2.4 Contaminant Transport Assessment and Management (CONTAM)

The CONTAM research area focuses on developing technology to observe and manage mass and energy distributions and fluxes across a range of temporal and synoptic scales. In 2009-10, the contaminant transport group continued its emphasis on integrated sensing and model-driven analysis. Projects continued to focus on closed-loop soil zone moisture, energy, and irrigation management demonstration, data assimilation approaches used to gain the maximum return on deployment investments, and high resolution river observation and modeling with respect to whole stream metabolism, groundwater-surface water exchanges, and hydrodynamic mixing.

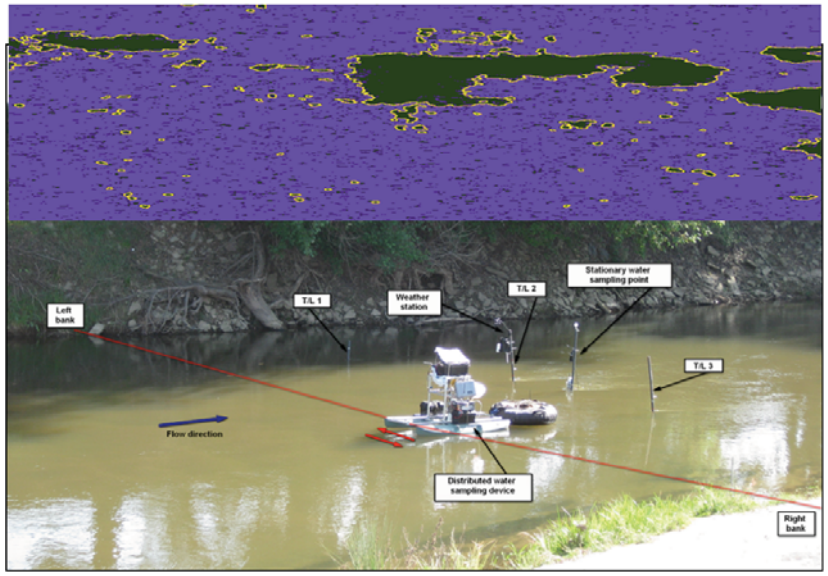


Figure 2. Stream metabolism spatial mapping experiment: (bottom) robotic and stationary water quality sensor stations on the Lower Merced River; (top) sample alteration detection algorithm results for shade/no-shade regions upstream of stations.

The major accomplishment in the CONTAM application area for 2009-10 was **the quantitative assessment of whole stream metabolism differences at unprecedented spatial resolution at the Lower Merced River test site** (see CoONTAM 02 report section). The layout of the full-scale river metabolism spatial observation test is shown in Figure 2. We are explicitly characterizing velocity, temperature, and light distributions while collecting high temporal resolution dissolved oxygen data to support metabolism calculations. The three main approaches explored over the past year are (1) high temporal resolution dissolved oxygen data collection and net daily metabolism estimation at high spatial resolution, (2) light intensity sensors and a network security camera were used at the field site to acquire the incident light data from the water surface over a river reach, and (3) the NIMS RD and AQ robotic systems were used to provide high resolution data on river flow fields, which were then used to parameterize a 2D (depth-averaged) river model.

CENS-developed sensor deployment platforms, such as the javelin, were also re-deployed during 2009-10 campaigns to begin to connect the flow path from terrestrial to the aquatic environment via groundwater-surface water exchanges. Using arrays of javelins at the same Lower Merced River test site discussed above, groundwater velocities were shown to be spatially heterogeneous about each transect with a small range (-1.82 to 4.80 cm/day) (see CONTAM 01 report section). Higher rates of groundwater discharge were found on the north side of the river in both transects. Groundwater discharge velocities were within range of previous studies at this site giving credence to the instrumentation, and method. In future field experiments, we will attempt to draw connections between these groundwater discharges, nutrient transport, and the stream metabolism observations discussed above.

In addition to these successes in the aquatic environment, CONTAM researchers continued to make substantial progress on the water resources management front, particularly in the context of stochastic data assimilation (see CONTAM 03 report). This CENS project builds off of earlier successes at the County Sanitation District in Los Angeles experimental site in Palmdale, CA, and continues to address the goal of safe wastewater reuse via irrigation. Wastewater often contains elevated solutes (e.g. sodium and/or nitrogen) and these excessive chemicals in soil could restrain crop growth and also pollute the groundwater beneath the irrigated lands. **We continued to add to the Palmdale soil moisture, temperature, and salinity data set with uninterrupted operation of this wireless sensor network since May 2008.** Over the past year, stochastic data assimilation experiments employing the Palmdale site have shown that even for a homogeneous soil, accurate estimation of soil states and fluxes requires simultaneous estimation of states and parameters. Estimation of states only can lead to significant errors in fluxes if the parameters are not specified accurately a priori. Further, **CENS researchers have shown that even in the more complicated heterogeneous case, their data assimilation approach (ensemble Kalman filter) is capable of**

providing better estimates of soil state and flux if measurement information content is sufficient. The preliminary outcomes of the assimilation of in-situ measurements also show that the filter estimates can improve the moisture estimates at different depths and also reduce the uncertainty of estimation compared to the open-loop simulation. Together, these results indicate that the data assimilation approach provides a relatively robust framework for the real-time estimation of states/fluxes in an irrigated agriculture context.

The CONTAM group's work on arsenic observation in subsurface sediments has also continued to make progress during 2009-10 (see CONTAM 04 report). Arsenic (As) in well water has led to the largest environmental poisoning in history, affecting tens of millions of people in the Ganges Delta and elsewhere. **Current CENS research has three components focused on comparing As release from mineral dissolution and Fe hydroxide respiration using Bangladeshi soils in laboratory microcosms.** Through these same experiments, we are testing the hypothesis that pond sediments are a major site of As release in Bangladesh through a comparison of As release from sediments collected from the paddy and the edge of the pond at our site.

CONTAM 01 Multi-Scale Soil Sensor Network in Support of Groundwater Quality Protection

CONTAM 01.1 Overview

This project has previously focused on moisture and chemical propagation in the soils undergoing irrigation. This aspect of the project has shifted primarily toward modeling and resource management questions, which are now being addressed in a separate project (see CONTAM-03 report). While some of these aspects of the project remain, the main emphasis of the CONTAM-01 project has shifted to the opposite end of the land use-to-waterway flow path, where agriculturally impacted groundwater discharges into a river.

Progress in this year's CONTAM-01 report was primarily in three areas:

- In a new direction, we extended the multi-scale soil sensor systems to the study of groundwater-surface water discharges. The quantification of groundwater discharge/recharge from surface water is poorly understood due to the heterogeneity of these processes within a given reach and a deficiency of instrumentation needed to obtain a high resolution for these interactions.
- We tested the response of potentiometric nitrate sensors to monitor nitrate impulses under controlled laboratory conditions. We have tested these sensors previously in the field, but all results to obtained to date have been ambiguous.
- We continued to add to the Palmdale soil moisture, temperature, and salinity data set with uninterrupted operation of this wireless sensor network since May 2008 (for typical results, see CONTAM-04 portion of the annual report).

Specific Objectives

The objective of this project was to evaluate inexpensive groundwater-surface water monitoring devices (temperature javelins) used to calculate groundwater-surface water discharge in a high spatial resolution. In addition, the response of low power, potentiometric electro-chemical sensors for nitrate sensing was further evaluated in a laboratory setting to determine whether groundwater-surface water chemical fluxes might also be determined using this approach.

CONTAM 01.2 Approach

Groundwater-Surface Water Discharge Mapping

We installed several of the previously developed temperature javelin sensor platforms at a site on the Lower Merced River. Temperature Javelins were composed of thick walled (schedule 80) PVC measuring 3 cm diameter and 3 m in length. Holes were drilled through both sidewalls of the pipe to accommodate small self-logging temperature sensors (Thermocron i Button). The holes were tapped on one side and counter bored on the other sidewall. Large set screws threaded into the sidewall secure the temperature probe in place (see Figure 1).

Initial testing took place at a known gaining reach of the lower Merced River near Livingston, California. Temperature javelins were tested to determine how accurately they are capable of gathering temperature data for interpreting groundwater discharge/recharge into the river. A steady state one dimensional groundwater transport model was used to determine vertical groundwater discharge/recharge through the use of surface water, groundwater, and streambed temperatures.

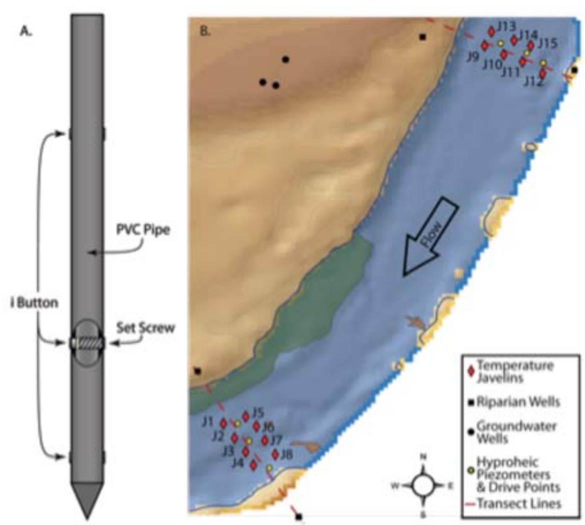


Figure 1 . Temperature Javelin installation site map of Flow Path site near Livingston, CA.

Laboratory Testing of Nitrate Sensors in Soil Columns

Large soil columns were fabricated at the Civil & Environmental Engineering Lab at Loyola Marymount University (LMU). Ion-selective sensors have proven effective in the laboratory using liquid solutions. However, sensor reliability is often affected in soil environments, which offer challenging conditions that include: saturated/unsaturated conditions affecting probe's moisture and non-uniform contact among sensor-water-soil-air. Experiments were conducted to test sensors' reliability and to help overcome these challenges. The experiment entailed injecting an instantaneous slug of nitrate in a 1-D steady up-flow field created inside a Plexiglas column packed with soil and equipped with up to 6 nitrate sensors (Figure 2). Sensors were pushed into low-moisture soil to simulate common "push-probe" field techniques. Sensors were calibrated in known nitrate solutions before and after the experiments to assess drift in calibrations. The sensors' temporal responses were assessed to determine whether or not the sensors captured the nitrate spike, and to study applicable principles of solute transport in saturated soil.

Figure 2. Soil column setup for testing sensor responses under unsaturated soil conditions.

CONTAM 01.3 Systems/Experiments

Groundwater-Surface Water Discharge Mapping

From October 16, 2008 through January 14, 2009 15 temperature javelins installed along two existing hyporheic piezometer transects approximately 100 meters apart. The Javelins were installed 5 meters apart and 4 meters on each side of the existing piezometer transects (see Figure 1). Streambed temperatures were measured in 30 sampling intervals at three depths below the streambed-surface water interface;

Groundwater temperatures were measured using Hobo water level loggers (U20-001-01) and found to be constant (19°C). Surface water temperature was assumed to identical to a downstream gauge station (MST). Upon retrieval of the temperature javelins it was found that there was an extremely high mortality rate (68%) of the Thermocron iButtons. Redundancy in the experimental setup ensured a minimum loss of data.

Vertical discharge velocities were calculated using an analytical solution to the convection-conduction equation for a saturated porous medium, allowing for the interpretation of discharge/recharge velocities through the use of surface and groundwater, and streambed temperatures. Uncertainty involved with this set up is less than 12 percent for the reasonably large temperature differences observed (>2°C) , however, when groundwater and surface water are not more than 2°C different, the uncertainty increases significantly (see Figure 4).

Laboratory Testing of Nitrate Sensors in Soil Columns

Sensors captured the injected nitrate spike in terms of signal strength and arrival time. Other sensors (not shown) exhibited similar responses. Results are promising in that the sensors may prove effective in detecting sudden nitrates spikes (e.g., as part of an alarm system in a field installation). Despite improvements, quantification of nitrate mass is not optimal due to sensor drift and uncertainty in background levels. Long-term use of sensor data for

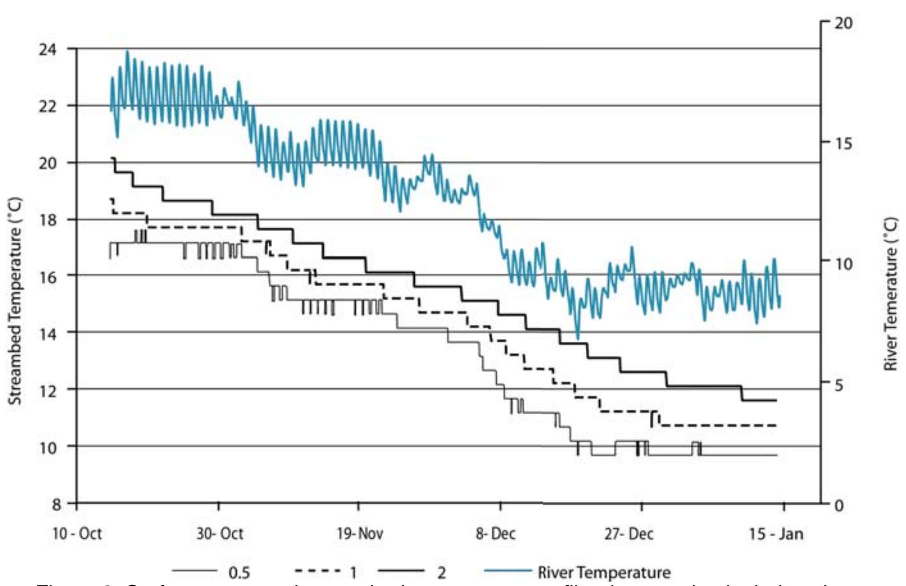


Figure 3. Surface water and streambed temperature profiles (sensor depths below river bed in meters)

quantification remains a challenge not only due to harsh field conditions, but also because newer sensors behaved better than older sensors

CONTAM 01.4 Accomplishments

Groundwater-Surface Water Discharge Mapping

Groundwater velocities were shown to be spatially heterogeneous about each transect with a small range (-1.82 to 4.80 cm/day) (Figure 5). Higher rates of groundwater discharge are found on the right side of the river in both transects. Groundwater discharge velocities were within range of previous studies at this site giving credence to the instrumentation, and method.

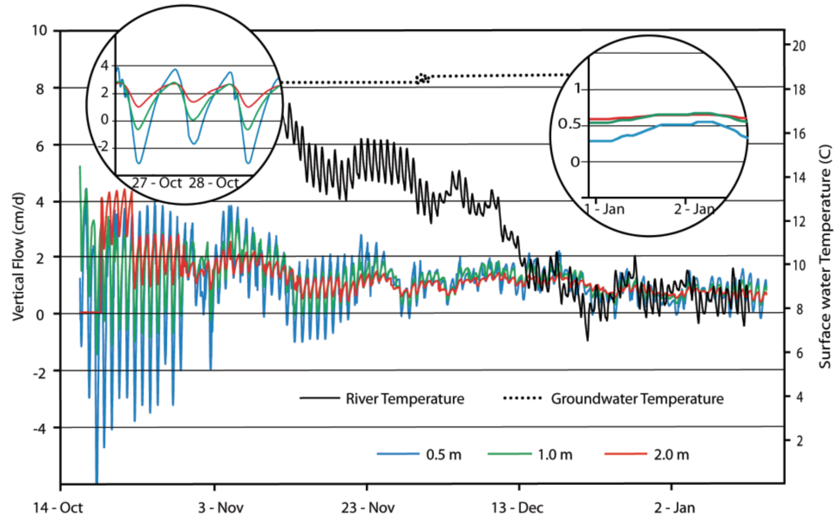


Figure 4. Estimated vertical groundwater velocities at various depths.

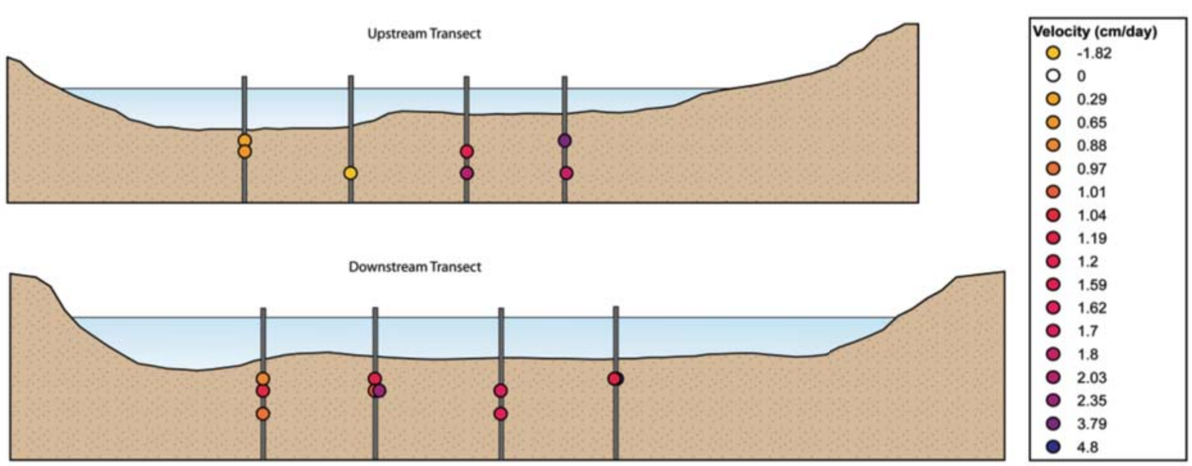


Figure 5. Mapping of groundwater-surface water discharges estimated for multiple locations in two cross-sections of the Lower Merced River.

Figure 5 shows groundwater discharge data for each depth of a selected temperature javelin over the monitoring period. After November 22 surface water temperatures diverge sufficiently from the groundwater temperature (2°C) to allow for groundwater discharges to be accurately calculated. Prior to November 22, the groundwater and surface water temperatures are too similar to utilize this model to calculate groundwater velocities, as is evident by the extreme noise in Figure 4. Small diurnal variations in groundwater discharge are evident from this point, and are in sync with surface water temperature cycling after December 22. Discharge values during this period are shown to be relatively small (~0.5 to 2 cm/day), which are consistent with findings by previous investigations in the region.

Laboratory Testing of Nitrate Sensors in Soil Columns

The nitrate sensors captured the injected nitrate spike in terms of signal strength and arrival time (Figure 6). Other sensors (not shown) exhibited similar responses. Results are promising in that the sensors may prove effective in detecting sudden nitrates spikes (e.g., as part of an alarm system in a field installation). Despite improvements, quantification of nitrate mass is not optimal due to sensor drift and uncertainty in background levels. Table 1 shows considerable uncertainty for the best two among six sensors tested.

CONTAM 01.5 Future Directions

Temperature Javelins as currently designed have proved effective in determining groundwater discharge or recharge. Future steps include the implementation of less expensive and higher resolution thermocouples in place of self logging thermistors, and the pairing of a more robust groundwater-surface water model capable of calculating both groundwater recharge and discharge. In addition the integration loggers, and radio modems connected to on site wireless sensor networks will allow for real time groundwater –surface water discharge monitoring. Long-term use of sensor data for quantification remains a challenge not only due to harsh field conditions, but also because newer sensors behaved better than older sensors.

From a broader perspective, the results and systems developed in this aspect (CONTAM 01) of the contaminant transport observation and management research thrust area will be integrated into synergistic projects (CONTAM 02 and SEN 04). The overall goal of these projects is to link water and chemical transport pathways from agricultural land uses, through groundwater, and into rivers.

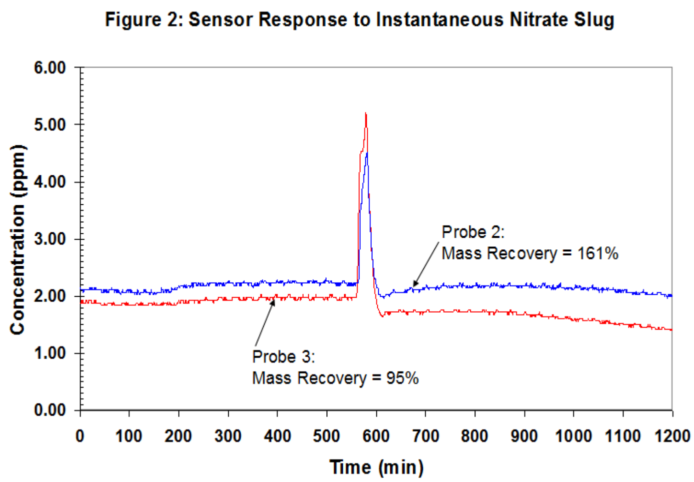


Figure 6. Responses of two nitrate sensors to injected nitrate pulse (10 ppm pulse injection).

CONTAM 02 Observations in Rivers and Urban Streams: San Joaquin River Mixing Dynamics and Mass Balances

CONTAM 02.1 Overview

Within river systems, stream metabolism may be used as a tool to evaluate river ecosystem structure and function because it directly assesses the balance between energy supply and demand within the system. By developing spatio-temporal assessments, we are looking for the association between metabolism rates and their variation, to water management and land use practices within a managed, agricultural system.

Specific objective:

The overall objective of this project is to create a quantitative link between land management activities and stream metabolism as an integrating measure of water quality change. In this year's report, we are specifically compare metabolic rates estimated within a lowland reach of the agriculturally dominated Lower Merced River using a conventional single station approach and a novel mobile station approach aimed at the first demonstration of high spatial resolution metabolic rate assessment in a river.

CONTAM 02.2 Approach

The assessment of the spatio-temporal variability of metabolism estimates occurring at a reach scale within the lowland section of an agricultural river system is of particular interest as this variability results not only from the position of the reach within the river continuum but from local natural and anthropogenic conditions. Such estimates have not been previously attempted at the spatial scale of interest here. Human-induced factors leading to alteration of the natural metabolic processes include (1) the alteration of the flow regime, reflected in changes in reach geomorphology, water temperature patterns, and groundwater-surfacewater flow exchanges, and (2) land use activities, reflected in changes in the riparian canopy cover -light/shade patterns-, reduction of light penetration by increase of the suspended sediment loads, and finally, potential eutrophication due to the excess in the nutrient loads reaching the river waters from agricultural drainage and sewage systems.

We are examining whole stream metabolism by using CENS systems to clearly define the physical aspects of the system in order to better understand the biological response and separate it from noise related to variation in these physical parameters. At this stage of the project, we are explicitly characterizing velocity, temperature, and light distributions while collecting high temporal resolution dissolved oxygen data to support metabolism calculations. The three main approaches are as follows:

- High temporal resolution dissolved oxygen data were collected and used to estimate net daily metabolism at high spatial resolution
- Light intensity sensors and a network security camera were used at the field site to acquire the incident light data from the water surface over a river reach.
- The NIMS RD and AQ robotic systems were used to provide high resolution data on river flow fields, which were then used to parameterize a 2D (depth-averaged) river model.

CONTAM 02.3 Systems Description and Experiments

High Resolution Metabolism Estimates

During a 6-day long experiment in the Spring of 2009, two monitoring systems were deployed within the lowland Merced River in order to study temporal and spatial variations of whole-stream metabolism. A stationary multiparameter sonde logging at a high resolution rate was set up in the mid point within a river transect providing us with data for the analysis of temporal variations of whole-stream metabolism during 4 diel cycles. Simultaneously, a networked info-mechanical system, NIMS-AQ, equipped with a multi-paramater sonde and an acoustic Doppler profiler (for velocity field measurements), was used to develop spatially distributed sampling within the same reach (see Figure 1). This distributed sampling system provided information for 11 sampling points along the river's cross section for three diel cycles (April 22 – 24).

The metabolism estimates were obtained using the open system oxygen change approach. This method states that within a system with no groundwater inputs, the rate of change of dissolved oxygen (Q) is the result of the development of an oxygen balance determined by the rates of change of Gross Primary Productivity (GPP), Community Respiration (CR), and diffusion of O2 to or from the atmosphere (D), all of them expressed in areal units (or volumetric units if the terms are divided by the averaged depth of the reach).

Light Intensity System and Experiment

Over the same reach of Lower Merced River, we began the development of an imaging sensor (camera) with algorithms to detect light/shadow patterns and pattern changes on the water surface (Figure 2). Inexpensive light intensity sensors (Hobo self-logging pendants) were used to provide calibration points in the field of view. The Multivariate Alteration Detection (MAD) technique with decision thresholds was used to identify changes in shadow for a given image pixel. The changes in shadow (increase or decrease) were classified based on scale, color (spectral properties), and shape (smoothness and compactness). A strong inverse relationship between changes in shadow and changes in light intensity was observed. The preliminary results suggest the feasibility of the proposed method for rapidly characterizing riparian vegetation-stream shading conditions over time and space, and their relation to river metabolism.

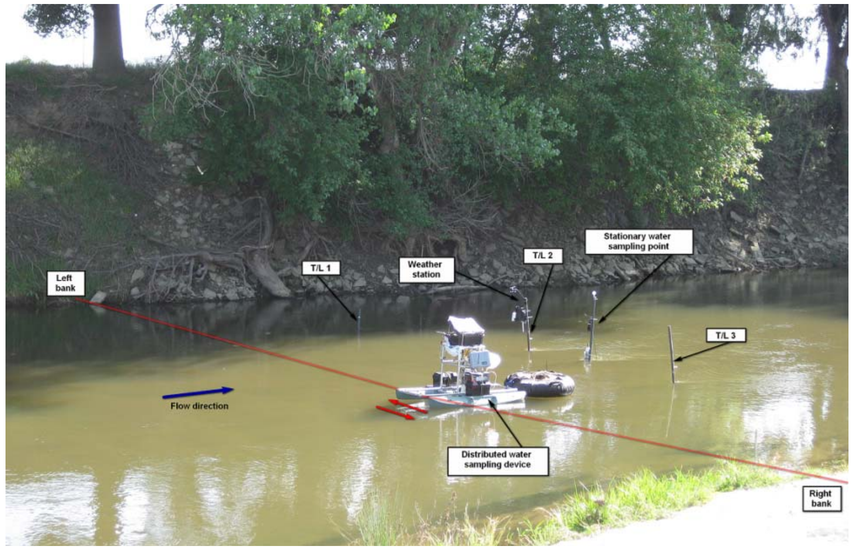


Figure 1. Experimental layout for river metabolism spatial assesment experiment.

Figure 2 - Light intensity sensors and PTZ security camera used for the river light incidence experiment.

High Resolution River Modeling

Using methods we developed in past reports for high resolution river characterization, we recently completed model development on the Lower Merced River. From field data, flow was calculated and elevation data was interpolated to provide proper boundary conditions for 2D (depth-averaged) hydrodynamic modeling. Flow and constituent flux estimates were calculated using point velocities and water quality parameters were measured using an acoustic Doppler velocimeter (Sontek ADV) and a multi-parameter probe (Hydrolab) respectively actuated in raster patterns using NIMS-RD. Flow calculations were compared with a nearby USGS gaging station for accuracy. River bed and floodplain geometry were directly measured by surveying (Leica) and echo-sounding device (Valeport). Further, parameterization determining how pressure is distributed in the hydrodynamic regime were also estimated from flow and geometry datasets but can be adjusted for model accuracy and stability.

Four cross sections were studied at the confluence: two upstream for inflow and two downstream for outflow. The furthest downstream cross section was near a local flow gauging station. The NIMS-RD system moved the sensor suite to each location to perform raster scans. To calculate flow through the cross section from individual velocity measurements, the typical vertical-velocity curve approximates an average velocity for a vertical rectangular subsection of the whole cross section. The sum of the subsections equals the total flow through the cross section. This whole process is known as the midsection method. The calculations are described below.

$$Q = \sum_{i}^{n} q_i = \sum_{i}^{n} a_i v_i$$

$$q_i = v_i \left[\frac{b_{i+1} - b_{i-1}}{2}\right] d_i$$

$$q_1 = v_1 \left[\frac{b_2 - b_1}{2}\right] d_1$$

$$q_n = v_n \left[\frac{b_n - b_{n-1}}{2}\right] d_n$$

$$v_i = \frac{\sum_j^m v_j R_j^{-1}}{m}$$

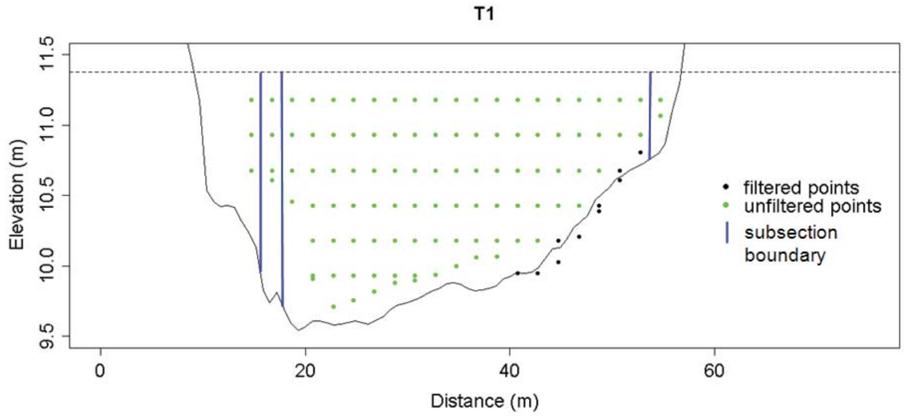


Figure 3. Sensor sampling locations for a raster scan at downstream cross-section (T1), where the black line shows the river bed bathymetry and dotted line shows the water surface elevation

Q is the volumetric flow, n is the number of subsections, q_i is the flow through a vertical subsection as defined in Figure 1, a_i is the area of the vertical subsection, v_i is the average velocity for the subsection, b_i is the distance from an reference to the observation point, d_i is the depth for the subsection found directly below a column of measurements (below any column of green dots shown in Figure 1), v_j point velocity measurement within the vertical subsection, and R_j is the ratio of point velocity with average vertical velocity defined by the measurement points depth to boundary.

The direct measurements of river bathymetry were interpolated using a multilevel B-spline. This helps with model stability and helps address sharp elevation differences between the measurement devices. Figure 4 shows the raw and interpolated field.

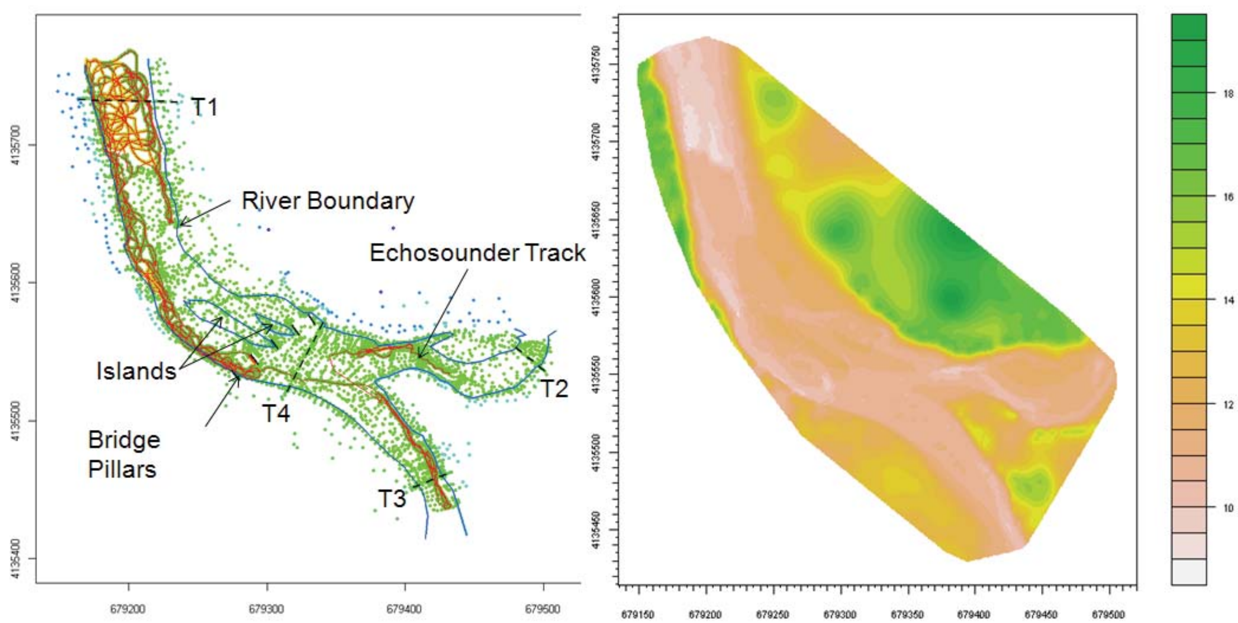


Figure 4. Left shows raw data points collected and right shows the interpolated topography from using RSurvey (an R-script developed by CENS research Jason Fisher).

CONTAM 02.4 Accomplishments

High Resolution Metabolism Estimates

The development of the high-resolution spatio-temporal analysis within this lowland agricultural river reach suggests that metabolism estimates obtained with the stationary system may not be able to characterize the spatial variation occurring along the cross section. This variation may be significant in the context of restoration, habitat assessment and/or similar investigations. Figure 5 presents the estimated values of Daily Community Respiration (CR24) and Gross Primary Productivity (GPP) for the two sampling strategies (stationary and distributed). Spatially, on an areal basis, an approximated three-fold variation exists in the estimates between the left bank (deep section of the channel) and the right bank (shallow zone). Temporally, a variability on a scale smaller than the typical seasonal analysis is appreciated.

Lower values of photosynthetically active radiation (*PAR*) during day 4 were reflected in the lower productivity estimates suggesting that *PAR* was a limiting factor during that day. The ratio of Gross Primary Productivity to Community Respiration (*P/R*) for the complete duration of the experiment ranged from about 0.65 to 0.85. Despite the fact that all of the estimated P/R ratios were less than one, the system does not rely exclusively on allochthonous carbon sources because none of the ratios obtained are significantly below 0.5.

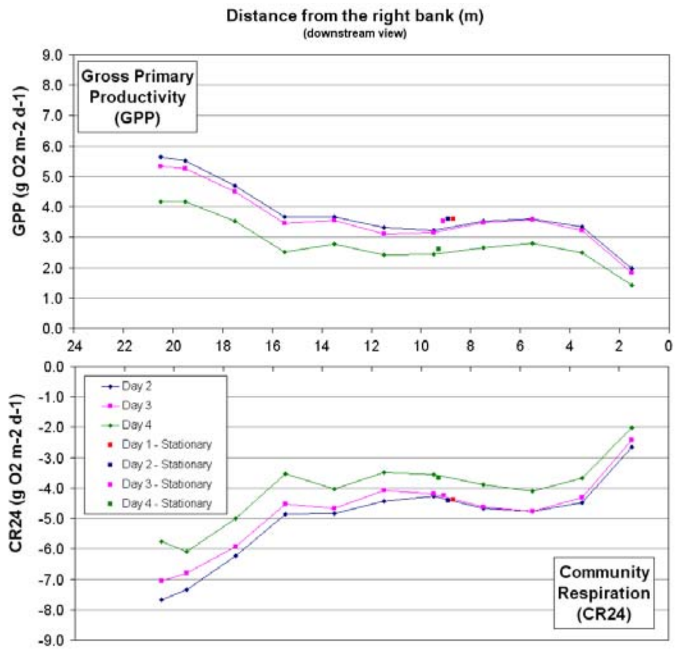


Figure 5. Stationary (dots) vs. Spatially distributed (lines) estimates of whole-stream metabolism.

Light Intensity System and Experiment

Using sequential images from a 50 m river segment and the aforementioned MAD technique, decision thresholds for change or no-change pixels can be set in terms of standard deviations about the mean for each component separately. In this research, pixels of MAD component Mi whose intensities are within ±2 σMi of zero, where σMi is the standard deviations of Mi, are no-change pixels. The changes in shaded area were calculated on object-based segmentation techniques. Shadow changes were most recognizable using the 2nd MAD component.

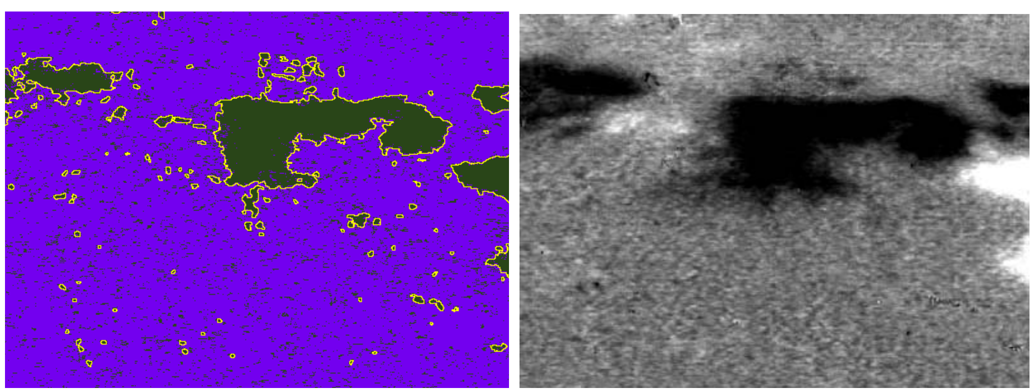


Figure 6 (left) describes the relative shaded area between 10:00 AM and 10:30 AM on September 10, 2009 (green area). Figure 4 (right) depicts changes in shade with dark pixels representing an increase in shaded area.

High Resolution River Modeling

Once the model is parameterized, the output typically generates fields for velocity magnitudes, velocity directions, and water surface elevations. The plots in Figure 7 show evaluate model output accuracy for three scenarios: element sizing, numerical model type (FESWMS vs. RMA2), and use of multilevel B-spline approximation for interpolation or the standard inverse distance interpolation provided by SMS.

The results showed better agreement for larger element spacing however the differences between element sizes were negligible. However, for numerical model and interpolation scheme, both FESWMS and the multilevel B-spline interpolation (MBI) performed noticeably better respectively. Additionally, the observed lateral velocity at the furthest downstream cross section, T1, suggests another channel that the model did not capture which may be due to inaccurate bathymetry data in that region.

CONTAM 02.5 Future Directions

Activities projected to be developed during the incoming year include:

Development of a tracer release experiment for the calculation of the reaeration coefficient (K2). The development of this experiment will improve our understanding of the air-water exchange process at our study site, leading us to a better estimation of the diffusion term within the O2 balance. We will compare the results of this experiment with values of K2 obtained through empirical equations or through the night-time method in order to define the methods applicable to our system.

Establishment of two semi-permanent monitoring stations located along the lowland Merced River. These stations will collect year-round data necessary for the development of the metabolism estimates. The ultimate goal of these stations is to investigate how the water management practices determine the metabolism rates temporally on a daily and seasonal scale, and spatially along the continuum within the lowland section of the River.

Employing additional light sensors in areas likely to exhibit more variations in shaded area to increase the spatial resolution could corroborate the observed trends. By also using polarizing film to prevent glare, and addressing potential image distortion due to camera position, this method of stream shading characterization can be further validated.

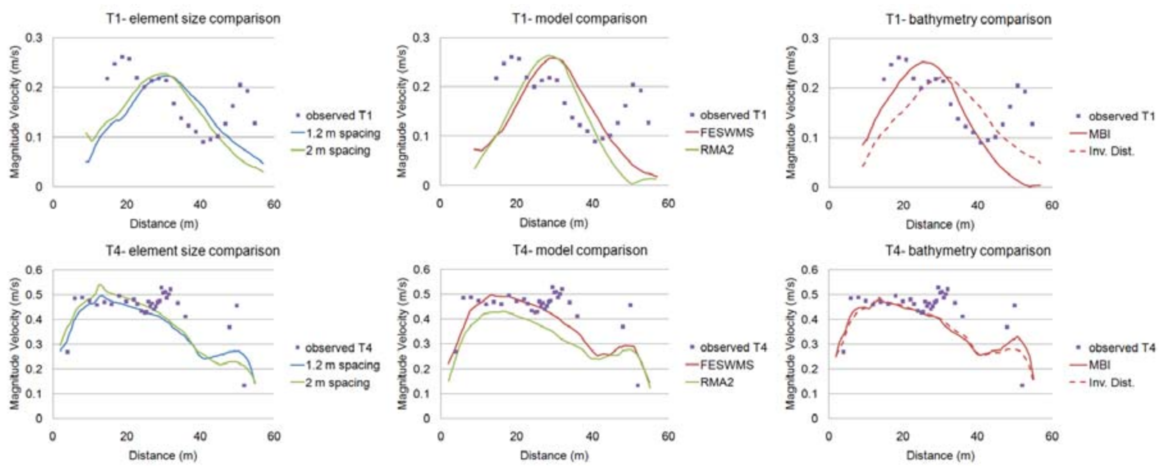


Figure 7. Results for downstream cross sections, T1 and T4, for the scenarios: (left) differing element spacing/sizing, (middle) numerical model, and (right) interpolation type . The lines represent model results while dots are the measured values.

Future work from this project aims to couple the multidimensional hydrodynamic models with other processes ranging from gross primary production to groundwater-surface water discharges and hyporheic exchange (see CONTAM-01 report). Also, the integration data from new sensors (acoustic Doppler profilers) and other spatial data to improve the simulation of these coupled processes.

CONTAM 03 Embedded Networked Sensing in Soils: A Stochastic Data Assimilation Approach to Network Design and Real-time State and Parameter Estimation

CONTAM 03.1 Overview

The County Sanitation District in Los Angeles applies four million gallons of treated wastewater per day to agricultural fields in Palmdale, CA, with a goal of wastewater reuse via irrigation. Wastewater often contains elevated solutes (e.g. sodium and/or nitrogen) and these excessive chemicals in soil could restrain crop growth and also pollute the groundwater beneath the irrigated lands. Thus, a monitoring and modeling system providing real-time soil state and flux estimates is needed to guide the management of wastewater release for the sustainability of these irrigated basins. In this project, the main goal is to use a data assimilation approach to merge soil state measurements from embedded sensor networks deployed in the Palmdale testbed into a coupled unsaturated water flow and solute transport model to provide sufficient, reliable soil state (moisture, temperature, nitrate and salinity concentration) and flux estimates for maximizing irrigation rates while preventing groundwater pollution and reducing restraints on plant growth.

CONTAM 03.2 Approach

The Ensemble Kalman Filter (EnKF) is chosen for this project because this approach can flexibly deal with the complexity and nonlinearities associated with hydrologic and solute transport processes in the unsaturated zone. The basic idea of this approach is that the EnKF propagates an ensemble of realizations (due to uncertain initial conditions, forcing, and model parameters) via the physical system model between measurement times, and updates the states of each realization using a Bayesian type update equation when measurements are available. In addition to states, model parameters can also be estimated with the EnKF framework using state vector augmentation. The idea of this method is that the parameters can be treated as time-invariant system states that are augmented to the original state vector and then estimated along with the state measurements. This method is applied to estimate soil hydraulic parameters (at different soil layers) to test whether the estimates of soil state and flux are improved when soil hydraulic parameters are updated.

CONTAM 03.3 System(s) Description and/or Experiments

Since the EnKF is able to estimate system states and/or model parameters, the primary experiments performed have been: (1) Determination of the best update strategy with the EnKF scheme and (2) Application of this strategy to the stratified soil system observed at the Palmdale site.

Experiment 1: Optimal update strategy with the EnKF scheme for homogeneous soils

In this observing system simulation experiment (OSSE), we explored the strengths and weaknesses of different update strategies with the EnKF (i.e. moisture update only, parameters update only, and moisture and parameters update simultaneously) for a simplified, homogeneous soil system. Fig. 1 shows the daily instantaneous soil moisture at midday for the truth, open-loop simulation, and filter estimates (with different update strategies). The ensemble mean of moisture in the open-loop simulation (Fig. 1b) is drier than the true moisture (Fig. 1a) since a higher ensemble mean (compared to the truth) of saturated hydraulic conductivity is applied in all the ensemble simulations. For the filter estimate with parameter update only, in the beginning of estimation period the moisture is drier than

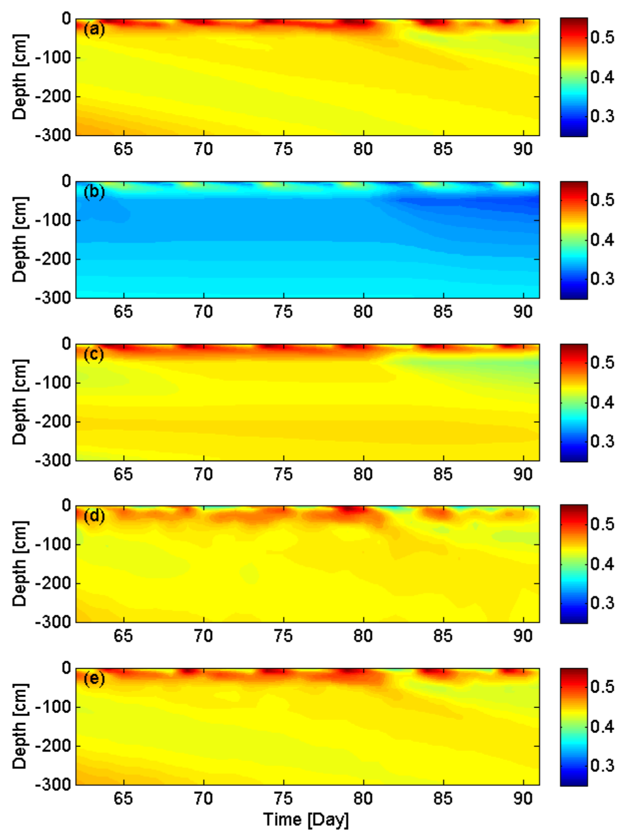


Figure 1. Daily instantaneous moisture saturation at midday for the: (a) truth; (b) open-loop simulation; (c) filter estimate with parameter update only; (d) filter estimate with moisture update only; and (e) filter estimate with moisture and parameter updates simultaneously. Results are shown during the final month of application period.

the value in the truth (not shown here) since the moisture is not updated and an initial bias exists in the saturated hydraulic conductivity. But at the end of the estimation (Fig. 1c), the soil moisture estimates are improved with the updated parameters. For the filter estimates with moisture update only (Fig. 1d), moisture is updated at each measurement time, but between measurement times the moisture diverges quickly due to the erroneous soil hydraulic parameters. For simultaneous moisture and parameter update (Fig. 1e), not only is the estimate of moisture corrected at each measurement time, but also the divergence of moisture between measurements is reduced due to the improved parameters. The estimation procedure not only improves the soil moisture state (which is the variable assimilated), but also improves parameter and solute estimates.

We are also interested in the flux estimation in the unsaturated zone. Fig. 2 shows the truth and ensemble mean of daily instantaneous water flux across the simulation domain. Note that the range of color bar in Fig. 2d is larger than the range in other sub-figures. Comparing Fig. 2b to Fig. 2a, a bias exists between the open-loop simulation and true flux. For the EnKF with parameter update only, the flux estimate is improved by the end of simulation period but still has remaining errors due to lack of moisture update (Fig. 2c). For moisture update only (Fig. 2d), since this filter estimate has larger saturated hydraulic conductivity and higher soil moisture (i.e. only moisture update), the flux estimate is significantly larger than the true flux. For the case of simultaneous moisture and parameter update (Fig. 2e), the flux estimate is closer to the true flux near the end of the simulation period and can reflect the true irrigation pattern near the surface. Based on these outcomes, it appears that the strategy with moisture and parameter update can lead to the best estimation of soil state, model parameter and flux.

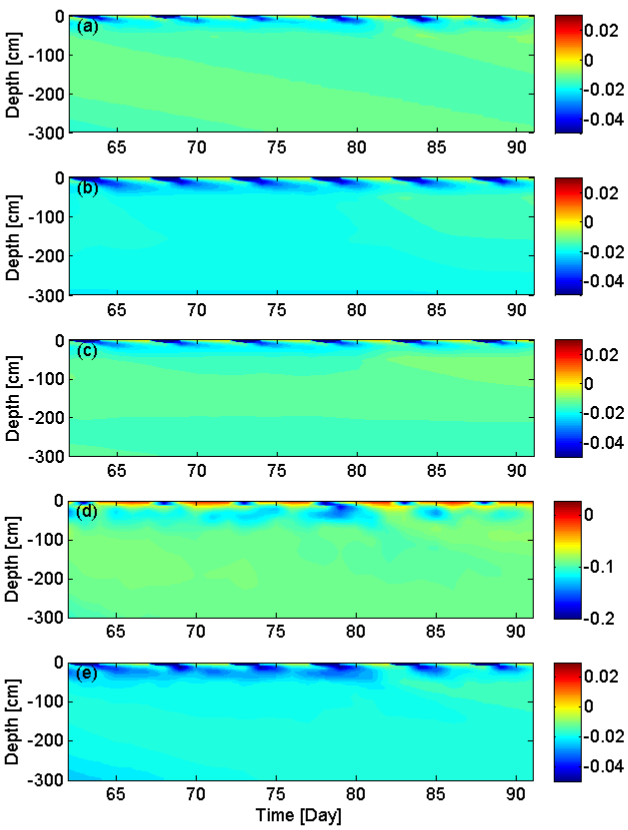


Figure 2. Daily instantaneous water flux at midday for the: (a) truth; (b) open-loop simulation; (c) filter estimate with parameter update only; (d) filter estimate with moisture update only; and (e) filter estimate with moisture and parameter updates simultaneously. Results are shown during the final month of application period.

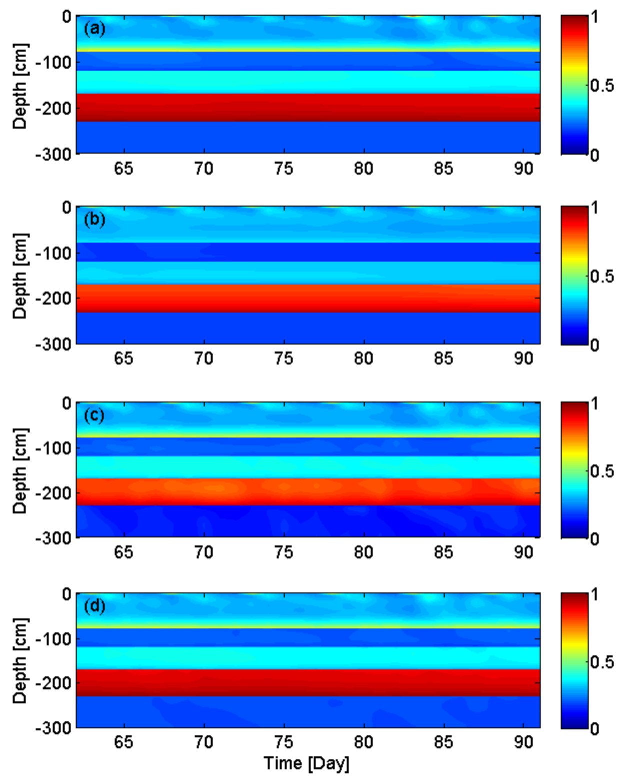


Figure 3. Daily instantaneous moisture saturation at midday for the: (a) truth; (b) open-loop simulation; (c) filter estimate with the near-surface observation network; and (d) filter estimate with the deeper observation network. Results are shown during the final month of application period.

Experiment 2: The effects of embedded sensor deployment with heterogeneous (stratified) soil media

The stratified soil system observed at the Palmdale site is investigated and two sensor configurations, near-surface (i.e. sensors are deployed only in the upper section of the simulation domain) and deeper observation (i.e. each soil layer has at least one sensor) networks, are applied to this heterogeneous soil column to assess if the EnKF scheme still performs well for the heterogeneous case. Fig. 3 shows the soil moisture estimates (expressed as relative saturation) compared to the truth. In Fig. 3c with the near-surface observation network, a better filter estimate in the upper three soil layers is obtained compared to the open-loop simulation (Fig. 3b). Since no measurements are available in the two deepest layers, the filter does not show an improvement in estimation for these two layers. However, when the deeper observation network is applied, the filter shows an obvious improvement in saturation estimate in these two layers (Fig. 3d). Fig. 4 shows the ensemble mean of nitrate concentration for the different estimates compared to the truth concentration. In Fig. 4, we can observe that the dynamics of nitrate evolution in both filter estimates are similar to the dynamics of the truth (i.e. the spatial extent of nitrate is mostly confined to the upper 100 cm of the simulation domain) compared to the open-loop simulation. This means that the estimates of solute concentration can be improved if the moisture and soil hydraulic parameters are updated correctly. Based on these results, it appears that with enough measurement information, the filter can significantly improve the estimates of soil state, soil hydraulic parameters and even fluxes.

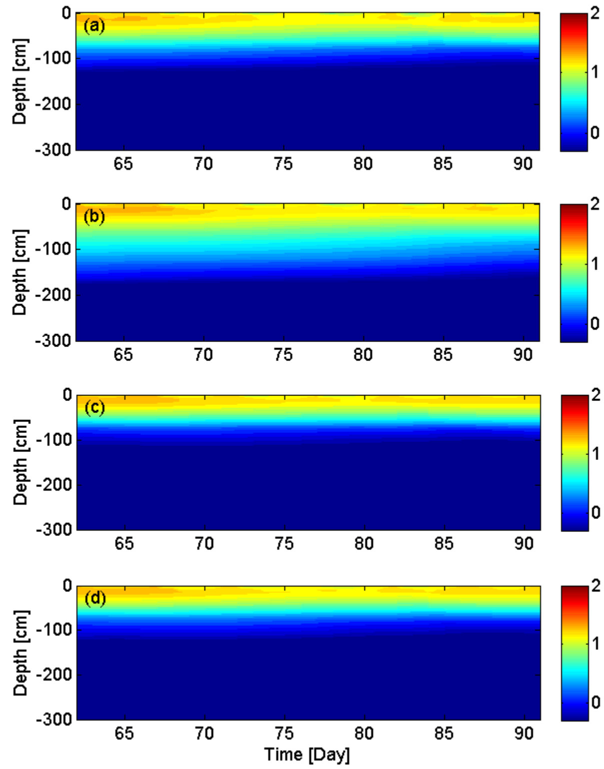


Figure 4.   Daily instantaneous nitrate concentration log[mg-N/L] at midday for the: (a) truth; (b) open-loop simulation; (c) filter estimate with the near-surface observation network; and (d) filter estimate with the deeper observation network. Results are shown during the final month of application period.

Experiment 3: Preliminary results from assimilating in-situ measurements into the coupled model

The feasibility of soil state and parameter estimation for the stratified soil system observed at the Palmdale site has been verified through the OSSEs shown above. The next step is to apply the proposed EnKF scheme to the site by assimilating real in-situ measurements into the coupled model. Fig. 5 and Fig. 6 show the filter estimate and open-loop simulation versus the moisture measurements at three depths (i.e. 25, 50, and 200cm) for sensor cluster 1 deployed at the site, respectively. In these two figures, the solid line represents the ensemble mean and the two dash lines represent the maximal and minimal values in the ensemble, and the red circles represent the moisture observations measured with sensors. Based on these two figures, the filter estimates can not only capture the moisture variation but also reduce the prediction uncertainty compared to the open-loop simulation. The preliminary results show that the EnKF is able to yield better estimates of soil states compared to the open-loop simulation. The next step in this experiment will be the development of a salinity transport model and the assimilation of the electrical conductivity measurements to assess salinity concentration at the site.

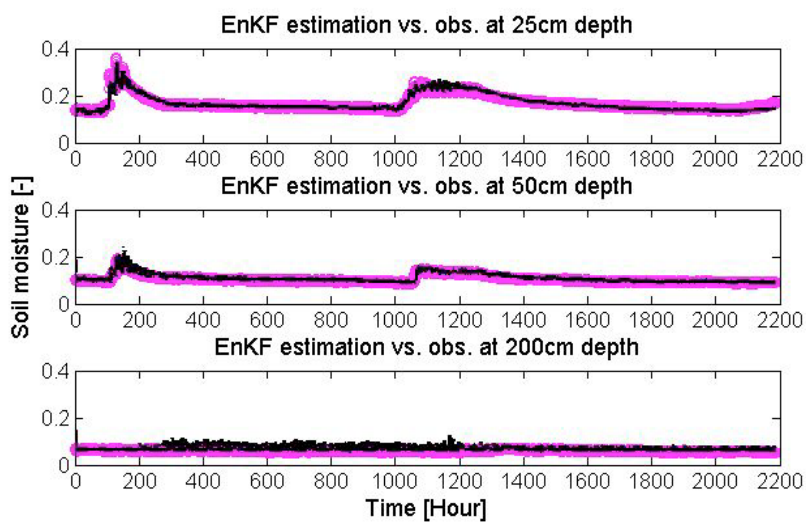


Figure 5.   Filter estimates of moisture versus sensor measurements at three different depths of sensor cluster 1 deployed at the Palmdale site. Solid line presents ensemble mean, dash line represents maximal and minimal realization, and red circle represents moisture observation.

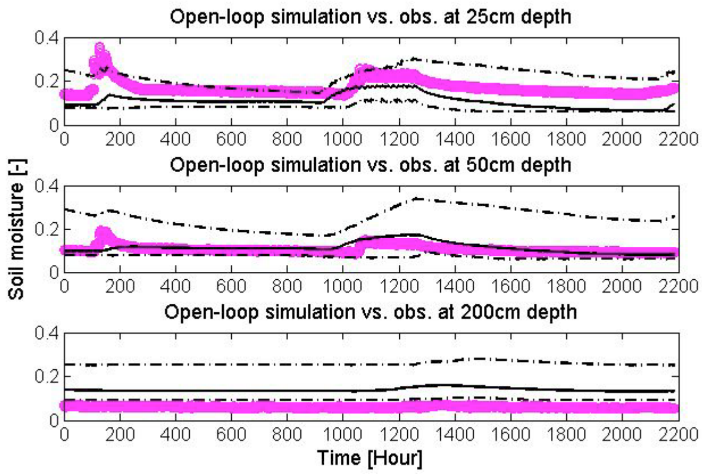


Figure 6. Open-loop simulation of moisture versus sensor measurements at three different depths of sensor cluster 1 deployed at the Palmdale site. Solid line presents ensemble mean, dash line represents maximal and minimal realization, and red circle represents moisture observation.

CONTAM 03.4 Accomplishments

Based on the results of experiment 1, we have shown that even for a homogeneous soil, accurate estimation of soil states and fluxes requires simultaneous estimation of states and parameters. Estimation of states only can lead to significant errors in fluxes if the parameters are not specified accurately a priori. Based on experiment 2, we have shown that even in the more complicated heterogeneous case, the EnKF is still capable of providing better estimates of soil state and flux if measurement information content is sufficient. The preliminary outcomes of the assimilation of in-situ measurements also show that the filter estimates can improve the moisture estimates at different depths and also reduce the uncertainty of estimation compared to the open-loop simulation. Together, these results indicate that the data assimilation approach provides a relatively robust framework for the real-time estimation of states/fluxes in an irrigated agriculture context.

CONTAM 03.5 Future Directions

The specific research tasks to be performed in the future are described briefly below.

Task 1: Development of salinity transport model

The wastewater applied for irrigation can generally contain elevated sodium that may pollute the soil and restrain plant growth. We would like to assess the transport of salinity at the Palmdale site and the potential for estimating the salinity flux through the system. To do that, the first step is to develop and incorporate a salinity transport model into the current coupled model. Then, a series of OSSEs assimilating electrical conductivity measurements will be performed to evaluate the capability of the EnKF to assess salinity concentration.

Task 2: Application of the data from the micro-meteorological station and sensor network deployed at the Palmdale site

Two experiments with real measurements will be performed to further test the proposed approach with real sensor data. First, a validation experiment (i.e. open-loop simulation) with updated states and parameters will be performed to assess the temporal interpolation/extrapolation capability of the EnKF. Second, measurements at a specific depth will be withheld from the assimilation to explore the spatial interpolation/extrapolation capability of the EnKF. Based on these two experiments, we will be able to evaluate the capability of the EnKF to estimate soil states, parameters, and even fluxes when real soil measurements are assimilated.

CONTAM 04 Deploying ion selective sensors to investigate how diurnal subsurface redox cycling influences arsenic mobilization in a Bangladeshi aquifer

CONTAM 04.1 Overview

Arsenic (As) in well water has led to the largest environmental poisoning in history, affecting tens of millions of people in the Ganges Delta and elsewhere. Despite the tragic public health implications of this problem, we do not yet have a complete answers to the questions of why dissolved arsenic concentrations are so high in the groundwater of the Ganges Delta, and how sulfur cycling affects the biogeochemistry of As in natural environments. Some literature indicates that seasonal, cyclic variations in redox conditions can lead to arsenic mobilization through a cycle of (1) oxidation of arsenic-sulfide solids and sorption of As(V) to Fe(III) oxyhydroxides and (2) respiration of AsV bearing Fe(III) oxydydroxides, leading to the release of As to the aqueous phase. Other recent studies have suggested an entirely new mechanism for arsenic mobilization. It may be that in phosphate limited conditions, microbial dissolution of minerals to gain phosphorus releases As incidentally from minerals such as apatite. Our activity over the past year has shifted to focus on laboratory microcosm experiments using soil and bacterial isolates from the site. We are investigation As release, sorption to biogenic minerals, and solubility in the presence of elemental sulfur.

CONTAM 04.2 Approach

Our current research has three components:

- We are comparing As release from mineral dissolution and Fe hydroxide respiration using the Bangladeshi soils in laboratory microcosms. Through these same experiments, we are testing the hypothesis that pond sediments are a major site of As release in Bangladesh through a comparison of As release from sediments collected from the paddy and the edge of the pond at our site.
- We are testing the hypothesis that As mobilization is largely controlled by sorption to biogenic minerals containing sulfide, as they appear to be far more sorptive to As relative to carbonate minerals. Using isolates from our site in Bangladesh, we are cultivating bacteria under conditions predicted by geochemical modeling software to result in the formation of differing types of minerals.
- We are investigating enhanced solubility of metals in the presence of polysulfides. The chemistry of As in sulfidic environments is extremely complicated due to the numerous soluble As-sulfide species predicted to form. The impact of elemental sulfur has been completed neglected in previous research and we hope to fill this gap.

CONTAM 04.3 Systems Description and Experiments

We are currently conducting experiments in the three areas described above.

- Comparison of As release mechanisms. To compare arsenic release from mineral dissolution and Fe hydroxide respiration, we incubated paddy and pond sediment under different conditions to measure the amount of As released. We designed the incubations to compare release by mineral dissolution (which should be higher under P limiting conditions and probably aerobic conditions) and reduction of arsenic-bearing Fe minerals. We did see some evidence for mineral dissolution (the live, P limited microcosm released more As than that with P added), but Fe mineral reduction led to greater release. Paddy and pond sediment behaved with similar trends (although we see more mobilization from pond sediment), but so far we have only tested the 0.5 m depth. When sulfide appeared, the arsenic decreased dramatically, but Fe stayed high. This is interesting, as it supports the preferential precipitation of As as As-S minerals over precipitation as Fe-As-S minerals (which has been a subject of some controversy in the literature). We are currently repeating this experiment at the 1m depth.
- Investigation of As sorption to biogenic minerals. From the Bangladeshi soil, we are maintaining three types of enrichment cultures: Fe-reducing, sulfate-reducing, and As(V) reducing. We are currently purifying isolates from all three enrichment cultures. We will investigate biogenic mineral formation by these isolates under varying chemistry (Fe/S(-II)/

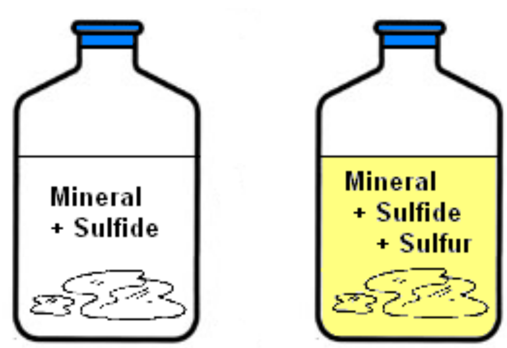


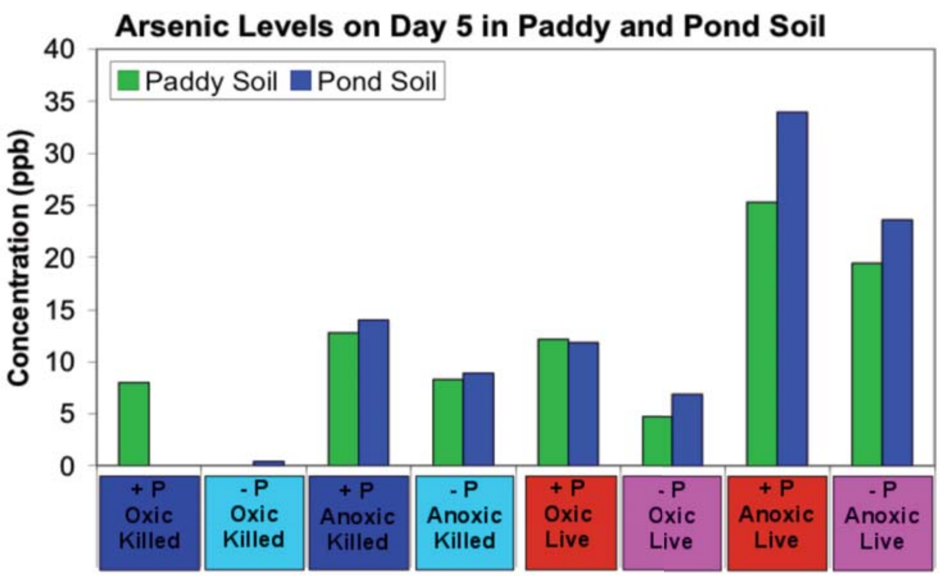
Figure 1. Schematic of metal solubility experiment. Bottles contain phosphate buffer, varying levels of sulfide, and the mineral of interest. Half of the treatments also contain elemental sulfur, resulting in a yellow color due to the formation of polysulfides.

S(0)/Carbonate) and how the biogenic minerals sorb arsenic. We will also test the availability of As(V) sorbed to standard minerals to the As(V) reducing isolates. Our first experiment uses FeRB in a solution only environment with As spiked and will compare it to one with S(II-) also spiked.

- Solubility of As, Pb, and Cd in the presence of elemental sulfur. We are looking at enhanced solubility of metals in the presence of polysulfides. See Figure 1 for a schematic.

CONTAM 04.4 Accomplishments

- See Figures 2 for Day 5 data for soluble As in sediment microcosms incubated under varying conditions.



	Oxic		Anoxic	
	+P	-P	+P	-P
Killed				
	+P	-P	+P	-P
Live		Mineral Dissolution	Iron Reduction	Iron Reduction/ Possible Mineral Dissolution

Figure 2. Soluble As at Day 5 for various microcosms. Text in the Table depicts the conditions for each treatment mobilization mechanism thought to be favored under a specific condition.

- We have enrichment cultures and isolates from our site, and have modeled the minerals predicted by geochemical modeling tools under varying conditions.

- Our preliminary data show that Pb(aq) and Cd(aq) concentrations are higher in the presence of S(0) than in the absence of S(0). Figure 3 shows the solubility of PbS(s) and CdS(s) in sulfidic solution in the presence and absence of elemental sulfur.

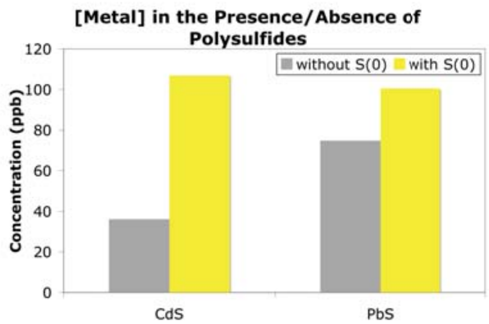


Figure 3. Solubility of Cd and Pb in a sulfidic system in the presence and absence of S(0).

CONTAM 04.5 Future Directions

This year's work will include follow up on all three areas:

- 1) New soil from the site is currently being obtained with the help of our Bangladeshi collaborators. We will repeat the As mobilization mechanism experiment at a range of depths at both sites. Additionally, we will add a mineralogical component to hopefully more directly detect which minerals are being consumed through microbial activity.
- 2) Laboratory-based and geochemical modeling investigation of As sorption to biogenic compounds. Isolates from Bangladesh site will be incubated at a range of Fe/S(-II)/S(0)/carbonate levels to result in formation of various biogenic minerals. Precipitated solids will be analyzed by standard mineralogical techniques with the help of collaborators.
- 3) We are currently repeating the experiment to include a bigger suite of pH's and S(-II) levels. Results will be modeled using FITEQL to determine best estimates for soluble complex formation constants.