

H11C-04 0915h INVITED

Hydrologic and Geochemical Transport Processes in Mine Waste Rock

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A mid-scale waste rock pile experiment (8 m x 8 m x 5 m high) has been ongoing at the Cluff Lake Mine in northern Saskatchewan since 1998. The gneissic waste rock, derived as run-of-mine rock from an open pit, has an average sulfide content of 0.6 wt% S, and yields drainage water with a pH between 3.2 and 4. Waste rock was placed upon a contiguous grid of 16 lysimeters located at the base of the pile. In addition, during construction of the pile, TDR probes and soil water solution samplers were located at various depths beneath the surface of the pile. Results are presented that summarize: (1) the behavior of unsaturated fluid flow and solute transport through heterogeneous waste rock, (2) the hydrologic response to placement of a low-permeability cover on the experimental pile in August 2002, and (3) solute loads released from the waste rock pile. The utility of small-scale laboratory tests to predict metal release at the field scale will also be considered.

H11C-05 0930h

Numerical modeling of soil covers for mine waste rock

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This project consists of studying some key hydrogeological properties of mine waste rocks and cover materials. The main objective was to evaluate the factors that influence flow of water in these materials, and to be able to improve the characterisation methods using numerical models. To do so, field work was completed on a waste rock pile of a mining operation in the southwest United States. Following this, a series of laboratory tests was done on samples of waste rock and of a potential cover material. Using these results, numerical calculations were performed to investigate the unsaturated flow conditions in the pile, for various configurations and properties. The numerical models, which were based on a typical geometry of waste rock dumps, show that the water entry value of the materials can play an important role in the amount of infiltration into the waste rock. The efficiency of covers was also investigated through these calculations. For a semi-arid climate, such as the one observed on the mine site, it is common to use the cover to try to limit water inflow (as opposed to limiting the oxygen flux) into potentially acid generating waste rock. A "Store, Divert and Release" cover (SDR) can typically be used to meet this objective. Different cover configurations have been studied, including a monolayer built with overburden from the mine site, and a multilayered cover composed of a coarse-grained material sandwiched between two layers of fine-grained material. The main results are presented and discussed in the paper.

H11C-06 0945h

Simulating Acid Mine Drainage Through Unsaturated Waste Rock Piles

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Acid mine drainage (AMD) through unsaturated waste rock piles is numerically simulated to gain insight into the governing physical and chemical processes. The simulations include unsaturated flow, oxygen diffusion, sulphide mineral oxidation, advective-dispersive transport of the oxidation products and pH-dependent geochemical reactions including mineral precipitation and dissolution. The waste pile models are considered as 2D structured porous systems under steady-state flow conditions. The simulations highlight the influence of grain size and moisture content on reaction rates and AMD. Fine-grained sulphide-bearing zones, proposed as internal capillary barriers for example, have a high specific surface area which tends to increase the local sulphide oxidation rate. On the other hand, these zones preferentially retain moisture which reduces the oxygen diffusion coefficient thereby decreasing the reaction rate. The results suggest that where these layers are not fully saturated, sulphide oxidation may continue at a high rate. A sensitivity analysis shows the effect of increasing the background quantity of buffering minerals, and the effect of moisture-dependent diffusion rates and sulphide mineral fractions. Issues related to flow instability and development of preferential flow zones are discussed. These types of simulations can be used to help design waste pile geometries and internal structures (e.g. capillary barriers) which will minimize or control discharge of acidic effluent.

H11C-07 1000h

Modeling Analysis for Characterizing Sulfate Reduction at an Acid Mine Drainage Site

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A field site has been established at Davis Mine, an abandoned pyrite mine in rural Rowe, Massachusetts in the United States. At the site, attenuation restricts the extent of AMD in both the groundwater and surface water of the area. Current research is examining the Fe(III) and sulfate reduction along with a complex community of acidophilic and acid-tolerant anaerobic microorganisms. In an effort to interlink the geochemical reduction with the microbial community existing in the site, the role of the Fe(III) and sulfate reducing bacteria is being investigated. Initial experimental data and column studies have shown the presence of sulfate reducing bacteria at the site. A detailed groundwater flow model for the affected site has been developed. A model is currently being developed of the various geochemical and biological processes at Davis Mine for use in distinguishing between sulfate reduction and dilution as they affect observed sulfate attenuation.

H12A CC: 520 C Monday 1030h

Isotope Tracing of Water and Carbon Cycling Processes in Large River Basins II (joint with B)

Presiding: P Aggarwal, International Atomic Energy Agency; J J McDonnell, Oregon State University

H12A-01 1030h INVITED

Stable Carbon Isotope Composition and Dynamics of Particulate Organic Carbon in the Basin of the Ganga-Brahmaputra River

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The Ganga-Brahmaputra River ranks first for sediment transport among world rivers, with high erosion rates in the Himalayan range driving the high suspended flux. The organic carbon (OC) burial flux in the Bengal fan has been estimated to be around $1.1 \times 10^{12} \text{ molC yr}^{-1}$ for the Neogene and could represent about 10% of the global burial flux of OC in continental margins. This stresses the importance of assessing the sources of the organic matter in the Himalayan watersheds and the chemical processing of organic matter on the flood-plain. To follow the dynamics of particulate OC, we used natural ^{13}C -labelling of OC, which is essentially linked to the variable proportion of C3- and C4- plants on the watersheds, together with the mineralogical, chemical and isotopic (ϵ_{ND}) data of the associated silicates. The stable isotope compositions of OC were measured (1) in bedrocks, soils, and river sediments from an Himalayan watershed (Narayani River, Nepal), (2) in river sediments at several outflows of the range, and (3) in soils and river sediments on the Bangladeshi flood-plain. In the watershed of the Narayani River, the $\delta^{13}\text{C}$ values of OC range from 26.3 to 22‰ for the bank sediments and from 24.2 to 22‰ for the suspended sediments. They present a narrow range of values around 24‰ at the outflow of the Himalayan range. They are less negative than those of OC in forest soils, hence indicating a significant contribution from the deforested, subtropical zone. On the Bangladesh flood-plain, sediments from the Ganga and Brahmaputra Rivers are enriched in ^{13}C (with $\delta^{13}\text{C}$ values around 22.5‰) relative to those collected at the range's outflow. This indicates addition of organic matter derived from the mixed C3-C4 biomass on the flood-plain. In sediments of the Ganga and Brahmaputra Rivers, the clay-size fraction is depleted in ^{13}C relative to the bulk sediment. A possible explanation is that the organic matter associated with the clay-size fraction is essentially originating from the Himalayan watersheds.

H12A-02 1045h

Isotopes of dissolved carbon and sulphur in large Canadian river basins: coupled sulphide-carbonate weathering and CO2 release

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Chemical weathering rates and associated CO2 fluxes have been calculated for three major watersheds of the western Canadian Cordillera and for the Ottawa River basin from major element concentrations and $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) in river water. Weathering rates and sources determined from major elements are consistent with $\delta^{13}\text{C}$ values (-17.0 to -2.7 permil vpdb) derived from the mixing of three sources of DIC: (i) silicate dissolution by carbonic acid (-17); (ii) carbonate dissolution by carbonic acid (-8.25); and (iii) carbonate dissolution by sulphuric acid derived by oxidative sulphide weathering (+0.5). Isotopes of sulphur and oxygen in the dissolved sulphate ion are used to separate the amount of sulphate released by sulphide weathering from that contributed by cyclic salts. In the Cordillera, DIC fluxes due to coupled sulphide-carbonate weathering are roughly equivalent to those for silicate weathering. This is less the case for the more geologically mature Ottawa basin. Coupled sulphide-carbonate weathering may therefore provide a long-term source of atmospheric CO2 offsetting silicate weathering CO2 drawdown. The magnitude of this source depends on the tectonic and geological setting.

H12A-03 1100h

Carbon Geochemistry in the St. Lawrence River: Isotopic Approach

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The St. Lawrence River ranks 16th in the world for its mean annual discharge and 13th for its watershed area (~1,000,000 km²). One of its major particularities lies in the size of the Great Lakes, at its head (245,700 km²). The mean residence time of water in the Great Lakes exceeds 100 years, resulting in relatively buffered physico-chemical properties of the water flowing through the river. The St. Lawrence

River carries very low suspended particulate matter to its estuary compared to other major rivers. As a result, low concentrations of particulate organic carbon (POC) are observed downstream in opposition to relatively high concentrations of dissolved organic carbon (DOC). We investigate sources, cycling and fluxes of both dissolved and particulate organic carbon in the St. Lawrence River from its source (the Great Lakes outlet) to its estuary, as well as in two of its tributaries. Special attention is given to seasonal patterns by using data collected on a bi-monthly basis from mid-1997 to late 2001. Concentrations and $\delta^{13}\text{C}$ measurements of dissolved inorganic carbon (DIC), DOC and POC as well as elemental dissolved organic matter (DOM) and particulate organic matter (POM) C:N ratios are used to calculate carbon fluxes and to discriminate aquatic vs. terrigenous sources. In the St. Lawrence River itself, POC is mainly of aquatic origin and is depleted in ^{13}C by roughly 13‰ vs. dissolved CO_2 . In the Ottawa River, St. Lawrence River's most important tributary, POM seems to be mainly terrigenous. In a small tributary of the St. Lawrence River, POM is aquatic in summer and terrigenous in winter. DOM seems to be terrigenous at all sampling sites with some influence of DOM derived from aquatically produced POC in summer in the St. Lawrence River at the outlet of the Great Lakes as well as one of its small tributaries. Flux calculations suggest that DOC is heavily degraded in the riverine portion of the St. Lawrence system in summer and fall. On a yearly basis, DOC losses represent about 10% of DOC exports to the estuary. The St. Lawrence River annually exports 1.38×10^{12} g of DOC (2000-2001), 0.11×10^{12} g of POC (average for 1999 and 2000) and 5.4×10^{12} g of DIC into its estuary. Finally, carbon fluxes from the St. Lawrence River to its estuary can be estimated from water discharge rates.

H12A-04 1115h

Constraining the Variability in Ages, Sources and Reactivity of Organic Matter Transported by Rivers of the Northeast U.S. to the Ocean Margin

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Riverine transport of organic carbon (OC) is a significant flux in the global C budget, representing major terms for both terrestrial losses and ocean margin inputs. Rivers are also dynamic systems where the chemical and isotopic character and reactivity of terrestrial OC is modified prior to its export to the margins. However, several major unknowns still exist in land-ocean OC fluxes, including: i) the amounts, ages and character of the OC reservoirs mobilized and transported; ii) the scales of variability in these parameters both within and among different systems; iii) the extent of modification of these parameters by microbial and abiotic processes during riverine and estuarine transport. The use of natural radiocarbon in aquatic and marine studies provides unique source, turnover and processing information with respect to local, regional and global carbon budgets. However, the number of C-14 analyses in most river systems is often too small, thus limiting the full potential of this isotope in carbon studies. As part of our on-going work, we are measuring the C-14 signatures and ages of dissolved and particulate organic carbon (DOC and POC, respectively), as well as dissolved inorganic carbon (DIC), in a group of northeast U.S. rivers. Here we report the ranges in radiocarbon signatures of bulk DOC, and POC, DIC and their associated $^{13}\text{C}/^{12}\text{C}$ ratios from measurements on seven different river systems. The rivers studied occupy a relatively small geographic range, yet individually they export both ancient and fully modern average-aged C to the coastal ocean. In addition, microbial heterotrophy appears to be responsible for the loss of both contemporary and highly aged OC, depending upon the dominant sources to a given system. While sample numbers still preclude an in-depth understanding of the sources and fates of different aged components in river systems in general, the data set permits some preliminary

conclusions concerning the relative importance of wetlands, ancient marine organic matter, and within-system modification as key potential controls on riverine C ages.

H12A-05 1130h

Results From A High Resolution In-Situ Water Quality Monitoring Program: What We Don't Know About Nitrate Flux from Watersheds

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Measuring the flux of nutrients from watersheds to the coastal ocean is important because increasing nitrogen, phosphorus and sediment loads in may rivers are degrading aquatic ecosystems. Management programs aimed at reducing nitrate contamination in surface waters need a comprehensive understanding of sources and fundamental processes that control water quality on a watershed scale. Over the past three years, the RiverNet Monitoring Program has made hourly measurements of nitrate concentrations at six stations in the Neuse River Basin, NC on the mid Atlantic coastal plain. Hourly nitrate concentrations exhibit significant variations on short (hourly to daily) time scales associated with point source dischargers. Nitrate fluxes calculated from hourly measurements differ from daily-calculated fluxes by 10% to 30% depending upon discharge conditions. These findings indicate that significant errors can be produced by monitoring programs that try to determine long-term trends of basin scale nitrogen flux without high-resolution data sets in basins with large point sources. Isotope techniques have been used to identify nitrogen sources and describe nitrogen transformations in watersheds and groundwater. Nitrogen, oxygen, and carbon isotopes of nitrate and POM indicate that in-stream nutrient consumption in the main channels is not an important process in nitrate transport to the estuary. This system is light limited by sediment turbidity, yet the concentration of nitrate decreases down basin. Geology and groundwater hydrology influence nutrient/discharge relationships. Dissolved phosphate and $\text{HD} / ^{18}\text{O}$ values of river and groundwater indicate that decreased nitrate concentrations in the lower basin result from significant deep groundwater addition and not in-stream consumption. In urban and agricultural watersheds, $^{15}\text{N} / ^{18}\text{O}$ relationship of nitrate indicates that atmospheric deposition may be important. ^{17}O measurements of riverine and groundwater nitrate indicate that atmospheric deposition can be a significant contributor (90%) to nitrate flux in urban watersheds, but contributes less than 10% of the nitrate flux in the basin as a whole. In the Neuse River basin, water discharge and nitrogen flux are positively correlated to ENSO variations (El Nino Southern Oscillation Index). Long-term nitrogen flux trends must take the ENSO cycle into account. These results indicate that current monitoring programs have tremendously underestimated the flux of nitrogen to the coastal ocean.

URL: <http://riversnet.ncsu.edu>

H12A-06 1145h INVITED

Hydrologic and Biogeochemical Controls on the C and N Isotopic Compositions of Particulate Organic Matter in Large US Rivers

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Particulate organic matter (POM) samples were collected bi-weekly to monthly from 40 NASQAN (National Stream Quality Accounting Network) river sites in the Mississippi, Colorado, Rio Grande, and Columbia River Basins from 1996 to 2001. These samples were analyzed for carbon and nitrogen stable isotopic compositions, and C:N ratios. The goal of our study was to use the isotopic compositions of POM samples, along with the abundant ancillary chemical and hydrological data generated by the NASQAN program at the same sites and dates (<http://water.usgs.gov/nasqan/>), to quantify seasonal and spatial changes in the POM and other nutrient sources, and to investigate in-stream biogeochemical processes in these large river systems. The d^{13}C values for these sites ranges from less than -40 to about -17 permil. The d^{15}N values range from about -30 to +30 permil. The combined use of the isotope data, C:N values, water chemistry, and hydrological data allow

the determination of the seasonal changes in the contributions of POM from different terrestrial and riverine sources. These data also provide insight into seasonal and spatial controls on sources of nutrients to the rivers and biogeochemical processes in the water column. On average, about half of the POM from these rivers is composed of plankton and/or heterotrophic bacteria. However, there is considerable seasonal variation in the relative proportions, mainly related to algal blooms and seasonal changes in discharge amounts from different upstream sources. Our data suggest POM derived from in-stream productivity, since it is biologically labile, may be an important but overlooked contributor to hypoxia in the Gulf of Mexico and other coastal areas.

H12B CC: 520 A Monday 1030h

Remote Sensing, Hydrology, and Field Experiments II

Presiding: T J Jackson, USDA Agricultural Research Service; B Crosson, Global Hydrology and Climate Center

H12B-01 1030h

Reanalysis Approach to Land Data Assimilation

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A reanalysis data assimilation framework in which remote sensing measurements are merged with a conventional land surface model to estimate soil moisture (surface and profile) and associated surface fluxes is presented. Formally known as smoothing in the control literature, the framework combines data from future and past an estimation time to form an estimate. This differs distinctly from filtering which uses data sequentially, yielding an estimate based only on current and past data. Through use of additional information on how the system evolves, the smoothing approach yields improved estimates of the state at the present time. Traditional smoothers such as the Rauch-Tung-Striebel (RTS) smoothers are optimal batch estimators as Kalman filters are optimal sequential estimators. Nevertheless in their traditional form both are limited to linear systems. Linearization of either the Kalman filter or the RTS smoother is seriously prone to unstable growth of the covariance matrices. Artificial limits on the propagation of the covariance matrix can result in suboptimal filters and poor estimation. Ensemble techniques have been developed for Kalman filters in order to avoid the linearization of the system equation. The framework presented here builds an ensemble smoother from a successful ensemble Kalman filter. An advantage of ensemble techniques is that we do not need to linearize or find the adjoint of the model, so we can use a mainstream land surface model (such as the NOAA Land Surface Model) in the data assimilation framework. By using a reanalysis rather than filtering approach, we can extract more information from the observational data available. The development and testing of the ensemble smoother as well as its application to land data assimilation is presented.

H12B-02 1045h

Variational Assimilation of Multi-Sensor Satellite Imagery for the Estimation of Evaporation from Soil and Vegetation

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Turbulent fluxes from the surface do not have a unique signature that can be detected by remotely deployed instruments. In order to retrieve the land evaporation, the remotely sensed measurements need to be merged into models that infer fluxes from their covariations. This study is based on variational assimilation of Land Surface Temperature (LST) into a surface energy balance model. It does not require empirical relations such as those relating evaporation to vegetation