

(October 5-13, 2002) and Earth Day Week (April 20-29, 2003).

To ensure that the soil moisture data collected is of scientific use, we are seeking the guidance of the scientific community - especially the global land surface modeling and soil moisture remote sensing community - to identify the optimal timing and spatial distribution of the semi-annual, coordinated soil moisture measurement campaigns.

URL: <http://www.globe.org>

## H61B-0782 0830h POSTER

### Climate Change Impacts on Hydrology in Taiwan

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The impacts of climate change on streamflows and groundwater recharge were evaluated for Taiwan. Rainfall unevenly distributes in a year in Taiwan Island, which May through October is a wet season and contains 67% and 90% of annual rainfall for North and South Taiwan, respectively. Increasing of frequencies of both flood and drought has been observed in recent years, which is coincided with the previous climate change impact study in Taiwan based on climate change scenarios from Country Studies Program. Further analysis of the influence of climate change on streamflows and groundwater recharge were evaluated based on IPCCs SRES scenarios in this study for providing more information of hydrologic conditions under possible future climates. Impacts on streamflows were assessed in a watershed scale by using the streamflow component of the GWLF model, while impacts on groundwater discharge was evaluate in an island wide scale by calculating water balance. Climate change scenarios were derived from three General Circulation Models (GCMs), including CGCM2 by Canadian Center for Climate Modelling and Analysis, HADCM3 by Hadley Centre for Climate Prediction and Research, and CSIRO-Mk2 by Commonwealth Scientific and Industrial Research Organization. These GCMs simulate climate based on SRES scenarios, which A2 and B2 scenarios were adopted in this study. The uncertainty of applying the predictions of global scale models and applying different GCMs are also concerned.

## H61B-0783 0830h POSTER

### Hyporheic Potential as a Mechanism for Variation in Stream Temperature Along the Umatilla River, Oregon.

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Groundwater and surface water interaction create patterns of thermal diversity crucial to normative ecosystem function. Native salmonids utilize upwelling hyporheic water, which both, create and expand critical cold water refugia. Using several known factors for hyporheic exchange, we created a potential hyporheic influence using 30-meter Digital Elevation Model data. Trend in valley width, stream slope, trend in floodplain width, variance in slope and sinuosity were derived from the DEM data and combined in to an estimate of hyporheic potential. We compared several known stream temperature influences to hyporheic potential. These influences include riparian shade, topographic shade, tributary influences, irrigation dam influence, and reservoir releases. FLIR - Forward Looking Infrared Radiometer data was used to create a longitudinal temperature profile for mainstem Umatilla River. Potential thermal influences were compared to a continuous temperature profile of the river. Hyporheic potential explains the majority of thermal variation during a peak temperature loading period. These results suggest, at river basin scales, that hyporheic exchange is an important driver in thermal variation.

## H61B-0784 0830h POSTER

### Surface Energy Balance and The Mixed Layer at Lake Tanganyika

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Lake Tanganyika is a very large (670 by 50 km) and deep rift lake (max depth 1.5 km) in East Africa between 3.5 and 9 degree south of the equator. Mixing of the upper layers in this meromictic lake is most intense in the trade wind season (May - September). Apart from increased wind speeds, lower air temperatures and evaporative cooling of the surface layer combine to enhance mixing. Previous work indicated that correlation of evaporation and heat loss from the lake leaves room for a significant portion in the variability of heat content to be explained by other factors. The components of the energy balance which contribute to mixing were compared among seasons and between the north and south ends of the lake, over diel and annual cycles. Sensible heat and latent heat fluxes were estimated with bulk aerodynamic formulas and the heat storage change in the surface water layer was determined. Solar radiation was measured and longwave and all-wave net radiation calculated. Evaporation provided a major contribution to mixing but varied per site and over seasons. Mixing intensity was related to oxygen and nutrient cycles. Apart from evaporative cooling, sensible heat transfer and the emission of long wave radiation were important mechanisms in cooling the surface layer at night. Sensible heat transfer and outgoing longwave radiation were relatively more important at the north end of the lake, compared with the south end, in explaining nocturnal heat loss from the surface.

## H61C MCC: Hall C Saturday 0830h

### Water Quality of Natural Systems

Posters (joint with B)

Presiding: J Kirchner, University of California, Berkeley; X Feng, Dartmouth College

## H61C-0785 0830h POSTER

### An Overview and Preliminary Data of a Five-year Water Quality Study of the Yukon River

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The U.S. Geological Survey is conducting a five-year water quality study of a 3000 km reach of the Yukon River from its headwaters in the Yukon Territory, Canada to Pilot Station, Alaska near its mouth and just above tidal influence. The water quality of the Yukon River, the fourth largest river system in North America, is poorly documented and may be changing in response to warmer temperatures. Permafrost regions in the Yukon River drainage basin are melting. As permafrost melts, the frozen soil is transformed into biogeochemically active zones. Runoff moving through and across these active zones is hypothesized to increase the flux of solutes to Yukon tributaries and the main stem, ultimately changing the Yukon River water chemistry. The objectives of the five-year study are: 1) Establish a baseline describing the general water quality of the Yukon River and its major tributaries as a reference to measure future changes. This objective will be achieved by sampling the Yukon River and two of its major tributaries at five fixed sampling sites every two weeks from March through September for a total of five years; 2) Identify processes that affect or control the water quality of the Yukon River and its tributaries. This objective will be achieved by intensive

sampling campaigns at high flow in June and low flow in late August during 2002-2004. The first reach and its tributaries from Eagle, AK to the Dalton Highway were sampled during the summer of 2002. The second reach, from the highway to Pilot Station will be sampled during the summer of 2003. The third reach from Whitehorse, Canada to Eagle, AK will be sampled during the summer of 2004.

Along with discharge, a suite of geochemical parameters, including suspended sediment, quantitative mineralogy, major ions, trace elements and nutrients are being measured with emphasis on dissolved and particulate carbon, gas flux and generation of methyl mercury. Discharge and water quality sampling using equal discharge increments provide instantaneous fluxes. In addition, the occurrence and fate of constituents of environmental concern, such as mercury and other toxic metals, are being addressed. Identification of the sources and sinks of these constituents, in addition to the processes controlling their fate and reactivity, will provide an important frame of reference to assess water quality changes in the basin that may result from permafrost melting and a warmer climate. Preliminary data from fixed station sampling and the 2002 summer sampling campaign indicate that water quality in the Yukon River drainage basin is sensitive to the hydrologic state of the river. Seasonally and spatially, dissolved organic carbon (DOC) ranges from 1 to 54 mg/L, carbon dioxide ranged from 33 to 735 umols/L, and major ions such as sulfate and calcium range from 4 to 74 mg/L.

## H61C-0786 0830h POSTER

### Export of Carbon From the Yukon River and Some of its Major Tributaries

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The fate of carbon (C) in the Yukon River, select headwater streams, and major tributaries is being investigated as part of a five-year study of the water quality of the Yukon basin. Preliminary calculations of C exports from the basin indicate that the Yukon River discharged an estimated 7.37 Tg of C during 2001, as measured at Pilot Station, just upstream of the Yukon delta. Approximately 70% of the C load was transported as inorganic C and 30% as organic C. The inorganic C load was almost entirely comprised of dissolved inorganic C (DIC). The relative importance of suspended particulate carbonates in the inorganic C load increases upstream, with the corresponding carbonate content of bar sediment increasing from about 2% by weight at Pilot Station to about 12% at Eagle, AK, about 2400 km upstream, near the Canadian border. Downstream reduction of sediment carbonate content, depletion of dissolved CO<sub>2</sub> in Yukon River water during summer, and under-saturation of river water with respect to calcite suggest dissolution of particulate carbonates in the river. Organic C load at Pilot Station is nearly equally divided between dissolved organic C (DOC) and suspended organic C (SOC). The relatively high proportion of organic C associated with suspended material is most likely due to adsorption of DOC onto suspended sediment and not to particulate biomass. DOC:SOC ratios are much greater in tributaries of the Yukon, such as the Porcupine River, that have relatively small suspended-sediment concentrations. C loads at Pilot Station for 2001 indicate a yield of about 0.46 moles DIC m<sup>-2</sup> yr<sup>-1</sup>, 0.10 moles DOC m<sup>-2</sup> yr<sup>-1</sup>, and 0.10 moles SOC m<sup>-2</sup> yr<sup>-1</sup> from the Yukon basin as a whole.

URL: <http://water.usgs.gov/nasqan>

## H61C-0787 0830h POSTER

### Atmospheric Deposition Effects on the Water Quality of High-Elevation Lakes in Grand Teton National Park, Wyoming.

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Atmospheric deposition is the primary cause of acidification in lakes and streams in the United States. Mountainous watersheds tend to have a low buffering capacity for nitrogen-based acidifying compounds

because of their sparse vegetation, short growing season, poor soil development and the presence of extensive areas of exposed bedrock. Consequently, lakes and streams in mountainous areas are especially vulnerable to acidification, and other water quality impacts caused by atmospheric deposition. Increased population growth in the western U.S., resulting in increased deposition of atmospheric pollutants, means that acidification of high elevation lakes and streams is a concern for resource managers, particularly in previously pristine wilderness areas.

Grand Teton National Park (GRTE) in northwest Wyoming encompasses some of the nations most spectacular mountain landscapes, and includes approximately ninety subalpine and alpine lakes. Atmospheric deposition impacts on water quality are an issue of concern in GRTE due to: (1) increasing residential and business development in Jackson Hole; (2) increasing use of prescribed burning in and around Jackson Hole; (3) proposed oil and gas development and associated activities south, east, and west of the park; (4) agricultural practices in Idaho west of the park; and (5) metropolitan and industrial development along the western slope of the Wasatch Mountains.

The objective of our study is to determine the status and trends in water quality of twenty high elevation lakes in GRTE with respect to atmospheric deposition impacts. In the summer of 2002 we sampled twenty lakes in GRTE and the Targhee National Forest, at elevations ranging from 2000 meters to 3100 meters. Sampling parameters included pH, conductivity, major anions and cations, DOC, total N and total P. Preliminary results from these analyses will be presented, and will be compared to data collected from the same lake sites during the Western Lake Survey of 1985 and another study conducted in 1995.

#### H61C-0788 0830h POSTER

##### Hydrogeomorphic Controls on Redox Chemistry Across Boreal Upland-Wetland Interfaces

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The reduction-oxidation (redox) state of wetland pore waters plays an important role in wetland biogeochemical processes. Many hydrological interfaces have been shown to be biogeochemical hot spots due to the supply of oxidized nutrients to more nutrient limited anaerobic environments. Methylation is a by-product of sulphate reduction, one of these redox reactions. In boreal forest catchments, hydrological interfaces such as upland-wetland groundwater connections have been found to be zones of elevated methylmercury concentrations. Little is known, however, about the spatial and temporal dynamics of the redox-cline, or the specific in situ biogeochemical controls on sulphate reduction and subsequent mercury methylation. As part of the Mercury Experiment to Assess Atmospheric Loading in Canada and the United States (METAALICUS), this study examined the spatiotemporal dynamics of the redox state of groundwater along several upland-wetland transitions by measuring concentrations of oxidized and reduced iron and sulphur, pH, and reduction-oxidation potential (Eh) using in situ platinum electrodes. Hydrological controls including water table elevation, precipitation, and hydraulic head were measured. It was found that although there was a clear chemical distinction between oxic upland and anoxic wetland waters, the extent of the zones of oxidized and reduced chemical species across the interface was highly variable throughout the summer, often responding to individual hydrologic events such as enhanced oxic groundwater flow due to precipitation inputs. Moreover, patterns of chemical distribution differed greatly between the two upland-wetland transects. Across one transect, the hydrological connection between upland and wetland was episodic and event-driven with large hydraulic gradients observed under storm conditions. This led to plug-flow through the wetland and a rapid gradient in oxic species reduction at the upland-wetland interface. The other transect had deeper upland soils and thus, a continuous hydrological connection between upland and wetland. Although large changes in chemical variability were also observed under storm conditions, the distribution of redox chemical species was more closely related to groundwater flow path. In situ Eh measurements across this transect revealed rapid changes between reducing and oxidizing conditions that were closely controlled by precipitation inputs and the subsequent input of oxic groundwater from the surrounding uplands. Contrary to some previous research, increases in water table elevation resulted in more highly oxidizing conditions that were sustained for one to two days. It is on this and shorter temporal scales that many biogeochemical transformations need to be studied. Implications of the dynamics of mercury methylation will be discussed in the context of the controls on sulphate reduction and oxidation.

#### H61C-0789 0830h POSTER

##### Nutrients, Water Temperature, and Dissolved Oxygen: Are Water Quality Standards Achievable for Forest Streams?

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Water quality standards provide a performance measure for watershed managers. Three of the most important standards for rivers and streams are the key nutrients, nitrogen and phosphorus; water temperature; and dissolved oxygen. The concentration of nitrogen and phosphorus in waterbodies affects primary production and productivity. Too little nutrients and streams are sterile and unproductive. Too much and they are eutrophic. Water temperature is important because it influences chemical reaction rates in streams and metabolic rates in fish. Dissolved oxygen is necessary for respiration. Salmon, the focus of much of the conservation efforts in the Northwest, are known as organisms that require cool, highly oxygenated water to thrive. Still, it is important when setting a performance standard to determine if those standards are achievable. A survey of nutrient data for small forested streams has found that the ecoregion guidelines proposed by EPA are often unachievable, sometimes even for small, unmanaged reference watersheds. A pilot survey of water temperatures in Oregon wilderness areas and least impaired watersheds has found temperatures frequently exceed the state standards. While natural temperature exceedances are addressed in the water quality standards for Oregon for unmanaged watersheds, these temperatures for managed watersheds might be presumed to result from management activities, precipitating an expensive Total Maximum Daily Load (TMDL) assessment. Less is known about dissolved oxygen for small forest streams because work 20 years ago showed little risk of significant dissolved oxygen concentrations where shade was maintained near the stream and fine slash was kept out of the stream. However, work from the 1970's on intergravel dissolved oxygen also shows that stream with greater large woody debris (LWD) can have lower intergravel dissolved oxygen concentrations, presumably due to trapping of fine organic and inorganic materials. Efforts to add LWD to streams could potentially depress intergravel dissolved oxygen. To avoid making inappropriate decisions based on these performance standards, watershed managers need to understand expected water quality patterns based on the physical, chemical, and biological factors that influence water quality.

#### H61C-0790 0830h POSTER

##### Nitrate and Aluminum Transport Through Soil Layers in a Clear-Cut Watershed

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The 24-ha Dry Creek watershed in the Catskill Mountains of New York State was clear-cut during 1997 to evaluate nutrient release to New York City reservoirs due to forest harvesting. The Dry Creek watershed is in the headwaters of the Neversink watershed, which is part of the New York City Reservoir system that supplies drinking water to over 20 million people. Soil water, groundwater seeps, and stream water chemistry were monitored to trace the transport of solutes before and after the timber harvest. Automated sequential zero-tension lysimeters and standard zero-tension lysimeters were installed at depths of 70, 300, and 500 mm to sample soil water in the O, B, and C-horizons, respectively. Pre-cut (water years 1993-1996) mean soil water concentrations from zero tension lysimeters indicate that O-horizon soil water (70 mm depth) had the highest nitrate ( $\text{NO}_3^-$ ) and monomeric aluminum ( $\text{Al}_m$ ) concentrations (73 and 18  $\mu\text{moles l}^{-1}$ , respectively). During that same time period water from ground-water seeps had lower  $\text{NO}_3^-$  and  $\text{Al}_m$  concentrations (22 and 0.88  $\mu\text{moles l}^{-1}$ , respectively) than any soil waters sampled. During the two years following the clear-cut, groundwater seep  $\text{NO}_3^-$  concentrations were 138-123  $\mu\text{moles l}^{-1}$  and  $\text{Al}_m$  concentrations were 50-30  $\mu\text{moles l}^{-1}$  lower than that measured in soil water. Throughout the same time period, B-horizon soil water had the highest mean  $\text{NO}_3^-$  concentration (345  $\mu\text{moles l}^{-1}$ ) while C-horizon soil water had the highest mean  $\text{Al}_m$  concentrations (51  $\mu\text{moles l}^{-1}$ ). But during storms in the first year after the clear-cut O-horizon soil water  $\text{NO}_3^-$  and  $\text{Al}_m$  concentrations often peaked at more than twice those measured in the B-horizon.

During the second year after the clear-cut, B-horizon storm  $\text{NO}_3^-$  concentrations were consistently greater than O-horizon concentrations. During the fourth and fifth years following the clear-cut, soil water  $\text{NO}_3^-$  concentrations had dropped below pre-cut concentrations however  $\text{NO}_3^-$  in groundwater seeps remained elevated. The  $\text{NO}_3^-$  concentration at the watershed outlet also remained above pre-cut levels. During the first years following the clear-cut, in the absence of watershed vegetation, soil  $\text{NO}_3^-$  was leached to watershed streams and to deeper groundwater. As the forest has regenerated soil  $\text{NO}_3^-$  has been immobilized while groundwater continues as a source of  $\text{NO}_3^-$  to watershed streams 4-5 years after the cut. Four to five years after the clear-cut  $\text{Al}_m$  concentrations were below pre-cut levels for all waters sampled. The elevated stream water  $\text{NO}_3^-$  concentrations that continue to be measured at the stream outlet, are not accompanied by elevated  $\text{Al}_m$  concentrations since the groundwater seeps that are the source of the  $\text{NO}_3^-$  have never been a significant source of  $\text{Al}_m$ .

#### H61C-0791 0830h POSTER

##### Nitrate and Pesticide Transport From Tile-Drained Fields in the Willamette Valley, Oregon

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Tile drainage affects the hydrology and thus the solute transport on agricultural fields by increasing the volume of water that drains from the subsurface. Previous NAWQA studies have shown elevated nitrate levels in wells and high detection frequencies for selected pesticides in Willamette Valley streams. As a substantial area of Willamette Valley agricultural land is tile drained, it is important to determine the role of tile drains in surface water and ground water pollution.

Four fields in the Willamette Valley were instrumented to monitor tile effluent for two winter seasons. On two fields, surface runoff was also monitored for the second season. Field areas ranged from 3 to 30 acres and were cropped in grass, corn, or a grass/corn rotation. Tile effluent nitrate concentrations frequently exceeded 10 ppm on some fields. Flow-weighted averages for each field were 0.87 ppm and 1.36 ppm for two established grass fields, and 8.1 ppm and 14.4 ppm for grass fields that had recently grown corn. Mass losses ranged from 1.15%-6.45% of the applied nitrate through the tile drains. Diuron, Metolachlor, and Chlorpyrifos were tested in selected surface runoff and tile effluent samples. On one field, Metolachlor concentrations were similar in the tile drains and surface runoff. Concentrations in both sources were 10 times lower than the drinking water advisory for Metolachlor. In a second field, Chlorpyrifos concentrations were two orders of magnitude lower than drinking water advisories in both sources. On the same field, Diuron concentrations were significantly higher in the surface runoff than in the tile effluent. Diuron concentrations were 1-2 orders of magnitude higher during the first precipitation events after application in the surface runoff. On a third field, Diuron was at least 10 times lower than drinking water advisories in the tile effluent, with the highest concentrations found in samples collected within 21 days of pesticide application.

#### H61C-0792 0830h POSTER

##### Discerning effects of crop management history on groundwater nitrate concentrations in two small adjacent watersheds

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Changes in agricultural management can minimize leaching of NO<sub>3</sub>-N to ground water. However the time needed to realize improvements in groundwater quality after management change is uncertain. This study was conducted in two small watersheds in the Loess Hills of southwest Iowa. They were similarly managed from 1964 through 1995, except one received large N applications (averaging 446 kg ha<sup>-1</sup> y<sup>-1</sup>) between 1969 and 1974. Our objective was to determine if NO<sub>3</sub>-N from these large applications have persisted in ground water. Transects of piezometer/lysimeter nests were installed, deep cores collected, and water levels and NO<sub>3</sub>-N concentrations were measured monthly. In June 2001, 33 water samples were analyzed for 3H, stable isotopes, and major cations. The watershed receiving the large N applications had greater NO<sub>3</sub>-N concentrations in ground water. Ground water time-of-travel estimates and tritium data support persistence of NO<sub>3</sub>-N from the historical applications. "Bomb-peak" precipitation (1963-1980) influenced tritium concentrations, especially near toeslope positions, while deep ground water was dominated by pre-1953 precipitation. Analyses of deep cores taken between 1972 and 1996 show that at the watershed divide, NO<sub>3</sub>-N takes nearly 30 years to reach groundwater at 20-m depth. Stable isotope and cation concentrations both suggest that runoff/infiltration processes contribute greater recharge to groundwater below the toeslope. Therefore both historical and current practices affect NO<sub>3</sub>-N concentrations in ground water near the stream. Impacts of recent management changes will not be clearly discerned by monitoring groundwater for many years. Management changes can take decades to fully impact ground water quality.

#### H61C-0793 0830h POSTER

##### Assessing Pesticide Contamination to Fresh Water in Some Agricultural Sites, Close to Oaxaca City, Mexico

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This study presents the results of a survey on pesticides in fresh water in shallow aquifers, rivers and dams in Zaachila, Tlaxiaco and Etla and agricultural valleys close to Oaxaca City, SW of Mexico. In the study zones, there are generalized uses of pesticides and the impact on the water resources by inadequate use of agricultural activities. Water is used for irrigation and drinking. Surveying criteria was to sample the aquifer (production wells), its water table (dig wells) and a regional water collector (Plan Benito Juárez Yuayapan dam). A total of 14 samples were analyzed for the identification and quantification of organochlorine and organophosphorus pesticides. Method was 508-EPA. Gas chromatographer was a 5890 series II Hewlett Packard, calibrated with several patterns. Results: 10 samples are contaminated with some pesticide of the used patterns; Dieldrin, Chlordano, Malathion, Mirex were not found; Traces of organophosphorus compounds were found in 8 samples, mainly Merphos, Parathion Ethylic and Disulfoton; There was detected traces of world-forbidden insecticides as Metoxychlor, Parathion Ethylic and Disulfoton; and In one sample (Cuilapam well #1) DDT exceeds, the Mexican maximum limit for potable water (1 mg/l),

#### H61C-0794 0830h POSTER

##### Spatial Dynamics of Nitrogen Hydrochemistry in a North Pennines (UK) Ecosystem

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Peat-dominated upland ecosystems represent major stores of a number of nutrient elements, including nitrogen. It is anticipated that climatic warming in such environments will increase the rate of nitrogen cycling,

potentially leading to the release of nitrogen into river waters. This could have negative effects on ecosystem function and downstream water quality. Thus, it is important to study the underlying hydrological and biogeochemical processes that control nitrogen flux and speciation in upland river waters. Currently, fieldwork aimed at improving understanding of these processes is being carried out at Moor House-Upper Teesdale National Nature Reserve, North Pennines, UK. The research focuses on two key areas: Hillslope hydrology, which is being examined using an EMMA (end-member mixing analysis) approach to identify the relative contributions of different source waters to overall channel flow under a range of conditions; and in-stream biogeochemical transformations of nitrogen species, which are being studied through chemical tracing experiments. The ultimate aim is to integrate these two pieces of research in order to improve understanding of how the hydrochemical signature of upland drainage waters is generated.

#### H61C-0795 0830h POSTER

##### Biogeochemistry of a Suburban Basin

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A long-term research effort was recently established in the Lamprey River basin in southeastern New Hampshire. The watershed is largely forested, and has significant amounts of wetlands due to the relatively low topographic relief. Human population growth is rapid, resulting in conversion of forest and agricultural land to housing tracts. The primary focus of the project will be to examine the relationships between land use, land cover and water quality as the watershed continues to increase in population density. A secondary emphasis will be to examine the interactions between hydrologic flow paths, climatic variability, and biogeochemical processes that drive groundwater and surface water quality in the basin. Our initial work has quantified landscape attributes and related them to water quality. Results to date show that small tributary streams are relatively high in nitrogen relative to the main stem of the Lamprey; that human population density drives nitrate concentrations in the basin; and that DOC flux is predicted well by the model of Aitkenhead and McDowell that links DOC flux to watershed C:N ratio.

#### H61C-0796 0830h POSTER

##### Linking Seasonal Variability in the Chemistry of Urban Streams to the Loading of NOMs and PAHs Through Storm Runoff

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Loading of organic contaminants from urban watersheds through storm runoff is considered a significant source of water quality degradation in urban streams during storm events. Yet, there is still much to be learned about loading pattern of natural and anthropogenic organic substances. This study investigates the variation in the loading pattern of natural organic matter (NOM) and polycyclic aromatic hydrocarbons (PAHs) in a time series in order to help to explain the seasonal variability in the chemistry of urban streams from the perspective of runoff-water quality. Two urban watersheds with different land-use practices were studied. Water samples were collected from both the receiving streams and the parking lots of urban shopping malls, during storm events in 1999-2002. Characterization of the samples was performed by TOC, HPSEC, GC-MS NMR, and impedance analyzer, as well as in-situ water quality parameters (pH, temperature, conductivity, turbidity, dissolved oxygen, and redox potential). The results show that light molecular weight PAHs were dominant in the first flush of storm runoff after long dry periods. High molecular weight PAHs were more evident in the trailing limb of the storms even though their concentrations were not high. The implication of the analysis is that NOM may be more responsible for the enhancement of solubility of PAHs in autumn than in any other season because the NOM appeared to be 5 times more concentrated in autumn stream samples. Thus, seasonal variability of the storm runoff has to be considered to determine the transport of NOM and PAHs. Interstorm period and precipitation intensity may also be dominant parameters controlling NOM and PAHs loading patterns along with seasonal effects.

#### H61C-0797 0830h POSTER

##### Chemical and thermal variations in seeps discharged from a burning coal refuse pile

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Acid mine drainage generated by coal refuse piles is affecting the Moxahala watershed in Southeastern Ohio. The major contributor of acidity to this watershed is the Misco refuse pile. This pile was formed during the exploitation of the Misco Mine in Perry County, Ohio, in the early 1950's. In addition to the generation of acid mine drainage, the Misco Pile is burning. There is an impounded pond on the southwest end of the west gob pile, which was created when the valley was filled with refuse. The water from this pond flows into and throughout the gob pile and discharges on the northeast end into Bennet Run. At an elevation close to the elevation of the pond, two seeps are discharged. Temperature, specific conductivity, and pH was monitored in these seeps and correlated to rainfall. A lack of response of water temperature to small rainfall events was observed. This behavior suggest channeling of water inside the pile from the source pond to the main seep, and probably evaporation effects. In comparison, during high rainfall events, transfer of heat from the burning spots to the infiltrating water occurred and an increase in seep temperature was observed. A decrease in conductivity and an increase in pH was observed during the studied period as a dilution effect produced by an increased water storage within the pond and pile. Diurnal effects were stronger in the smaller seep, probably due to lower water velocities and greater residence time at the air-pile interface. From the location of the burning spots and seeps, a water velocity of 1 to 5 feet/s (0.3 to 1.7 m/s) was estimated. The pile can be viewed as a dual-porosity system of continuous conduits and matrix porosity. Only flow with sufficient head can penetrate and transfer heat from the hot areas in the matrix.

#### H61C-0798 0830h POSTER

##### Real-time Monitoring and Internet Publishing of Organic Carbon Concentrations in the Sacramento-San Joaquin River Delta

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Historically, continuous monitoring of water quality has been limited to parameters such as temperature, electrical conductance, and turbidity. The growing availability of process analyzers has expanded the range of parameters that can be monitored and has increased the frequency of measurements. When combined with the Internet, process analyzers allow real-time access to high frequency water quality data that is valuable for resource managers, utilities and researchers. In the Sacramento-San Joaquin River Delta, high frequency organic carbon (OC) data are needed: 1) to compute daily to annual loads, 2) for forecasting source-water quality at municipal water-treatment plants, and 3) for research on C biogeochemistry in the Delta estuary. The California Department of Water Resources has installed a network of OC analyzers to provide real-time monitoring of total and dissolved OC (TOC and DOC, respectively) at key points in the Delta and along the State Water Project. These analyzers perform measurements using wet chemical oxidation (Sievers TOC 800), catalyzed combustion (Shimadzu TOC 4100), and UV absorbance (Tytronic UV-254). Data are recorded on dataloggers, telemetered to a central database and published on the Internet.

Method inter-comparisons have shown that the oxidation method typically underestimates TOC and DOC concentrations. This bias was greatest during the winter months when organic carbon levels are highest and contributions from terrestrial carbon sources were at maximum. Relative-percent difference for grab samples measured with the on-line analyzers and at DWRs

analytical laboratory was less than 25%. The UV-254 sensor was the most reliable of the three methods and had a average precision of 4.4% and accuracy of 88 to 117% relative to laboratory measurements. Instrument downtime did not exceed more than 50% for any month or more than 25% for any six-month period. The main operational difficulties encountered with all analyzers were an inconsistent supply of filtered water (0.45 micron absolute) for DOC measurements. We found that appreciable amounts of organic carbon were lost when filtration efficiency fell below 0.45 microns as filters clogged.

#### H61C-0799 0830h POSTER

##### Simple Syringe Filtration Methods for Reliably Examining Dissolved and Colloidal Trace Element Distributions in Remote Field Locations

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Methods for obtaining reliable dissolved trace element samples frequently utilize clean labs, portable laminar flow benches, or other equipment not readily transportable to remote locations. In some cases unfiltered samples can be obtained in a remote location and transported back to a lab for filtration. However, this may not always be possible or desirable. Additionally, methods for obtaining information on colloidal composition are likewise frequently too cumbersome for remote locations as well as being time-consuming. For that reason I have examined clean methods for collecting samples filtered through 0.45 and 0.02 micron syringe filters. With this methodology, only small samples are collected (typically 15 mL). However, with the introduction of the latest generation of ICP-MS's and microflow nebulizers, sample requirements for elemental analysis are much lower than just a few years ago. Thus, a determination of a suite of first row transition elements is frequently readily obtainable with samples of less than 1 mL.

To examine the "traditional" (<0.45 micron) dissolved phase, 25 mm diameter polypropylene syringe filters and all polyethylene/polypropylene syringes are utilized. Filters are pre-cleaned in the lab using 40 mL of approx. 1 M HCl followed by a clean water rinse. Syringes are pre-cleaned by leaching with hot 1 M HCl followed by a clean water rinse. Sample kits are packed in polyethylene bags for transport to the field. Results are similar to results obtained using 0.4 micron polycarbonate screen filters, though concentrations may differ somewhat depending on the extent of sample pre-rinsing of the filter. Using this method, a multi-year time series of dissolved metals in a remote Rocky Mountain stream has been obtained.

To examine the effect of colloidal material on dissolved metal concentrations, 0.02 micron alumina syringe filters have been utilized. Other workers have previously used these filters for examining colloidal Fe distributions in lake and sea water. Filters are pre-cleaned in the lab using clean pH 2 water followed by a clean water rinse and then dried with clean air. Because of the significant pressure that must be placed on the syringe for some minutes to effect a filtration, a simple plastic press and stand has been devised. Polarization artifacts, which can affect this type of ultrafiltration, do not appear to be significant. This may be due to the comparatively large pore size of these filters (equivalent to approx. 40 kDa). These filters, in combination with the 0.45 micron filters, are being used in a multi-year study of trace elements in the Yukon River system.

#### H61C-0800 0830h POSTER

##### Long-term Change of a Dissolved Humic Acid as Studied by Kinetic In-situ Heating UV Spectroscopy

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Humic substances are the most abundant natural organic matter (NOM) in groundwater and sediments. Although they are considered to play important roles at the earth's surface, especially in environmental pollution, their detailed characters are not well known, because of their complexity in chemical structures. Humic substances have many functional groups capable of forming very stable complexes with heavy metals and can also retain some toxic organic and inorganic chemicals dissolved in groundwater. Therefore, structural and functional properties of humic substances and their changes with time and space are essential in evaluating their environmental impacts. In order to study first long-term thermal changes of humic substances dissolved in groundwater, we have performed a heating experiment of a representative dissolved humic

acid (a chemical reagent extracted from soil). Based on our preliminary batch experiments at 90-70 °C, the reaction rates are relatively slow and many long runs were needed to determine kinetic parameters. Therefore, we have employed here an in-situ heating cell for ultraviolet-visible spectroscopy for the real time tracing of the decrease of the humic acid by means of absorption intensity at 254 nm, which is generally used as a measure for concentrations of humic substances (also for some dissolved organic substances (DOC)). Firstly, we conducted continuous monitoring (every 10 seconds) of decrease in absorbance at 254 nm of the standard humic acid at 180 °C for accelerating the reaction. The absorbance showed a gradual decrease during one hour period suggesting 2 different linear stages in a semi-logarithmic diagram. The combination of 2 first order reactions gave a very good fitting of the experimental data points and the following 2 rate constants were obtained with high accuracy:  $1.0 \times 10^{-3}$  and  $4.6 \times 10^{-6} \text{ s}^{-1}$ . We will conduct the same type of experiments at lower temperatures to determine decrease rate constants and activation energies. The mechanisms of thermal changes of the humic acid and its life-time in groundwater and soil environments will be discussed.

#### H61C-0801 0830h POSTER

##### Organic matter sources and transport in an annually flooded alluvial fan, the Okavango Delta, Botswana.

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The Okavango Delta of northwestern Botswana is a large inland delta and alluvial fan consisting of over 25,000 square kilometers of permanently and seasonally flooded wetland. Surface waters of the seasonal swamp contain high concentrations of dissolved organic matter (DOM) which vary significantly during inundation by the annual flood. Dissolved organic carbon (DOC), the largest pool of organic carbon in Okavango Delta waters, constitutes an important component of the carbon cycle and energy balance in water systems. Results from water chemistry sampling indicate flushing of DOC during the rising limb of the hydrograph and a dilution/consumption effect on DOC during the peak flood. This increase in DOC concentrations with the onset of flood correlates with an increase in conductivity, suggesting that two dominant hydrologic mechanisms are responsible: the concentrating of dissolved ions in the groundwater by evapotranspiration and the release of dissolved ions from the groundwater during flood and recharge of the groundwater aquifer. In the absence of surface inflows, the water table drops by 1.5 to 2 meters due to transpiration, and ions become so concentrated that the groundwater is saline. Inundation of the Okavango Delta by the annual flood replenishes the groundwater aquifer and mobilizes DOM. We postulate that DOM and ions are flushed from sediment interstitial waters with the onset of the flood. A decrease in conductivity and DOC concentrations at peak flood indicates a dilution effect and an increase in zooplankton concentrations at peak flood suggests consumption of newly released organic matter by zooplankton and higher trophic organisms. Spectral properties of fulvic acids isolated from filtered water samples were also analyzed and show that the sources of organic matter vary significantly between perennial and seasonal swamp areas.

#### H61C-0802 0830h POSTER

##### Residence Time of Groundwater and its Application to Aquifer Characterization in Jeju Island, Korea

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The environmental tracers of  $^3\text{H}$ ,  $^3\text{He}$  and CFC-12 (chlorofluorocarbon-12) were employed to determine the residence time of groundwater sampled from three springs and twenty municipal wells of a basaltic aquifer and underlying sedimentary aquifers in Jeju volcanic island, Korea. Mantle He significantly affected apparent

$^3\text{H}/^3\text{He}$  ages in half of the samples. Apparent CFC-12 ages show time lag up to 17 years relative to  $^3\text{H}$  in mountainous area, which is attributed to the thick unsaturated zone.  $^3\text{H}/^3\text{He}$  systematics are in relatively good agreement with the reconstructed  $^3\text{H}$  input history in the island though some samples show higher initial  $^3\text{H}$  value than  $^3\text{H}$  input because of residence in the unsaturated zone or selective  $^3\text{H}$  diffusion from the portion of bomb  $^3\text{H}$ .

The mean residence time of groundwater is estimated in the range of 6 to 15 years in basaltic aquifer and U formation, and greater than 60 years for the wells completed in Seoguiipo formation in western coastal area by the application of lumped parameter models. The remarkable distinction of residence time in Seoguiipo formation can be attributed to the low permeable layers distributed widely enough to limit leakage from the overlying basaltic aquifer. Some groundwater samples including springs show characteristics of low degree of mixing, which indicates groundwater flow in basaltic aquifer is not significantly affected by mixing between highly permeable layers such as interflow zones. Nitrate concentrations are on the background level in the wells of Seoguiipo formation in western coastal area though nitrate contamination is conspicuous in coastal area throughout the island. This is in good agreement with the results of environmental tracer analysis.

#### H61C-0803 0830h POSTER

##### Geochemical fingerprints of waters in the Lake Baringo-Bogoria region, Kenya: Implications for hydrogeochemical processes and water quality

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Lake Baringo and Lake Bogoria lie within an asymmetric half-graben in the East African Rift, Central Kenya. Lake Baringo to the north is fresh because of subsurface outflow ( $\sim 0.8 \text{ g/l TDS}$ ;  $\text{pH} = 8.9$ ) whereas to the south, Lake Bogoria, which is hydrologically closed, is saline/alkaline (mixolimnion:  $\sim 40 \text{ g/l TDS}$ ;  $\text{pH} = 10.2$ ). The climate is semi arid ( $\text{P} < \text{ET}$ ). P on the valley floor is  $\sim 700 \text{ mm/yr}$  and  $\sim 1200 \text{ mm/yr}$  on the adjacent highlands; ET is  $\sim 2500 \text{ mm/yr}$ . The Loboi Plain ( $\sim 200 \text{ km}^2$ ) between the two lakes is comprised of Pleistocene and Holocene alluvium and lake sediments  $> 1 \text{ km}$  thick. The primary sources of water in the area are rivers draining the highlands, and hot, warm and cool springs and seeps of different salinities associated with the faults. Freshwater wetlands and rivers traversing the Loboi Plain represent a limited resource in this semi-arid environment and are heavily utilized for drinking water by the resident population, livestock, and wildlife, and for crop irrigation. To better understand the hydrogeochemical processes affecting the freshwater sources in the southern Loboi Plain, water samples that were collected from lakes, rivers, springs, and one of the large wetlands (Loboi Swamp) were analyzed for a full suite of major and minor elements. The objective of the study was to determine the extent to which the composition of water from a variety of environments could be used as geochemical fingerprints for hydrogeochemical processes.

Conservative mixing between the most dilute river-water endmember ( $\sim 0.1 \text{ g/l TDS}$ ) and the most concentrated Lake Bogoria surface water, is indicated by the covariation of  $\text{Na}^+$  with  $(\text{Alk}_T + \text{Cl}^-)$  and with  $\text{F}^-$  content for nearly all surface and spring waters in the region. This trend is consistent with an overall process of evapoconcentration of dilute meteoric water containing dominantly  $\text{Na}^+$ ,  $\text{HCO}_3^-$ , and  $\text{Cl}^-$  derived from weathering of intermediate (trachyphonolite) and basaltic volcanic rocks in the region. Spring waters feeding the Loboi Swamp are warm ( $\sim 35^\circ\text{C}$ ), with  $\text{pH} \sim 6.4-6.9$ , and compositions ( $\sim 0.25 \text{ g/l TDS}$ ) consistent with interaction of relatively shallow meteoric water with host rocks. Surface waters in the wetlands are more concentrated ( $\sim 0.3-0.5 \text{ g/l TDS}$ ) and more alkaline ( $\text{pH} = 7.1-8.2$ ) than associated springs consistent with degassing of dissolved  $\text{CO}_2$ , evaporation, and redissolution of previously deposited salts. Porewaters in marsh sediments contain higher concentrations of dissolved inorganic carbon,  $\text{NH}_4^+$ , and Fe than overlying surface water consistent with biologically-mediated organic-matter oxidation under reducing conditions. Each aqueous setting has a distinctive geochemical fingerprint that reflects the initial composition (i.e. source water) and the effects of subsequent physical, chemical and biochemical processes operating in the environment.

## H61C-0804 0830h POSTER

## Changing Water-Resources on Ile de la Gonave, Haiti

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Ile de la Gonave is a 750-square-kilometer island off the western coast of Haiti. The island is composed of Eocene and Miocene limestones unconformably overlain by Pleistocene limestone. The highest elevation is 778 meters. Annual precipitation varies across the island because of the orographic effect and ranges from 800 to 1,400 millimeters. There is no surface water except immediately after large storms. Droughts, some extending for more than one year, and frequent crop failures due to droughts have been reported. Potential evaporation is estimated to be about 2,000 millimeters at the coast, but less at higher elevations. Consequently most rain is lost through evapotranspiration; recharge to the limestone aquifers apparently occurs only after large storms and is estimated to be about 4 percent of the mean annual precipitation based on a chloride mass balance. Depth to the water table ranges from less than 30 meters in the Eocene and Miocene limestones to over 60 meters in the 300-meter thick Quaternary limestone. Average annual precipitation at Port au-Prince (50 kilometers to the east and on the main island of Hispaniola) has decreased from about 1600 millimeters in 1860s to about 1300 mm in the 1950s. Precipitation data from Port-au-Prince after the 1950s are sporadic, making further comments about climate change difficult. Even without decreasing precipitation, which may be due in part to climate change or the deforestation of Haiti, the increasing population on Ile de la Gonave has and will continue to exacerbate the scarce water supply, particularly because of the small number of sources (springs, cave pools, and wells) where people can obtain water. Women take an average of almost three hours per day to travel an average of 2.5 kilometers (one-way) to obtain water for their families. Because of the difficulties in obtaining freshwater, the 100,000 inhabitants use an average of only 7 to 13 liters per person per day. Reconnaissance field analyses indicate that ground water in the interior of the island is of a calcium-bicarbonate type, while water at the coast is of a sodium-chloride type and has mixed with as much as 20 percent seawater. Tests for the presence of hydrogen sulfide-producing bacteria were negative in most drilled wells, but positive in most capped springs and positive in all springs, cave pools, and hand-dug wells, indicating contamination of most drinking-water sources. Widespread bacterial contamination of the water is not surprising, in that there are few latrines on the island and livestock grazes everywhere, enabling waste to be washed into the drinking water sources. The contaminated drinking water likely causes typhoid fever, which is frequently seen in the one hospital on the island.

URL: <http://pr.water.usgs.gov/public/webb/>

## H61C-0805 0830h POSTER

## Water Quality of Drinking Water Supplies in Socorro, New Mexico

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Socorro, a small town with a population of about 8,000, is located in central New Mexico along the Rio Grande within the Rio Grande rift, at the edge of an extensive volcanic field. Socorro has six sources of supply for drinking water. Two of these sources are thermal springs and four are wells ranging in depth from 97-500 ft. The water is not blended into one source for distribution, but rather each source serves as drinking water for those in the immediate area surrounding the well or spring. Each source was sampled and analyzed monthly over a 2-year period. The following parameters were determined and compared: temperature, pH, conductivity, TDS, hardness, alkalinity, Cl, SO<sub>4</sub>, F, Br, NO<sub>3</sub>, Na, K, Ca, Mg, SiO<sub>2</sub>, As, Ba, Cd, Cr, Co, Cu, Fe, Pb, Li, Mn, Mo, Ni, Se, Sr, Ag, Th, U, and Zn. The monthly water usage from each source was also determined.

High levels of arsenic (up to 42 ppb) and uranium (up to 55 ppb) occur naturally in the water sources, but not together in the same sources. Based on water quality parameters, the water may be grouped into three types with two sources in each type.

Type 1. Low hardness (~70 ppm), low TDS (~240 ppm), no Fe (<5 ppb), no Mn (<5 ppb), very low U (3 ppb), and high As (~40 ppb). Type 2. High TDS (~700 ppm), high hardness (~260 ppm), high Fe (~100 ppb), high Mn (~650 ppb), low U (~6 ppb), and mid-level As (~24 ppb). Type 3. High TDS (~430 ppm), high hardness (~200 ppm), mid-level Fe (~50 ppb), mid-level Mn (~10 ppb), high U (25-55 ppb), and low As (~8 ppb).

Considering the arsenic and uranium values, type 2 water appears to be a dilution of type 1 and type 3. This does not appear to be the case when comparing

Fe, Mn, hardness, and TDS. Type 2 contains the highest Fe, Mn, TDS, and hardness. One possible explanation is that as type 1 and type 3 groundwater mixes and flows toward the river, some of it flows through areas higher in calcium carbonate and Fe and Mn mineralization producing the type 2 water which results in higher Fe, Mn, TDS, and hardness.

Interestingly, the sources with the lowest TDS or the best quality water contain the highest arsenic levels. Four of the six sources contain arsenic above the USEPA's new MCL of 10 ppb.

## H61C-0806 0830h INVITED POSTER

## Calcium Dynamics in a Marine Terrace Chronosequence: New Insights From Calcium Stable Isotopes

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Understanding the origins, distribution, transport and cycling mechanisms of calcium during progressive mineral weathering and soil development is critical to determining the status of this important ecosystem nutrient. In previous studies of Ca dynamics at the watershed scale, strontium isotopes have proven useful for identifying mineral sources of calcium and for distinguishing mineral weathering from atmospheric sources of calcium, but are inherently unable to provide information about Ca cycling during processes such as biological uptake and ion exchange. In order to gain a more direct understanding of Ca dynamics during mineral weathering, soil development and ecosystem evolution, we have initiated a study of the Ca stable isotope systematics of a chronosequence of marine terrace deposits north of Santa Cruz, California. The five terraces that comprise the chronosequence range in age from 65 ka to 226 ka, and are made up of reworked granitoid minerals derived largely from the Miocene Santa Margarita sandstone and Santa Cruz mudstone. In soil profiles collected from each terrace, Ca is concentrated mainly in plagioclase feldspar in the deepest samples and on soil exchange sites near the surface, but has been largely depleted due to weathering from intermediate-depth samples.  $\delta^{44}\text{Ca}$  values of deep porewaters from each terrace are uniform and identical to that of Ca in plagioclase (~-0.6‰/‰), consistent with a purely weathering source.  $\delta^{44}\text{Ca}$  values of shallow porewaters systematically increase with increasing terrace age from values similar to that of Ca in grasses collected from each site (~-2.0‰/‰) toward that of Ca in seawater and local precipitation (~0.0‰/‰). In contrast,  $\delta^{44}\text{Ca}$  values of intermediate depth porewaters decrease with increasing terrace age, in opposite sense to the variation observed for the shallow porewaters. We attribute this contrasting variability to the progressive development of a clay fraction over the soil profile that promotes preferential retention of relatively heavy Ca in the shallow soils and allows downward transport of relatively light Ca to intermediate depths. Our results reveal that both biotic and abiotic processes are responsible for determining the Ca stable isotope distribution in these soils.

## H61C-0807 0830h POSTER

## A Strontium Isotope Reconnaissance of a Marine Terrace Chronosequence in Central California, USA.

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Long-term sampling locations have been established on a chronosequence of marine terraces north of Santa Cruz, CA. Investigation of these sites will allow a multidisciplinary assessment of mineral weathering and soil formation processes. The five surfaces comprising the chronosequence (terraces 1-5) have been dated at 65ka, 92ka, 137ka, 139ka, and 226ka, respectively, by Perg et al. 2001 using cosmogenic radionuclides (CRN). Soil horizons have developed in the sediments covering the terraces, derived locally from the Miocene Santa Margarita sandstone, Santa Cruz mudstone, and the Cretaceous Ben Lomond Granodiorite. The terrace sites have been sampled and instrumented with suction water samplers and precipitation collectors. Bi-monthly collection of soil waters, surface waters, precipitation, and vegetation are on going. This component of the study will use Sr isotopes (87Sr/86Sr) to understand

sources, cycling, and behavior of strontium and associated base cations.

87Sr/86Sr measurements have been made on a variety of materials from terrace sites 1-5, including precipitation, soil waters, ground and surface waters, vegetation, ammonium-acetate extractable soil Sr, and soil digests. Additionally, 87Sr/86Sr measurements have been made on local bedrock and beach sands. The measured values of 87Sr/86Sr in the samples range from 0.706 in deep soil water and soil exchange extracts to 0.710 in surface waters and soil digests. Isotopic values for eight precipitation samples at the terraces average 0.7091, reflecting the marine influence. Depth profiles of ammonium-acetate exchangeable soil Sr and soil waters from equivalent depths yield similar values and trends in 87Sr/86Sr (from 0.709 at the top toward 0.706 at 6 meter depth), suggesting that equilibrium is established between exchange sites and associated waters. Decreasing 87Sr/86Sr values with depth suggest a dominant influence of precipitation derived Sr on the cation exchange pool at the surface and emergence of a mineral weathering signal at depth. The Sr isotopic data in conjunction with cation chemistry will allow for formulation of Sr budgets on each of the terraces and ultimately, temporal comparisons of Sr behavior across the chronosequence.

## H61C-0808 0830h POSTER

## Silicate Weathering of Marine Terraces North of Santa Cruz, California

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Flights of marine terraces provide a natural laboratory to study silicate weathering, soil development and hydrologic evolution of the vadose zone. Terraces north of Santa Cruz, California were cut successively into the slowly rising coastline by high stands of sea level during the Pleistocene. Subsequently, they were covered with 1 to 5 meters of sediment derived locally from Miocene sedimentary formations and Cretaceous Ben Lomond granodiorite. Terrace surfaces have been dated using cosmogenic radionuclides (CRN) Be<sup>10</sup> and <sup>26</sup>Al by Lesley Perg and others as 65 ka, 92 ka, 137 ka 139 ka and 226 ka. Soils from five terraces have been sampled and instrumented with suction water samplers, tensiometers, and soil gas samplers. Physical characterization of the sediments includes bulk chemistry, grain size, and specific surface area. Chemical analyses of the sediments were done by XRF.

Mass transfer coefficients indicating how much of a component has been lost due to weathering, were calculated using SiO<sub>2</sub> as the initial proxy for a conservative component based on a high content of detrital quartz. Iron and Aluminum were lost from the topsoils (<0.5 m) and gained in the subsoils (0.5m to 2m) relative to Si. Evidence for the transfer of Fe and Al from upper to lower horizons is consistent with pedogenic formation of aluminosilicate clays and iron oxy/hydroxides in the subsoil. The argillic B horizons contain significant amounts of kaolinite and extractable iron oxides at roughly the same depths where net gains of Al and Fe occur. The progressive development of these argillic horizons with time has a strong influence on pore water hydrology and solute fluxes.

In contrast to Al and Fe, base cations become progressively depleted in the terrace soils with age. The strong correlation between Na and Ca loss indicates rapid plagioclase weathering. Mg and K exhibit less consistency in weathering trends corresponding to partial retention of mica in the weathering profiles. The high intensity of weathering in the Santa Cruz chronosequence compared to other chronosequences in California is attributed to wet climatic conditions.

## H61C-0809 0830h POSTER

## Biogeochemical Weathering Processes in a California Marine Chronosequence as Implicated by Pore-Water Major-Constituent Concentrations and Germanium-Silicon Fractionation

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Silicate weathering processes dominate weathering rates from terraced grassland surfaces in the drainage basin of Wilder Creek (Wilder Ranch State Park, Santa Cruz County, California). This study uses Si, Na, and Ge concentrations from soil pore-water samples taken from a flight of five marine terrace locations in the watershed. A sample-concentration procedure preceded ICP-MS instrumental analysis in order to determine Ge at parts-per-trillion levels. At two sites (Terraces 3 and 4), higher Si and Na concentration levels at the surface or near-surface depths showed the effect of evapotranspiration. Minimum levels of these two elements occurred from 15 cm to 90 cm deep, and for each the concentration increased gradually with depth. These increases showed that plagioclase dissolution controlled pore-water Si and Na deep in the respective soil profiles. Samples from both Terrace 3 (137 ka in age) and Terrace 4 (139 ka) had Ge/Si ratio values ranging from  $0.3 \times 10^{-6}$  to  $5 \times 10^{-6}$ . For both terrace sites, larger ratios occurred in samples taken from shallower depths. The ratio values progressively decreased with increasing depth, down to about 1 to 2 meters below the surface. Larger Ge/Si values provided evidence of uptake and incorporation of Si into phyloliths in leaf structures by prevailing native grasses that depleted Si at shallower depths. As the end of the annual growth cycle for the grasses coincides with the onset of seasonal rains, the phylolithic Si becomes readily available for fluvial transport. These results have important ramifications in interpreting Si fluxes for the estimation of weathering rates in watersheds.

#### H61C-0810 0830h POSTER

##### Sequential Extraction of Mercury from Sediments in San Francisco Bay Estuary

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Mercury is found as both a natural component of weathering and as an industrial contaminant in sediments in central California. Although the mercury in most of California's coastal rivers is primarily derived from natural weathering processes, the bulk mercury in San Francisco Bay is derived from historic mining. In the northern reach of the estuary, this contamination is largely from elemental mercury used in gold mining in the Sierra Nevada and California Coast Ranges; whereas in the southern reach of the estuary the contamination is from weathering of mercury sulfide deposits and mining wastes in the nearby New Almaden mercury mining district. This disparity in sources is consistent with the results of our investigation of phase distributions of mercury in sediments using a sequential extraction method proposed by Bloom and Katon (2000). The extractions show that in the northern reach about 90% of the mercury was strongly complexed or elemental mercury, but only about 60% was strongly complexed in the southern reach. Moreover, almost all (greater than 90%) of the mercury at the New Almaden mine site was in the refractory sulfide fraction (cinnabar), but only 15% of the mercury was in that fraction downstream in the southern reach, showing the effects of chemical weathering and physical processes on mercury speciation in this system.

Bloom, N. and Katon, J., 2000. Application of Selective Extraction to the Determination of Mercury Speciation in Mine Tailings and Adjacent Soils, Assessing and Managing Mercury from Historic and Current Mining Activities, San Francisco, CA.

#### H61C-0811 0830h POSTER

##### Quantification of Potential Arsenic Bioavailability Using Chelating Resins in Spatially Varying Geologic Environments at the Watershed Scale

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Elevated concentrations of arsenic and other uranium-associated elements have been observed in surface and ground waters of the Nueces and San Antonio River watersheds, Texas. These watersheds drain

the Catahoula formation which is enriched in trace elements including As, V, and U, through natural geochemical weathering over geologic time scales and intensive U mining from the 1960s to the 1980s. Mining activities have potentially impacted groundwater quality through infiltration and lateral migration of mineral-rich plumes generated by rainfall infiltration and leaching of ore bodies and spoil piles, recharge from contaminated rivers and streams, and infiltration from mine pits.

The objective of this project is to quantify the potential availability of arsenic in different geologic environments at the watershed scale using chelating resins as infinite sinks. Such information has been identified as a critical need for protecting the agricultural and aquacultural resources, and the ecological quality of the Nueces Estuary system, a designated Estuary of National Significance by the U.S. Congress via the Water Quality Act of 1987.

Iron-loaded resin (Dowex M4195) was exposed to spiked and equilibrated soil samples (pond sediment, river sediment, and ephemeral stream sediment) over a ninety day time period. Once removed, the resin was subjected to a 2 M NH<sub>4</sub>OH stripping procedure where the effluent was analyzed using Graphite Furnace Atomic Adsorption Spectrometry to quantify total As (average 73% sorption ability and 50% recovery). Additionally, the iron resins were subjected to competition studies between arsenate and phosphate and arsenate and vanadate. Preliminary results show there is little change in sorption ability as a result of the presence of the competing ion. The use of refrigeration as a means of storage showed no decreasing effect on stripping recovery of these resins over a 28 days period.

Simultaneously the laboratory technique was applied to loaded resins placed in field sampling devices and exposed over a twenty-eight day period to different geologic environments (lake, river, stream, ephemeral stream, pond, and wetland). This experiment yielded a twenty-fold range in arsenic content sorbed to the resins with the wetland (2.62E-3 mmol) and river sediments (1.11E-4 mmol) representing the maximal and minimal sorption, respectively. Although these results may suggest that a higher fraction of potentially bioavailable As is present in wetland environments, stripped As concentrations will be compared to total As content in soil and water samples collected at each site to test for the influence of environmental conditions and overall concentrations on availability of this metal.

Potential toxicity in different geologic environments along the watersheds is dependent on the total concentration and bioavailability of arsenic. It is important to identify those geologic environments that sequester contaminants because these systems retard contaminant transport, limit toxicity, and can act as long-term sources for the contaminant.

#### H61C-0812 0830h POSTER

##### Arsenic and Associated Trace Metals in Texas Groundwater

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The value of groundwater has increased substantially worldwide due to expanding human consumption. Both the quantity and quality of groundwater are important considerations when constructing policies on natural resource conservation. This study is focused on evaluating groundwater quality in the state of Texas. Historical data from the Texas Water Development Board and the National Uranium Resource Evaluation were collected into a GIS database for spatial and temporal analyses.

Specific attentions were placed on arsenic and other trace metals in groundwater. Recent studies in the United States have focused on isolated incidences of high arsenic occurrence, ignoring possible connections between arsenic and other trace metals. Descriptive statistics revealed strong correlations in groundwater between arsenic and other oxyanions including vanadium, selenium and molybdenum. Arsenic and associated trace metals were clustered at three physiographic hotspots, the Southern High Plains, the Gulf Coastal Plains of Texas, and West Texas. A geologic survey showed that arsenic and other trace metals in Texas groundwater follow local geologic trends. Uranium deposits and associated mineralization were found to occur in the same physiographic locations. Uranium mineralization may be a significant natural source of arsenic and other trace metals in Texas groundwater. Recharge, evaporative concentration, and aquifer characteristics were also contributing factors to the occurrence of trace metals in Texas groundwater. Spatial statistics were used to delineate natural sources from anthropogenic inputs. Similarly, the natural background was estimated from the spatial distribution of trace metal observations in Texas groundwater.

#### H61C-0813 0830h POSTER

##### Selenium Removal and Mass Balance in a Constructed Flow-through Wetland System

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A constructed flow-through wetland system was established in 1996 in the Tulare Lake Drainage District (TLDD) of San Joaquin Valley, California for studying Se removal from agricultural subsurface drainage. The system consisted of ten 15x76 m cells with either monotype or combination of plants with one cell non-vegetated. The system was run till Feb. 2001. Selenium removal efficiency was evaluated and mass balance on Se was carried out. The inflow drainage water to the cells had yearly average Se concentrations of 19-22 ug/L dominated by selenate (SeVI, 95%). Average weekly Se concentration ratios of [outflow]/[inflow] ranged from 0.45 to 0.79 and mass ratio (concentration \* water volume) from 0.24 to 0.52 for year 2000, i.e., 21 to 55% reduction in Se concentration and 48 to 76% Se removal in mass by the wetland. The non-vegetated cell showed the least Se removal. The global mass balance showed that on the average about 58.8% of the total inflow Se was retained in the cells and Se outputs were outflow (35.3%), seepage (3.6%), and volatilization (2.2%). In an independent measurement of internal compartments, about 53.1% of the total Se from inflow was determined within the cells, including surface (0-20 cm) sediment (32.5%), organic detrital layer above the sediment (17.9%), fallen litter (1.9%), standing plants (0.6%), and surface water (0.3%). There was about 5.7% of the total Se from inflow unaccounted for.

#### H61C-0814 0830h POSTER

##### Metal Attenuation in an Acid Mine Drainage Impacted System: a Study at the Abandoned Spenceville Copper Mine, Nevada County, California

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Acid mine drainage (AMD) from the abandoned Spenceville copper mine contributes toxic levels of metals to nearby streams. Aqueous concentrations of copper and zinc exceed California water quality criteria just downstream of the mine. The majority of the metal contamination however is removed from the system over a short spatial distance. The primary mechanism responsible for this geochemical scavenging is adsorption onto Fe, Mn, and Al hydroxide precipitates that are clearly visible in the streambed. A five-step sequential extraction procedure modified from Leinz et al (2000) was performed on the streambed sediments in order to characterize solid phase speciation of metals in this area. The first two fractions (carbonate and amorphous Fe-Mn hydroxide) were considered to be bioavailable, with the possibility of the metals in these phases being remobilized under changing pH or redox conditions. Copper and zinc were found to have the highest bioavailability, followed by Cd, Pb, and Al.

Leinz, R. W., S. J. Sutley, et al. (2000). An investigation of the partitioning of metals in mine wastes using sequential extractions. Mine Waste Characterization, ICARD Publications. II: 1489-1499.

## H61C-0815 0830h POSTER

## Alkylphenol Polyethoxylate Metabolite Behavior During Short-Term Soil Aquifer Treatment

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The attenuation of alkylphenol polyethoxylate (APEO) metabolites was studied at a soil aquifer treatment (SAT) facility located in Mesa, Arizona, USA. SAT is a technique commonly used in arid environments to augment groundwater supplies. In SAT, municipal wastewater is discharged into basins and allowed to infiltrate into the subsurface; the basins are most often filled for several days and then allowed to dry out. During SAT the quality of the recharged water is substantially improved. Because this water may eventually be used to augment drinking water supplies, there is a concern whether organic contaminants survive SAT.

APEO metabolites are among the most frequently detected anthropogenic contaminants in the environment. The ubiquitous presence of these compounds may be of concern because they are relatively recalcitrant, can sorb and accumulate in soils and sediments, can bioaccumulate in plants and animals, and can be estrogenic to wildlife at low concentrations.

In this study, two parcels of water were monitored during SAT – one aerobic, the other anaerobic. During infiltration, under aerobic and anaerobic conditions, both alkylphenol ethoxycarboxylates (APECs) and carboxyalkylphenol ethoxycarboxylates (CAPECs) were substantially attenuated (> 90%) within 3 m. As expected, nonylphenol was removed under aerobic conditions, but produced under anaerobic conditions. Interestingly, no short-chained APEOs were detected. The rapid attenuation of CAPECs was surprising, as other researchers have found these metabolites to be very persistent. During infiltration, APEO metabolites with the longest ethoxycarboxylate side chain are attenuated fastest. Unlike several recent studies, alkylphenoxyacetic acids (APIECs) and carboxyalkylphenoxyacetic acids (CAPIECs) were almost twice as abundant as alkylphenoxyethoxyacetic acids (APEECs) and carboxyalkylphenoxyethoxyacetic acids (CAPEECs). Nonylphenol concentrations in both the wastewater and effluent SAT water were > 10 µg/L; these concentrations are high enough to induce estrogenic responses in certain animals.

The ability of the SAT system to remove APEO metabolites decreased over time; this was indicated by the accumulation of NP and breakthrough of longer ethoxy chain metabolites at 1.5 m and 3 m during the study period. These observations suggest that the drying cycle is necessary to maintain high APEO metabolite attenuation efficiencies in SAT systems. Overall, short-term SAT appears to be very effective at eliminating APEO metabolites.

## H61C-0816 0830h POSTER

## Reduction of aqueous perchlorate by iron surfaces in batch and column studies

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The rate and extent of perchlorate reduction on several types of iron metal was studied in batch and column reactors. Mass balances performed on the batch experiments indicate that perchlorate is reduced to chloride. Perchlorate reduction was proportional to the iron dosage in the batch reactors, with up to 66 percent removal in the highest dosage system. Surface normalized reaction rates among three commercial sources of iron filings were very similar for acid washed samples. The most significant perchlorate transformation occurred in solutions with near neutral initial pH values. Surface mediation of the reaction is supported by the absence of reduction in batch experiments with soluble Fe(II). Elevated chloride concentrations significantly inhibited perchlorate reduction, and lower removal rates were observed for iron samples with higher amounts of background chloride contamination. Perchlorate reduction was not observed on electrolytic sources of iron or on a pure mixed phase oxide (Fe<sub>2</sub>O<sub>3</sub>), suggesting that the reactive iron phase is not pure zero valent iron but is instead a combination of the elemental metal coated by a mixed valence iron hydr(oxide)

phase. The observed reaction rates are too slow for direct use in remediation system design, but the findings may provide a basis for future development of cost-effective abiotic perchlorate reduction techniques. Further work to elucidate the mechanism of perchlorate reduction on iron media is in progress.

## H61C-0817 0830h POSTER

## Factors Controlling DNAPL Migration in a Fracture Network: Experiments and Simulations

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Groundwater contamination by dense nonaqueous phase liquids (DNAPLs) has received considerable attention in recent years, and the attention on characterizing and quantifying the migration of DNAPL in geological formations has been given to the migration of DNAPL in porous media, not much in fractured rock. The spilled DNAPL that is heavier than water migrates downward to fractured bedrocks under the influence of gravity and is a long-term contaminant source. Although the progress has been accomplished on the development of algorithms for the numerical solution of the macroscopic models of contaminant transport in rock fractures, a lack of fundamental understanding exists concerning the interactive effects of the structural characteristics of fractures and fluid rheology on the patterns of DNAPL migration in a fracture network. In particular, little experimental work has been done on DNAPL migration in a fracture network. The two-dimensional fracture network was built up. Water was applied to both sides of a fracture network to have intended hydraulic head, and TCE was injected into one of vertical fractures. TCE migration process was recorded with digital camcorder. The dynamic macro-modified invasion percolation (DMIMP) model is suggested by integrating groundwater flow factor with MMIP that reflects the capillary effect, gravity-destabilization condition and viscous force of DNAPL. The information gained from experiments was analyzed and used for testing the DMIMP model to characterize the DNAPL migration pathway in a fracture network. DMIMP simulations and laboratory experiments show a good agreement. The results of DMIMP simulations and laboratory experiments show that in addition to gravity force, water viscous force considerably affects migration of DNAPL in rock fractures. This study will provide a step-stone for further developing reliable numerical simulators of the DNAPL migration in a fracture network that are required for the implementation of rational and cost-effective risk assessment procedures to DNAPL-contaminated rock fractures.

## H61C-0818 0830h POSTER

## Density-Controlled Remediation of DNAPL in a Fracture Network

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Dense non-aqueous phase liquids (DNAPLs) are a common groundwater contamination source, because of extensive use in industrial processes. While DNAPL travels rapidly downward through rock fractures because of the high density relative to groundwater, DNAPL is retained in rough fracture surfaces and dead-end fractures, due to capillary and gravity forces. DNAPL retained in rock fractures continues to dissolve slowly because of low solubility, which produces a serious long term dissolved contamination plume exceeding drinking water standard. Therefore, the efficient remediation of DNAPL-contaminated fractured site is to remove DNAPL source from rock fractures. Remediation technologies to remove DNAPL contamination usually involve the delivery of remedial fluids to the contamination source (e.g., water for pump-and-treat, surfactant for surfactant flushing, solvent for cosolvent flushing, and air for air sparging), but the fractured rock environment makes effective delivery of remedial fluids very difficult to achieve. It is more true of dead-end fractures than of rough fracture surface, because in dead-end fractures, fluid flow does not occur and remedial fluids is rarely delivered to dead-end fractures. We have applied density-controlled remediation technique to a fracture network. The idea of this method comes from the mechanism that DNAPL flows into dead-end fractures and displaces groundwater mainly due to higher density than water. The main idea of this study is that dense fluid injected into fracture network turns DNAPL into LNAPL relative to the

density of surrounding aqueous fluid, which results in the floating of DNAPL from dead-end fractures. The two-dimensional fracture network with dead-end fractures was built up. Denser fluid with much less toxicity than DNAPL is injected at the side of the two-dimensional fracture network, and is pumped out at constant rate from the other side, using syringe pump. The removal process of DNAPL is monitored with digital camcorder and the density change of surrounding aqueous fluid is also monitored to test the applicability of density-controlled remediation technique to DNAPL-contaminated fracture network.

## H61C-0819 0830h POSTER

## A New Paradigm of Modeling One-Dimensional River/Stream Watershed Water Quality

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This paper presents the development of sediment and reactive chemical transport under non-isotherm condition in one-dimensional river/stream watershed system. We assume that effect of temperature cannot be omitted, so that the distribution of temperature needs to be calculated and biogeochemical parameters can be assigned according to temperature to compute sediment and chemical transport. Through decomposition of reaction network via Gauss-Jordan column reduction, (a) redundant fast reactions and irrelevant kinetic reactions are removed from the system; (b) fast reactions and slow reactions can be decoupled; (c) species reaction equations are transformed into two sets: equilibrium species mass action equations and kinetic-variable reaction equations. This enable our model to include as many types of reactions as possible, choose kinetic-variables instead of chemical species as primary dependent variables, and simplify the reaction terms in transport equations. In our model, production-consumption rate of chemical species is determined by reaction-based formulations, and two options are provided to solve the advection-dispersion transport equation: Lagrangian-Eulerian approach and Finite Element Method in Conservative Form. An example problem is employed to demonstrate the design capability of the model and the robustness of the numerical simulations.

## H61C-0820 0830h POSTER

## Relating Weight and Count Distributions of Stream Bed Gravel

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The size distribution of particles in a stream bed reflects the stream hydrology as well as its physical and chemical water quality characteristics. In environmental assessments, the sediment particle size distribution indicates habitat quality for aquatic insects and stream suitability for spawning by various fish species. A common monitoring approach (e.g., Wolman count) assesses surface particles as size-count distribution. The method is convenient, but the distribution of subsurface particles, which cannot be assessed by size-count is also needed for water quality assessment. We collected surface and subsurface substrate samples from several coastal and inland streams in Oregon to develop methods of relating size-count and size-weight distributions of the surface material and their relationships with the size-weight distribution of the subsurface sample. In this study, we present examples of relationships of size-count and size-weight distributions of the surface particles. These distributions differ substantially, and depending on the method of calculation, the distribution means for the same sample can differ several

fold. We converted the size-count to size-weight distribution using log-normal functions between two consecutive size groups. When used to calculate the median and the standard deviation of the distribution, the method yielded a more stable approach than two alternative calculations.

#### H61C-0821 0830h INVITED POSTER

##### Design Considerations for Continental-Scale Water-Quality Networks

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The U.S. Geological Survey recently completed the redesign of two continental-scale networks, the National Stream Quality Accounting Network (NASQAN) and the Hydrologic Benchmark Network (HBN). In both cases, although the original networks provided useful data, the networks failed to achieve as much as was originally hoped when they were implemented approximately 30 years ago (NASQAN) and 40 years ago (HBN). Although both networks focused on water quality, the lessons from these networks are applicable to the network of research watersheds currently under consideration.

The most important lesson was that network objectives must be stated with sufficient precision to define the intended interpretation and analysis of data collected by the network. For example, many monitoring networks have the objectives to determine the status of a resource and the trend in that status. These generic objectives were too imprecise to determine the NASQAN and HBN network design: how are the data going to define the status? For NASQAN, we decided that estimation of the annual load of selected water-quality constituents was our central objective because it permitted us to determine the source, transport, and delivery of constituents using the principle of conservation of mass. Once this objective was specified, the details on network design fell into place. Sampling strategy, sampling methods, and minimum sampling frequency could be determined, which, in turn, determined the cost of operating stations. Methods and quality-assurance plans could be specified to meet this objective, as well as the requisite data-handling system. When combined with the budget, these elements defined the maximum number of stations that could be operated. In general, resource constraints will require iterating between defining objectives and determining whether environmentally meaningful data that meet those objectives can be collected within budget. Often, objectives will have to be redefined to meet the budgetary constraints.

The second lesson to be drawn from the operation of long-term networks like NASQAN and HBN is the need for on-going data interpretation to be integral to the program. Such interpretation will determine whether the data truly meet the objectives of the network and if any adjustment to the network operation is required. Such interpretation maintains the vitality of the network and ensures the continued merits of its operation.

#### H61C-0822 0830h INVITED POSTER

##### Modeling and Monitoring Soil Erosion, Sediment Movement, and Sediment Storage in the United States

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The U.S. has in place the National Resources Inventory (NRI), a large and efficient system for collecting data for prediction of soil erosion using the Universal Soil Loss Equation (USLE). What seems required now is a worldwide verification scheme, with network design, that would account for earth-mass fluxes in sample stream basins chosen to be representative of global climatic zones and hydrogeomorphic systems. Each sample basin would terminate in a reservoir that stores water and sediment and thus permits the calculation of sediment yield. Stream channels and valleys, as well as sample upland areas, would be monitored by surveys and cosmogenic tracers. Ideally, streamflow and sediment transport in each basin would be monitored, at least just upstream of the reservoir. Such a scheme would not only allow for verification of the USLE or related technologies under different conditions on an areal basis, but it would allow powerful insights into sediment movement and storage and associated fluvial processes.

URL: <http://www.geog.ucla.edu/>

#### H61D MCC: 105 Saturday 0830h

##### Drought Analysis and Prediction I

(joint with A, GC)

**Presiding:** J Valdes, University of Arizona; J Salas, Colorado State University

#### H61D-01 0830h INVITED

##### The Evolution of 20th Century Drought Monitoring Tools Leading to a 21st Century North America Drought Monitor

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The monitoring and analysis of drought have long suffered from the lack of an adequate definition of the phenomenon. As a result, drought indices have slowly evolved during the last two centuries from simplistic approaches based on some measure of rainfall deficiency or streamflow, to more complex problem-specific models. The incorporation of evapotranspiration as a measure of water demand by C. Warren Thornthwaite led to the landmark development in 1965 by Wayne Palmer of a water budget-based drought index that is still widely used. The 20th Century concluded with the development of the Drought Monitor tool, which incorporates Palmer's index and several other indices to provide a universal assessment of drought conditions across the entire United States. The 21st Century is seeing the coordinated operational monitoring of drought on a continental scale as experts from Mexico, Canada, and the United States develop the North America Drought Monitor.

By placing the development of these drought indices into a historical perspective, this paper will provide a better understanding of the complex Palmer Index and of the nature of measuring drought in general. Drought patterns over the United States during the last 100 years will be illustrated using several of these indices.

#### H61D-02 0845h INVITED

##### Stochastic Modeling of La Niña Influence on Meteorological Droughts in the South Cone of America

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The objective of this work is to characterize and to establish quantitative relations between the properties of meteorological droughts in the geographic scope of the South Cone of America and the extreme phases of ENOS. From the quantitative point of view it also of interest to be appraised the existence of non linearities and effects of temporary phase angle between both phenomena. Stochastic models were used to relate the temporary structure of dependency between the field of Standardized Anomalies of the Sea Surface Temperature, SST, fields in the Pacific Ocean, and fields of monthly values of the Standardized Precipitation Index in those continental regions of South America, to the south of the Tropic of Capricorn, where the homogeneous influence of ENOS has been previously identified, particularly La Niña events related with the occurrence of droughts.

Transfer Function and NARMAX models were applied to model relationships between both phenomena, applied to all the phantom of both phenomena as a first approach. This sample that are no significant differences between both types of modeling, linear and non linear. In addition, since evidence exists of which the extreme events La Niña are associate with the occurrence of meteorological droughts in this region, with the intention of modeling the nonlinear relation presents between both types of events, these same models are applied in a threshold scheme, considering the percentile of the main component of the SST that identifies conditions of La Niña, like indicating variable. The modeling indicates that while these models applied to the whole set of the variables allow to explain not more of the 0.10 of the variance of the first main component of the monthly precipitation field in the analyzed continental zones, get to explain more of the 0.50 of her if they are applied as much considering only conditions

of the colder extreme phase, corresponding to La Niña, like exogenous variable in the Transfer Function like in NARMAX models, and without significant differences among them are detected.

#### H61D-03 0900h

##### Characterizing the Recurrence of Hydrologic Droughts

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Characterizing periods of deficit and drought has been an important aspect in planning and management of water resources systems for many decades. An extreme drought is a complex phenomenon that evolves through time and space in a random fashion. It may be characterized by its initiation, duration, severity (magnitude or intensity), spatial extent, and termination. These characteristics may be determined by comparing the water supply time series versus the corresponding water demand series in the area of consideration. Because the water supply quantities such as rainfall and streamflow are stochastic variables the ensuing drought characteristics are random and must be described in probabilistic terms. Let us consider a periodic stochastic water supply and a variable water demand series. A drought event is defined as a succession of consecutive periods (run) in which the water supply remains below the water demand. Thus, the drought length  $L$  (negative run length) is the number of consecutive time intervals (seasons) in which the water supply remains below the water demand, preceded and followed by (at least one season where) the water supply is equal or greater than the demand. Likewise, the difference between the water demand and the supply at time  $t$  is the magnitude of the deficit at time  $t$  so that the accumulated deficit  $D$  (drought magnitude) is the sum of the deficits over the drought duration  $L$ . In the study reported herein, the probability density functions (pdf) of drought length and drought magnitude and their low order moments are derived assuming that the underlying water supply series after is clipped by a constant or periodic water demand results in a periodic dependent binary series that is represented by a periodic two-state Markov chain. The derived pdfs allow estimating the occurrence probabilities of droughts of a given length where either the drought begins in a given season or regardless of the initial season. In addition, the return periods of droughts (based on length and magnitude) are determined. The applicability of the drought formulations is illustrated using several series of precipitation and streamflow in Sicily, Italy and Colorado, USA. The results obtained show an excellent agreement between the observed and theoretical results. In conclusion, the proposed methods appear to be a useful addition for drought analysis and characterization using stochastic methods.

#### H61D-04 0915h

##### Stochastic modelling of regime changes

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Graphical and numerical techniques exist to represent the duration, magnitude, and intensity not only of droughts, but of any climatic episode. We present here statistical decision and limit methodologies for quantifying regime shifts through their duration and magnitude. Duration is defined as the number of consecutive values above (or below) a reference level, and magnitude is the sum of all values for any given duration. Assuming that a regime shift can occur every year, independently of prior years, we naturally obtain a class of standard waiting time distributions (waiting times for the regime shift). Because magnitude can be expressed as a random sum of  $N$  random variables (where  $N$  is duration), its probability distribution is evaluated using limit theory for random sums. Here we analyze a reconstructed time series of the Pacific Decadal Oscillation (PDO), explicitly describe the probability distributions, and estimate their parameters from the PDO data obtaining a reasonably good fit. Our stochastic approach to modeling duration and magnitude of multi-annual events (such as droughts) enables the computation of statistical significance for those episodes, and provides a rigorous solution to deciding whether two droughts are significantly different from one another.