

**H22A-05 1430**

Importance of Methylated Arsenic Species in the Biogeochemical Cycling of Arsenic in two California Semiarid Lakes: Salton Sea and Davis Creek Reservoir

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Methylated arsenic species have been reported emanating from cultures of algae, bacteria, invertebrates and vertebrates, but there have been few reported measurements of methylated arsenic species in natural waters. We found methylated forms of arsenic in water samples from the Salton Sea and Davis Creek Reservoir, two lakes in semiarid regions of California. Total arsenic gradually increases with depth in the Salton Sea ( $As_T = 88 \text{ nM}$  at 1m;  $As_T = 98 \text{ nM}$  at 9m). Methylated arsenic species decrease, both in concentration and percent of total, with depth (27% to 4%). Concentrations of total arsenic in Davis Creek Reservoir also increase with depth ( $As_T = 1 \text{ nM}$  at 2m;  $As_T = 22 \text{ nM}$  at 21m) and the percent of methylated species decreases from 44% to 3%.

Methylation of metals and metalloids has been demonstrated to facilitate their uptake by biota (e.g., mercury) and thus increase their potential for toxicity. Therefore measurement of total arsenic or solely of inorganic arsenic may not indicate its potential hazard. In our water sample survey of a number of lakes and rivers in arid areas, there appears to be no correlation between the total concentration of arsenic and the percent of the total methylated. In fact, several lakes with very elevated arsenic concentrations (Mono Lake,  $As_T = 130,000 \text{ nM}$ ; Pyramid Lake,  $As_T = 840 \text{ nM}$ ) have no detectable methylated species, whereas Davis Creek Reservoir ( $As_T = 13 \text{ nM}$ ) has up to 44% of methylated arsenic forms. In systems where methylated species are the prevalent form of arsenic, understanding the factors that control their distribution will be critical to understanding the cycling of arsenic. In addition the form of arsenic may have profound implications for its geochemical and biochemical reactivity or behavior.

**H22A-06 1445**

An Evaluation of Water Hyacinth (*Eichhornia crassipes* Mart.) Solms) as an Indicator of Water Quality

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The water hyacinth (*Eichhornia crassipes*) is an abundant free-floating macrophyte found in many low gradient rivers of the world. It exhibits a high accumulation capacity for many elements and may provide an integrated record of contamination in an area. This study examines the potential of this species for water quality assessment in a river impacted by agricultural drainage. River water and hyacinth root tips (5-8 cm) were sampled bimonthly at six stations along the middle reach of the San Joaquin River and its tributaries during June to December 1985 and in November 1986. Sediment particles ( $\leq 62 \mu$ ) washed from hyacinth roots were also collected in November 1986. Elemental compositions of river water (total and dissolved fraction), sediment and water hyacinth were determined by emission spectroscopy (ICP) and atomic absorption. In root tips, the concentrations of major elements required for plant growth decreased in the order:  $K > Mg > Ca > P > Na$ . Significant positive correlations between concentrations in root tips and dissolved concentrations in river water were observed for Mn, Na and Se. Solute concentrations of these elements in river water decreased with distance downstream. Negative correlations were observed between concentrations in root tips and dissolved concentrations of Al, Cu and Fe. Concentrations of Cu in root tips were negatively correlated with Cu in associated sediment, whereas concentrations of Fe in root tips were positively correlated with Fe in sediment. Analyses of root tips allowed greater differentiation of element contamination at stations than was possible using water data alone, especially for elements which were at or below detection limits in river water.

**H22A-07 1520 INVITED**

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Experimental Results of Wet Immobilization Techniques for Selenium Detoxification at Kesterson Reservoir, 1986-8.

Wetlands contaminated by selenium, or other pollutants, can only be restored to their full economic and ecological value if they remain wet. This is because wetlands are the most important diminishing resource in many areas. Laboratory and field experiments were combined with an extensive fluid measurement program to test if the severely selenium-polluted Kesterson Reservoir (a marsh) could be detoxicated to an acceptable level for wetland wildlife. The method tested, wet immobilization, submerges the marsh with low-selenium water but does not require removal of contaminated sediment or biotic selenium. Mean concentrations of selenium in wetlands biota fell from over 200 ppm (dry wt.) to 6-50 ppm in

1 year (summer to summer). A seasonal cycling of selenium with winter maximum was discovered. Declines to even lower levels occurred the next summer (1988). Seasonal patterns were not similar in Se-contaminated drier parts of the system. The success of failure of wet immobilization in heavily or lightly contaminated wetlands appears to depend on limiting backfluxes of selenium from sediments to the free water. Control techniques based on those often used for control of sewage phosphorus seem most appropriate.

**H22A-08 1540**

Selenium Concentrations in Ephemeral Pools at Kesterson Reservoir, Field and Laboratory Observations

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At Kesterson Reservoir, wildlife exposure to toxic concentrations of selenium have been attributed to Se in surface water environments resulting from ponding of agricultural drainage waters. High concentrations of soluble selenium are also prevalent throughout soil profiles at Kesterson Reservoir as a result of past disposal of seleniferous agricultural drainage waters. While discharge of these waters has been discontinued, the Se inventory in Kesterson Reservoir soils can continue to pose a threat to wildlife. Among the remedial action plans considered was the "On-site Disposal Plan" (ODP), which would involve excavation of at least 0.15 m of surface soils from much of the Reservoir, and containment of this highly seleniferous soil ( $>4 \text{ mg Se/kg soil}$ ) in an on-site facility. One potential scenario for continued pool chain exposures to Se involves the formation of seasonal ponds due to the annual rise of the local shallow water table. The combination of the water table rising to the soil surface and low rainfall will result in seasonal ponding with highly seleniferous waters (100 to 5000 ng/l) which largely reflect the upward displacement of soil water. Accumulation of Se and other soluble salts in the upper portions of the soil profiles prior to the wet season is enhanced by the combination of high potential evaporation and the presence of a shallow water table. Soil water and surface water quality data from a variety of field and laboratory experiments will be presented. It will be shown that the ODP would be counterproductive with respect to preventing seleniferous ephemeral pool formation.

**H22A-09 1555 INVITED**

Is Selenium Volatilization a Viable Technique for Cleaning up Kesterson?

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Microbial volatilization of selenium (Se) was studied as a cleanup method for contaminated sediments at Kesterson Reservoir, Merced County, California. Tests were conducted *in situ*, in simulated field experiments, and controlled laboratory environments. Soils were kept moist and were aerated frequently. They were amended with straw, manure, citrus peel, gluten, casein, zinc, cobalt and nitrogen to stimulate bio-methylation of Se. Gaseous products were trapped in alkaline  $H_2O_2$  and activated carbon. Soil Se depletion was monitored by monthly soil analyses. *In situ* experiments were conducted in field plots at Kesterson. In simulated field experiments, contaminated soil collected at Kesterson was ground, sieved and mixed, and was placed 12-15 cm deep in 60 x 60 cm wide plastic containers and kept open in the field. Controlled laboratory experiments employed closed continuous-flow systems and were conducted in the greenhouse with a day/night temperature regime. The highest Se removal was observed with citrus peel, followed by casein and gluten. Strong stimulation of Se evolution was also observed upon combined application of straw and nitrogen. The time required to achieve cleanup goals at Kesterson was estimated.

**H22A-10 1615**

Geochemical Controls on Selenium Mobility in Ground Water at the Kesterson Reservoir.

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The geochemical characteristics of shallow ground water, including elevated concentrations of sodium, sulfate, and boron, indicate significant infiltration of surface pond water at Kesterson coupled with the general immobilization of selenium by anaerobic bacteria in the organic-rich bottom muds. However isolated plumes of Se have penetrated to depths of 20m beneath the reservoir. Even after an extensive drilling and research effort, the exact cause of such penetration at specific locations is unclear. The following general observations however are apparent: A strong correlation exists between elevated Se and transport of dissolved oxygen and nitrate from the surface water. Se does not occur in either natural or infiltrated waters that contain measurable concentrations of ferrous iron or manganese. The Eh of the oxidizing plume corresponds

generally to the selenate-selenite redox couple and the reducing aquifer Eh to the ferrous iron-ferrous hydroxide couple. The penetration of the plume is related to dynamic equilibrium between the rate of surface water infiltration and the rate of Se depletion in the aquifer caused by microbial uptake and dissolution of minerals contributing ferrous iron and manganese to the ground water. The importance of the last observation is that a decrease in the source term, i.e. surface infiltration, has led to a rapid decrease in selenium concentrations which supports the conclusion that long-term far-field groundwater selenium contamination is not likely to occur at Kesterson.

**H22A-11 1630**

Saline Groundwater Plume Mapping With Electromagnetics

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There is growing interest in the mapping of contaminant plumes migrating from unlined storage ponds. At the Kesterson Reservoir, Merced County, California we had the opportunity to map a plume of saline drainage water that had migrated from several flooded ponds into the underlying shallow alluvial aquifer. Extensive sampling of ground-water beneath the ponds showed that drainage water had penetrated to depths of from less than 6 m to as much as 40 m, with an average depth of 20 m, and had conductivities of 1000 to 1700 mS/m compared to native ground-water conductivities of 300 to 400 mS/m. Although computer modeling studies gave a quantitative estimate of plume movement, there was no other measurement of plume migration on private lands downgradient of the reservoir. To obtain that information we conducted detailed ground conductivity measurements using two direct-reading EM instruments, the Geonics EM31 and EM34-3. To complicate the plume mapping problem, we found highly variable soil salinization features due to past irrigation practices and accumulation of salts from evaporative fluxes of saline groundwater from the shallow water table. Differentiation between saline soils and the deeper plume was made possible by using three intercoil separations and a dense grid of measurements. Plume migration distance was reasonably close to that calculated from a numerical groundwater transport model.

**H22A-12 1645**

Tracer Experiments for Evaluating Non-Reactive and Reactive (Nitrate and Selenium) Transport Under Kesterson Reservoir

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Tracer experiments have been carried out at Kesterson Reservoir, Merced County, Ca., for evaluating transport of non-reactive and reactive solutes (selenium and nitrate) in the shallow aquifer underlying the Reservoir. From 1981 to 1986 an estimated 4000 acre-feet/year of high salinity (10,000 ppm) agricultural drainage water seeped into the sandy aquifer underlying the Reservoir. In general, the selenium (ave. 300 ppb) and nitrate ( $< 1$  to 400 ppm as  $NO_3^-$ ) in the drainage water was removed by microbial interactions with the bottom sediments. However, in several limited areas, selenium and nitrate migrated to depths of up to 25 m in the aquifer. Migration of the large plume (approx. 3 km x 1 km) of high salinity drainage water and the smaller plumes (less than 250 X 250 m) of selenium bearing waters are of concern even though operation of the Reservoir has ceased.

Two medium scale (travel distance of 30 m) multi-well tracer experiments showed that non-reactive transport is controlled largely by the micro-scale structure of the aquifer and is only minimally influenced by pore-level mixing (longitudinal dispersivity values of several centimeters were measured). The individual flow paths are typically less than 0.5 m thick and are continuous over distances of at least 10's of meters. Flow velocities vary within a factor of  $\pm 2$  of the average value. Reactive tracer experiments confirm that under slightly reducing conditions the highly soluble species of selenium, selenate and selenite, are quickly immobilized by interactions with the aquifer sediments. The half life for selenate was several days. Selenium immobilization was almost completely inhibited by nitrate concentrations in excess of several ppm. Rapid denitrification was observed, with an average half life of 7 days. These experiments indicate that without a sustained supply of nitrate, denitrification will proceed quickly and that selenium immobilization will follow shortly. These conclusions are supported by field observations showing the decay of the small nitrate and selenium plumes.

**Hierarchy in Subsurface Transport (H22B)**  
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Scale-Dependent Variability in Subsurface Hydrology: Self-Similarity and Spectral Conditioning

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