

# ACTIVITY REPORT



**Natural  
Gas &  
Oil  
Technology  
Partnership**

**December 2003**

Bringing Department of Energy national laboratories capabilities to the petroleum industry.

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Note: Natural Gas and Oil Technology Partnership projects are reported according to the following schedule:

**January, March, May, July, September, November**  
Drilling, Completion, and Stimulation Technology  
Oil and Gas Recovery Technology  
Diagnostic and Imaging Technology

**February, April, June, August, October, December**  
Natural Gas Technology  
Upstream Environmental Technology  
Downstream Environmental Technology

**Natural Gas and Oil Technology Partnership on the World Wide Web: <http://www.sandia.gov/ngotp/>**

## Upstream Environmental Technology

### Ecological Framework to Evaluate the Effect of Size and Distribution of Releases at Upstream Petroleum Sites

(American Petroleum Institute, BP Amoco, ChevronTexaco, Exxon-Mobil, Gas Technology Institute, Unocal, ORNL, and LLNL)

#### Highlights:

- Continued work on manuscripts
- Groundwork for expansion/generalization of models

The intensive modeling phase of the project is complete and manuscripts are being finalized. Two models have been developed that can be used to determine the threshold frequency, size and/or distribution of habitat loss resulting from exploration and production activities that would have a significant impact on the persistence of herbivore and/or predator populations. Models are currently parameterized for the Tallgrass Prairie Preserve in Osage County, Oklahoma.

LLNL completed a series of experiments using the simulation tool Spatially Explicit Rodent DYNamics Computations and Analysis (SERDYCA) to study the effect of spills on artificial square habitats. Spills may cause fragmentation of the habitat (i.e., isolation of habitat patches), but most often spills induce inhomogeneities in the landscape (i.e., loss of habitat in a Swiss-cheese-like pattern without isolation of habitat patches).

Both ORNL and LLNL have begun work to modify and generalize their respective models in anticipation of applying the models to additional sites. Future work will utilize these models at sites near Vernal, Utah owned by the U.S. Bureau of Land Management that are undergoing oil and natural gas development. ORNL is investigating expanding the badger model to species such as the prairie chicken or raptors. While badgers hold the same home range their entire lives, other species may occupy different areas during breeding and other times of the year. Therefore, ORNL is adding an algorithm for abandoning a home range and establishing a new one. LLNL is investigating expanding the vole model to other rodent species such as the prairie dog.

#### Publications

The chapter "Toward A Framework For Assessing Risk To Vertebrate Populations From Brine And Petroleum Spills At Exploration And Production Sites" that was submitted for a book to be published by ASTM International was accepted for publication in 2004.

The LLNL team completed a paper entitled "The Effect Of Area Size And Predation On The Time To Extinction Of Prairie Vole Populations. Simulation Studies Via SERDYCA: A Spatially-Explicit Individual-Based Model Of Rodent Dynamics." The paper was submitted to the journal *Ecological Complexity*. Researchers at LLNL are also preparing a paper that studies the effect of spill inhomogeneities on prairie vole persistence.

ORNL revised the paper "Unnatural Landscapes In Ecology: Generating The Spatial Distribution Of Brine Scars" based on reviewer comments from the journal *Environmetrics*.

ORNL is revising the manuscript entitled "Simulated Effects Of Habitat Loss And Fragmentation On The American Badger (*Taxidea taxus*)" for submission to *Ecological Modelling*. Additional sensitivity analysis is being conducted to determine how two main types of mortality (habitat-related and movement-related) control the population's response to fragmentation.

ORNL submitted an abstract to the International Association for Landscape Ecology entitled "Spatial Life History Influences The Risks Associated With Habitat Loss And Fragmentation Associated With Petroleum Exploration And Extraction." The abstract was invited for a session on "Landscape Ecological Modeling And Ecological Risk Assessment: At The Crossroads."

## Estimation and Reduction of Air Quality Modeling Uncertainties

(Envair, EPRI, and LBNL)

No report received.

## Remote Sensing for Environmental Baseline and Monitoring

(US Geological Survey (USGS), and USDA Agricultural Research Service (ARS), and ORNL)

### Highlights:

- Received remote hyperspectral data measured in Osage County.
- Verified the data from the seven study areas.
- Revised the cluster algorithm.
- Found 69 distinct spectral clusters for USGS Site B.
- Submitted journal paper.

The US Geological Survey (USGS), the USDA Agricultural Research Service (ARS), and ORNL are collaborating to develop remote (airplane or satellite) hyperspectral sensor techniques to identify areas impacted by oil production. On November 10, ORNL received the hyperspectral data that the HyVista Corporation (<http://www.hyvista.com/>) had measured in Osage county, OK on October 12. ORNL asked HyVista to image seven distinct areas that total 39 square kilometers (km). HyVista created a flight path that imaged three regions with overlapping strips. Each strip is 512 three-meter-pixels wide, for a total of 1536 meters. The north region has three strips with a total length of 12 km and a total area of 18 square km. The south region has six strips with a length of 69 km and an area of 106 square km. The west region has five strips with a total length of 40 km and an area of 61 square km. The total area is 185 square km. The data was received on five DVD and totals 14.4 gigabytes. The latitude and longitude of each pixel was provided. ORNL verified that the data covered the seven study regions.

ORNL is analyzing the HyVista data for a region that includes the USGS research site B. The region is 130 pixels by 98 pixels for a total of 12,740 pixels. Each pixel has 126 bands of hyperspectral data. The large number of pixels has required a revision of the clustering algorithm, which was developed for a field data set with 211 measurements. Previously, the algorithm began with the correlation matrix between all of the measurements. The revision is to calculate the correlation between a selection of the pixels and all of the other pixels (to calculate selected rows of the full correlation matrix). The preliminary analysis has found 69 distinct clusters for the study region. The spatial locations of the clusters are being analyzed to find clusters that only occur in the areas with brine scars.

### Publications

In previous work on this project, ORNL and the ARS wrote a paper on a new clustering algorithm for hyperspectral data and submitted it to the *IEEE Transactions on Geoscience and Remote Sensing*. After some very constructive comments by the reviewers, the revised paper "A New Clustering Algorithm for Unsupervised Classification" was resubmitted to the journal on December 17.

## Modeling of Water-Soluble Organic Content of Produced Water

(ChevronTexaco, ConocoPhillips, Shell, Statoil, and ORNL)

### Highlight:

- Published data on produced water was surveyed, including information from the Gulf of Mexico, the North Sea, and on-shore gas wells.

Produced water data sets from the Gulf of Mexico, the North Sea, and on-shore gas wells show a great degree of variation of organic compounds, but a few trends are apparent. These general statements appear to apply to water produced from onshore, offshore, and near-shore sources.

Unless contamination of the reservoir occurs, the paraffinic oil and grease load in produced water is very low, within National Pollution Discharge Elimination System permits for offshore oil and grease. Entrained droplets can contribute up to 40 ppm to the measured total petroleum hydrocarbon, and cannot be removed by gravity because of their small size, <20 microns.

Oxidized organics are more soluble than aliphatic hydrocarbons, and their concentrations are difficult to predict from knowledge of the geochemistry of formation waters because oxidation often occurs during separation and treat-

ment. These organics, however, represent a large fraction of the total extractable material sampled using EPA methods. Organic acids, which have a relatively high prevalence in all produced water fractions, can have concentrations as high as 1000 ppm.

Other heteronuclear organics are not particularly prevalent in the water soluble fraction, unless introduced to enhance production, e.g., amines.

Volatile aromatic compounds can represent a significant fraction of the water soluble organic material, depending on the source of the oil and the degree to which the oil and the water has been outgassed before sampling. The concentrations of volatile aromatic compounds is difficult to predict with models based strictly on thermodynamic equilibrium calculations. Non-volatile polyaromatic hydrocarbons are much less soluble, and these are present in ppb amounts in the water.

There are few data on some organic compounds that may be relatively soluble in produced water, such as ketones, aldehydes, mixed heteronuclear organics, mercaptans, and thiols.

The range of produced water data sets, the quality of the data, and the variability within the data set affect the choice of the predictive model (phenomenological or statistical).

## Science-Based Methods to Assess Risks Attributable to Petroleum Residues Transferred from Soil to Vegetation

(ChevronTexaco, PERF UC-Berkeley, UC-Davis, and LBNL)

### Highlights:

- Initial set of extractions complete
- Presented results at SETAC conference
- Presented detailed progress report at PERF 99-13 meeting

LBNL and UCD researchers completed the initial set of chemical extractions and analyses of grass, soil, and air samples that were collected during the controlled plant uptake exposure study performed at UCD. Both polycyclic aromatic hydrocarbons (PAH) and n-alkanes were quantified in the samples. Resulting plant/soil concentration ratios (dry weight basis) were compared to modeling results from both the empirical Travis and Arms soil-to-plant bioconcentration model and the more process-based mass balance plant uptake model that LBNL researchers developed during year one of this project. Preliminary findings for the 12 PAH's in the exposure experiment indicate that

(1) the concentration ratio between grass and soil were linear over the three order of magnitude concentration range used in the study demonstrating that uptake processes were not saturated,

(2) the concentration ratios for the PAHs were not influenced by elevated levels of n-alkanes in the soil,

(3) the measured concentration ratios were below those predicted by the empirical Travis and Arms model, particularly for the 2- and 3-ring PAHs, and

(4) the measured values were higher than the values estimated by the mass balance model run with default inputs (not calibrated) but the measured values showed the same parabolic function as predicted by the mass balance model.

Measurements of the concentrations of n-alkanes (with even carbon numbers from C20-C30) in soil and grass revealed no accumulation in the above-ground portion of the plant over a wide range of contaminant concentrations in the soil. LBNL researchers speculate that the soil-borne petrogenic n-alkanes (even carbon numbers) may not be transferred through root tissue to the above ground plant parts because of the high level of biogenic n-alkanes (odd carbon numbers) in plant tissue including the root epidermis. The petrogenic n-alkanes may also be readily metabolized within the plant thereby preventing accumulation in the above ground tissue. These explanations need to be evaluated further by analyzing contaminant levels in the roots.

Results from the plant uptake study and modeling research related to this project were presented by LBNL researchers at the Society of Environmental Toxicology and Chemistry (SETAC) conference in November (Maddalena et

al 2003a; Kobayashi et al 2003). LBNL researchers also presented a detailed progress report (Maddalena et al 2003b) to members of the PERF 99-13 (Petroleum Environmental Research Forum) at their annual meeting organized by researchers at ChevronTexaco. LBNL and UCD researchers submitted an abstract to the SETAC Europe conference to be held in Prague, Czech Republic, April 18-24, 2004.

#### Publications

Maddalena, R.L.; R. Kobayashi, T.E. McKone, and N.Y. Kado. "Controlled Chamber Measurements of the Multipathway Uptake of PAHs from Soil into Wheat." Paper presented at Society of Environmental Toxicology and Chemistry Annual Meeting, Austin TX. 2003a

Kobayashi, R.; R.A. Okamoto; R.L. Maddalena and N.Y. Kado. "Measurement of Polycyclic Aromatic Hydrocarbons in Wheat Grains." Poster presented at Society of Environmental Toxicology and Chemistry Annual Meeting, Austin TX. 2003

Maddalena, R.L.; R. Kobayashi, T.E. McKone, and N.Y. Kado. "Controlled Chamber Measurements of the Multipathway Uptake of PAHs and n-alkanes from Soil into Wheat." Presentation at PERF 99-13 Annual Meeting, Richmond CA. 2003b

### Interactive Information System on Drilling Waste Management Practices (ChevronTexaco, Marathon, and ANL)

The decision tree flowcharts for the technology identification module were programmed into a first draft early December. The project team reviewed them and made suggestions for improvements.

Text for the regulatory module was completed in late December, and will be programmed during January.

Several of the technology fact sheets were drafted in December, and will be completed in January.

It is anticipated that a full draft website will be finished during March or April and then undergo testing by a selected review panel.

### Use of Ionic Liquids in Produced Water Clean Up (ChevronTexaco, Shell, Conoco-Phillips, ORNL)

#### Highlight:

- Quartz crystal microbalance apparatus commissioned

A quartz crystal microbalance apparatus was commissioned for the detection of organic molecules in produced water. The apparatus has been previously used at Oak Ridge National Laboratory for the detection of CO<sub>2</sub> in air, and of acetone in aqueous solution. The detection works by the uptake of organic into a film of ionic liquid coating the quartz crystal. In the simplest formulation, the measured frequency shift is related to the mass of uptake by the Sauerbrey equation, although viscosity changes in the surface layer and changes in the fluid density can also affect the oscillation frequency.

The goal of the first commissioning tests was to reproduce the earlier ORNL data on CO<sub>2</sub>/air and organic systems. The ionic liquid that showed promise in liquid-liquid extraction tests, butyl-methyl imidazolium Tf<sub>2</sub>N, was used on the crystal. The tests will continue with the analysis of brine solutions spiked with organic compounds typical of produced water contaminants. The solutions will be sparged with nitrogen, which will transport the organics to the sensor. From earlier work, it is expected that the change in frequency will be related quantitatively to the concentration of organic in aqueous solution.

## Hydrophobic Membranes for Removal of Organic Impurities in Production Water (LLNL)

No report received.

## Downstream Environmental Technology

### A Predictive Model of Indoor Concentrations of Outdoor PM<sub>2.5</sub> in Homes

(Aerosol Dynamics, Western States Petroleum Association, and LBNL)

No report received.

### A Predictive Model of Indoor Concentrations of Outdoor Volatile Organic Compounds in Homes

(American Petroleum Institute, Western States Petroleum Association, and LBNL)

No report received.

### Characterization and Reaction Behavior of Sterically-Hindered Sulfur Compounds in Heavy Crudes with Nano-Sized Molybdenum Disulfide

(ChevronTexaco, BNL, and ANL)

Project suspended pending renewed funding.

### Development of a Solid Catalyst Alkylation Process Using Supercritical Fluid Regeneration (Marathon-Ashland and INEEL)

Three new catalysts were explored in the reaction/regeneration system; a new USY zeolite, a Beta zeolite, and a Mordenite zeolite. Reaction conditions were 60 °C, an isoparaffin to olefin ratio of 20:1, and an olefin weight hour space velocity of 0.265 hr<sup>-1</sup>. The USY had the highest activity followed by the Beta zeolite, with the Mordenite zeolite having the lowest activity. Despite the lower activities, both the Mordenite and Beta catalyst regenerated very well without any appreciable loss in activity maintenance over 50 hours of study. Under the same regeneration conditions, the USY activity maintenance dropped under 90% in initial activity in just over 30 hours. Activity maintenance studies using the Beta zeolite were performed at a lower olefin weight hour space velocity of 0.20 and 0.1 hr<sup>-1</sup>. The activity improved as the space velocity decreased and the activity continued to be regenerated well over the length of the experiments. At the olefin weight hour space velocity of 0.1 hr<sup>-1</sup>, the Beta zeolite catalyst regenerated to initial activity levels for 124 hour, or over 5 days of continuous operation while providing conversions and yields comparable to that of the USY zeolite.

A manuscript titled "Recovery of Alkylation Activity in Deactivated USY Catalyst Using Supercritical Fluids: A Comparison of Light Hydrocarbons" was accepted for publication by the journal *Applied Catalysis A: General*.

### Secondary Organic Aerosol Research in the Sierra Nevada Foothills

(Aerosol Dynamics, Independent Petroleum Association of Mountain States, and LBNL)

No report received.

## Proton Exchange Reactive Membranes for Conversion of Light Alkanes to Clean Liquid Fuel

(Ceramatec, Inc. and INEEL)

A new proton conducting membrane with platinum mesh electrodes was received from Ceramatec. The membrane was cycled up to 800°C and found to maintain seal integrity. After system evaluation, it was determined that the membrane generated an electrical potential and a current. The current at 700 °C was measured as 300 mA, corresponding to 0.0021 cc/min of hydrogen flow. That flow rate is below the detection limit of the residual gas analyzer system. Ceramatec is in the process of making a new membrane with better transport properties.

New ruthenium/molybdenum ZSM-5 zeolite catalysts were prepared and tested under dehydrocyclization reaction conditions. No liquid reaction products were observed using this batch of catalyst; however, a significant conversion of methane to hydrogen transpired. Modifications of the catalyst preparation processes have been developed to focus on liquid yield.

## Bioupgrading of Heavy Crudes Using Temperature and Oil Tolerant Enzyme Catalysts

(ChevronTexaco and ORNL)

No report received.

# Natural Gas Technology

## Molecular Engineering: Next Generation of Gas Purification Technology

(ChevronTexaco, Virginia Commonwealth U, and BNL)

No report received.

## Coiled-Tubing-Deployed Hard Rock Thermal Spallation Drill and Cavity Maker

(Nextant, NM Tech, and LANL)

### Highlights:

- NM Tech successfully modified their prototype, lab-based, flame jet burner design to achieve a stable burner operation at 90% of the targeted fuel rate.
- The subcomponents needed to fabricate a 200-ft long coiled-tubing with support utilities and attach it to the coiled tubing unit have been procured.

Los Alamos completed a specification for a fabricated 200-ft long coiled tubing with internal umbilicals and placed an order with Precision Tube Technology to procure it. The internals include a 0.125-inch OD 316 stainless steel tubing (fuel line) and an eight-conductor, 0.220-inch OD cable (telemetry plus power for igniter) inside a 0.500-inch OD 316 stainless steel tubing (water line) that will be inside the 1-inch coiled-tubing (air line). Delivery of the coiled tubing is expected in February.

Los Alamos completed the specifications and placed an order with Dynamic Sealing Technologies for a two-port rotating union with an integrated 10-circuit electrical slipring (swivel-commutator) unit to be used for connecting the top end of the coiled tubing to the surface supply for fuel, cooling water, and electrical power and telemetry systems on the coiled-tubing unit. The existing swivel on the coiled tubing unit will be used to connect the air supply to the coiled tubing on the opposite hub.

NM Tech continued bench testing of the burner with the modified flame holder. Air flow rates of more than 900 standard liters per minute were achieved after the air supply system was modified to achieve higher combustion chamber pressures. This air flow rate is more than 92% of the air rate required for stoichiometric combustion and more than 88% of the target air rate needed to supply 5% excess air at the design target of 10 lb/hr propane. When a smaller nozzle was installed to produce a supersonic exhaust from the burner, the maximum air flow achieved was reduced to 750 standard liters per minute.

The burner noise increased substantially which may have been the result of achieving a supersonic flame-jet. When the burner was positioned to impinge on a spallable rock sample, the spalling rate and velocity of the rock fragments observed was significantly increased over that observed during earlier burner demonstrations at lower fuel and air rates.

The air supply pressure was increased 10 psi to about 110 psig at the compressor receiver to see if the limit was due to the air supply pressure or the result of sonic conditions at the exit nozzle throat. However, inspection of the combustion chamber showed that the flame holder had melted and the test was not continued. Burner testing will not be pursued on the test burner until modifications, based on what has been learned, have been implemented on the drill stage burner.

Based on the test burner results, the drill stage burner was modified to include an enlarged flame holder section and a modified in-line mixer. Rates and flame stability were only marginally improved, if at all, and the mixing section was again redesigned and fabricated with a narrower throat to produce more change in the flow streamlines and, hopefully, improved mixing. The narrower throat resulted in a maximum air rate that was half the design air rate, but about 2.5 times the rates achieved previously when a stable flame was observed.

### Scintillating Fiber Neutron Detectors for Well Logging

(CompuLog, Precision Drilling, Technology Services Group, and PNNL)

#### Highlight:

- Detector signals undergoing optimization

Current work continues to focus on optimizing the readout electronics for the photomultiplier tubes (PMTs). All work is based on the low temperature version of the detector. Background (dark current), gamma ray, and neutron response were collected for each PMT as a function of voltage over the manufacturer's recommended operating range. Lower voltages give better discrimination between neutron and gamma ray events with good noise suppression. The PMT's differ by about a factor of two in sensitivity but are still within manufacturer's specifications. The PMT's do not show signal saturation at ambient temperatures. Signal saturation is probably designed to happen only at elevated temperatures.

Moderator materials are still under evaluation for the high temperature version (200°C) of the detector.

### 225° C MWD Using Silicon-On-Insulator (SOI) Electronics

(Baker Oil Tools, Eagle-Picher, Honeywell SSEC, General Atomics, Noble Engineering, Quartzdyne, and SNL)

No report received.

## Partnership Office

The Upstream Environmental Technology Forum will hold a review on existing projects on February 25 in Houston. Details of venue and schedule will be announced when available. Existing projects requesting

fiscal 2004 funding are to submit proposals by January 16. Due to budget constraints, no new-start projects will be solicited for fiscal 2004.