Surface Water Interactions and Floodplain Hyporheic Processes in a Highly Permeable Coastal Watershed: Implications for Management of the Cheakamus River Valley, British Columbia, Canada.

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Groundwater-surface water interactions control the extent and character of floodplain hyporheic zones, and play an important role in the quality of riparian habitats. Effective management of British Columbias coastal watersheds can be difficult, in part, because studies that investigate hyporheic zones within highly permeable floodplains are lacking. This paper describes the results of a geologic and hydrogeologic investigation of a section of the Cheakamus River Valley floodplain where groundwater-fed salmonid spawning habitat has been recently rehabilitated. Knowledge of the river-groundwater (hyporheic) processes is required for the preservation of off-channel and riparian habitat quality. Well logs, ground penetrating radar, seismic refraction, shallow pit sedimentology and geological reconnaissance mapping have been used to construct hydrostratigraphic models of the Cheakamus valley-fill. Measurement of floodplain water tables, and groundwater and surface water geochemical sampling have been used to refine the conceptual models for future numerical modelling of floodplain hyporheic processes at the regional and reach-scale.

H11C MC: Hall D Monday 0830h

Current Issues in Hydro-Ecological Controls on Nutrient Dynamics and Export From Forested Catchments I *(joint with B)*

Presiding: **I F Creed,** The University of Western Ontario**; C L Tague,** San Diego State University

H11C-0247 0830h POSTER

Potential Controls of Nitrate Losses From Forested Basins in the Oregon Coast Range

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Numerous factors may control losses of dissolved nutrients from forested basins in the Oregon Coast Range. Potentially important factors include forest composition, stand age, forest management, grazing, agriculture, sewage inputs and bedrock types, as well as others

perhaps not previously appreciated. With understanding of processes and controls may come the ability to model, predict and extrapolate current and future conditions across the Coast Range. To better understand the controls on nutrient losses from coastal watersheds, we sampled over 45 sites on the main stem and tributaries of the Salmon River in the Oregon Coast Range monthly since January 2000. The Salmon River basin is characterized by old soils with large stores of soil nitrogen, presumably resulting from long-term inputs by nitrogen fixing red alder. We measured all major chemical constituents, with a focus on organic and inorganic nitrogen, and also determined instantaneous stream flow at approximately two-thirds of our sites.

Nitrate concentrations in these streams ranged from zero to nearly 200 ueq/l nitrate-N. Our data to date show a surprising correlation between losses of nitrate from the basin and losses of chloride, indicating that the inputs of chloride from sea spray play a role in nitrogen losses from these watersheds. In addition, at equal chloride concentration, areal coverage of alder within sub-basins is positively related to stream nitrate concentration.

H11C-0248 0830h POSTER

Origins and Bioavailibility of Dissolved Organic Nitrogen Exported From Undisturbed Watersheds

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Dissolved organic nitrogen (DON) comprises approximately 50% of the soluble fixed nitrogen exported from unaltered watersheds, yet little is known about its chemical composition, origins, and biological lability. Seasonal changes in the chemical composition and bioavailibility of DON were investigated in two second-order streams draining subalpine watersheds that receive low rates of N deposition (ca. 3 kg/ha/yr). Concentrations of DON peaked sharply during early spring runoff and were weakly related to discharge over a two-year period. Concentrations of nitrate were related strongly to water temperature and were influenced by biotic factors. Chemical fractionation using XAD-8 resin indicated that DON was a dynamic pool of organic matter that undergoes temporal changes in composition. During the study period, approximately 60-80% of DON was of non-humic origin. The proportion of humic DON increased during snowmelt. The relative carbon and nitrogen content of each fraction also changed at this time, but displayed contrasting patterns. The C:N ratio of humic substances increased during snow melt, and the C:N ratio of non-humic substances decreased to values below 10 suggesting a release of highly labile DON from the watershed. Over an annual period, concentrations of non-humic DON were strongly related to concentrations of nitrate suggesting the importance of biotic influence on production of this fraction of DON. Bioavailibility assays indicated that changes in the lability of DON were related to composition. The pool of non-humic organic matter, which is the main source of DON in undisturbed watersheds, is likely to be affected in the future by increased atmospheric N deposition and subsequent increases in N availability and mineralization in soils.

H11C-0249 0830h POSTER

Spatial Variability of Nutrient Concentrations and Stream Temperatures within the McKenzie River Basin: Abiotic and Biotic Controls

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Ecosystem controls of nutrient dynamics and of stream temperature are complex, especially as we scale from headwaters to larger systems. Water temperature is influenced by biotic, climatic, hydrologic and geomorphic factors, yet the interactions of these factors contributing to spatial variation in temperature is not well understood. Similarly, how well can we predict nutrient dynamics with increasing drainage area of streams? Can nutrient concentrations be interpolated or extrapolated from known points within the stream network?

Independent measures of stream temperature and stream nutrient concentrations within the McKenzie River Basin reveal the influences of flow path and hydraulic retention times as dominant factors for stream temperature and phosphorous. Stream flows originating from subsurface aquifers have distinct phosphorous and temperature signals compared to those from near surface sources. In this region, P concentrations are highly influenced by volcanic bedrock and streams with the highest P also have cold summer temperatures, suggesting that their source of water is deep aquifers, with long residence times of water. Geomorphic controls (substrate type, hyporheic flow and groundwater inputs) can have as large an impact on diurnal stream temperature dynamics as the removal of riparian vegetation. Conversely, nitrogen dynamics and dominance of DON versus DIN are less predictable. Previous experiments showed rapid transformation of ammonia to nitrate, leading to a hypothesis of increased nitrate concentrations with distance downstream at low flow. However, synoptic nutrient sampling from first- through eighth- order streams and rivers found the highest nitrate concentrations and greatest variability among first- and second-order streams. Larger streams within the H.J. Andrews Experimental Forest and downstream to the confluence of the McKenzie River with the Willamette showed less variability. Surprisingly, downstream sites had lower nitrate concentrations than upstream, even with point and non-point anthropogenic inputs. These results confirm that abiotic processes are controlling availability of P in streams, while species of N are more tightly coupled to biotic mechanisms and transformations. Synoptic nutrient sampling along the longitudinal gradient of rivers coupled with mechanistic studies at headwater sites will increase our understanding of biotic and abiotic interactions which influence nutrient retention and release from basins.

H11C-0250 0830h POSTER

Nitrate and Phosphate Concentration Trends in Selected Puerto Rico Rivers over the Past Four Decades–The Impact of Human Activity on Tropical Island Landscapes and Water Quality

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For more than four decades, the U.S. Geological Survey (USGS) has collected riverine nutrient concentration data in Puerto Rico, a mountainous Caribbean tropical island. During the last forty years the population of this 9043 square km island has increased from about 2.4 to 3.8 million people. Much of the island has been developed for agriculture, and later for industry and urbanization. Data from gaging stations located within four of the larger, mixed land-use drainage basins of Puerto Rico were compiled and analyzed. The stations selected were the Rio Grande de Manati at Highway 2 (Station 50038100), Rio de la Plata at Highway 2 (Station 50046000), Rio Grande de Patillas near Patillas (Station 50092000), and Rio Grande de Anasco near San Sebastian (Station 50144000). Analytical results were compared with a shorter-term data set from smaller forested watersheds (that are part of the USGS Water, Energy, and Biogeochemical Budgets (WEBB) Program) to evaluate the impact of human activity on the water quality. During the 1960's, discharge weighted average concentrations (DWAC) of dissolved nitrate-nitrogen (nitrate-N) ranged from 0.10 to 0.51 mg/L in the four rivers. DWAC of nitrate-N increased and peaked in the 1970's and 1980's (range of 0.35 to 1.00 mg/L), and have subsequently decreased (range of 0.30 to 0.95 mg/L). DWAC of nitrate-N declined, even though the average nitrate-N concentration continued to increase in three of these rivers. The decrease in DWAC of nitrate-N may reflect the changes in land use from the 1960's to present, which includes an increase in forest and a decrease in cropland throughout much of Puerto Rico. However, the largest decrease (from 0.77 to 0.34 mg/L) occurred in the Rio de la Plata after it was dammed in 1974.

DWAC of nitrate-N in the four rivers were several times higher than the total nitrate-N observed at gaging stations in undisturbed forested watersheds, such as at the Rio Mameyes near Sabana (Station 50065500) and the Rio Icacos near Naguabo (Station 50075000), where DWAC of the total nitrate-N were 0.09 and 0.10 mg/L, respectively. Forest disturbance associated with the passage of Hurricane Hugo, in September 1989, more than doubled the nitrate concentration in streams draining the forested watersheds for a number of months afterward. But Hurricane Georges, which greatly affected the entire island in September 1998 did not cause a similar increase in dissolved nitrate concentrations in the larger rivers. The average nitrate-N yields (calculated by multiplying the DWAC by total runoff) at the gaging stations on the larger rivers ranged from 2.0 to 8.6 kg/ha/yr, which is only slightly higher than the range of 1.8 to 4.6 kg/ha/yr observed for streams draining forested watersheds.

DWAC of total phosphate-phosphorous (phosphate-P) have remained comparatively constant through three decades of measurement in both the larger, mixed land-use basins and the smaller forested watersheds. In the four larger rivers the DWAC of total phosphate-P ranged from 0.03 to 0.32 mg/L, while in the smaller forested watersheds, DWAC of total phosphate-P were lower, and ranged from 0.001 to 0.003 mg/L. The average total phosphate-P yields at the gaging stations on the larger rivers ranged from 0.5 to 1.4 kg/ha/yr, which is much higher than the range of 0.03 to 0.07 kg/ha/yr observed for streams draining forested watersheds. These low concentrations suggest the rivers are phosphate limited.

URL: http://pr.water.usgs.gov/webb/

H11C-0251 0830h POSTER

Long-term Changes in Lake Nutrient and Trophic Status in the Sierra Nevada: Results From Synoptic Surveys and Intensive Monitoring of Emerald Lake, California

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Long-term monitoring of nutrient and seston conditions in subalpine Emerald Lake (Sequoia National Park) has revealed several significant trends during the last two decades. Nitrate, both during spring runoff and during growing seasons declined by more than half from 1988 through 1998. Declining snowmelt nitrate peaks were associated with changes in snow regime induced by the 1987-1992 drought. Our evidence suggests that growing season trends were primarily the result of increased P-supply to the lake and the release of phytoplankton from P-limitation. Contemporaneous with these nutrient supply changes was an increase in phytoplankton biomass and a shift towards more frequent N-limitation of phytoplankton growth. Particulate carbon levels in the late 1990s were more than 3-fold greater than in the early 1980s; Emerald Lake may have experienced mild eutrophication due to increased P-loading. These site specific trends in nitrogen and phosphorus were also reflected in a larger set of Sierra Nevada lakes (n = 38) sampled as part of synoptic surveys conducted in 1985 and 1999 suggesting that lakes throughout the Sierra Nevada are becoming more productive in response to increased nutrient loading. Our data indicate that critical loads for nutrient deposition in the Sierra Nevada appear to be $<$ 5 kg/ha/yr for N and $<$ 0.1 kg/ha/yr for P. Possible causes for higher P-supply to Sierra Nevada lakes include: (1) atmospheric transport of organo-phosphate pesticides and fertilized soils from the Central Valley of California, (2) increased cycling of sediment P and (3) increased weathering of P-bearing minerals within catchments.

H11C-0252 0830h POSTER

Nutrient Storage and Release Following Perturbation of an Experimental Forest Ecosystem

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Chemical weathering and chemical denudation are being studied in a sandbox red pine ecosystem at the Hubbard Brook Experimental Forest. The sandbox is a 7.5 m x 7.5 m x 1.5 m granitic sand-filled lysimeter with suction porewater samplers installed at 15 cm, 35 cm, and 95 cm depths, and a tipping-bucket drainage collector at the bottom. In May of 1998, photosynthetic input to the subsurface was halted by removal of the above-ground portions of the 15-year-old trees. The purpose of this perturbation was to study subsurface hydrology and decomposition in the absence of physical disturbance, and their effects on nutrient loss from the system.

Elimination of transpiration has increased water and nutrient export while drainage concentrations have remained the same if not increased. The greatest concentration increases for all ions occur at the 15 cm porewater depth. Potassium and chloride both show large increases shortly after the tree cut, and calcium, magnesium and nitrate all show large increases the second growing season after the tree cut. Sodium and fluoride concentrations have shown little change in response to the cut. For all ions, concentrations are markedly independent of discharge and porewater residence time, i.e. there is little evidence of kinetic water-mineral reactions. Nutrient mass balances and nutrient ratios in drainage indicate that most of the nutrients released are from the litter layer. Results of this study suggest that a combination of soil-chemical and decomposition mechanisms along subsurface flow pathways can attenuate nutrient loss from perturbed sites, whereas surface runoff pathways may amplify nutrient loss.