Project ID: 70050: "Novel Optical Detection Schemes for In-Situ Mapping of Volatile Organochlorides in the Vadose Zone"
Grant FG07-99ER62881
June 15, 2001

S. Michael Angel: Principal Investigator, Department of Chemistry and Biochemistry, The University of South Carolina, Columbia, SC 29208,
(803) 777-2779 office, (803) 777-9521 FAX, Email: angel@mail.chem.sc.edu

Molly M. Gribb: Co-Investigator, Department of Civil Engineering, Boise State University, Boise, Idaho 83725,
(208) 426-5707, Email: mgribb@boisestate.edu

Bill W. Colston Jr: Lab collaborator, Medical Technology Program, Lawrence Livermore National Laboratory, PO Box 808, Livermore, CA 94550,
(925) 423-0375, Email: colston1@llnl.gov

***Number of graduate students and/or post-doctorates actively involved in the project*:**
3 graduate students at USC
1 post-doctorate at Boise State

Research Objective
Long-term objective: To develop a system for measuring and identifying a wide range of volatile organic hydrocarbons, including aromatics, carbon tetrachloride, TCE and other organochlorides, at ppb levels *in-situ* in the subsurface ("at-depth") using a fiber-optic REMPI probe in a cone penetrometer.

Specific focus of much of the proposed work is to identify and optimize those experimental parameters which effect the *in-situ* determination of organic molecules in the subsurface using resonance-enhanced multi-photon ionization (REMPI).

Emphasis is placed on visible excitation so that the high transmission of fiber-optics at visible wavelengths can be fully utilized.

A fiber-optic REMPI system is being designed and integrated into an existing cone penetrometer system at LLNL. The design will be compatible with existing Raman and fluorescence probes.

Research Progress: Second year of project
This report summarizes work during Year 2 of this 3-year project.

- USC compared UV (1+1) and visible (2+2) REMPI excitation of toluene using the coaxial fiber/electrode REMPI probe and obtained detection limits of 1.7 ppb and 7.5 ppb of toluene using UV and visible excitation, respectively.
- USC and LLNL demonstrated *in-situ* measurements at 20 ppb benzene and 43 ppb toluene using the coaxial fiber/electrode REMPI probe with 15 mJ/pulse (Figures 1 and 2).
- USC and LLNL demonstrated ~4 orders of magnitude linearity for visible wavelength, 4-photon REMPI of toluene and benzene with the coaxial fiber/electrode REMPI probe.
- Invited to deliver a plenary lecture at the **Tenth International Symposium on Resonance Ionization Spectroscopy.**

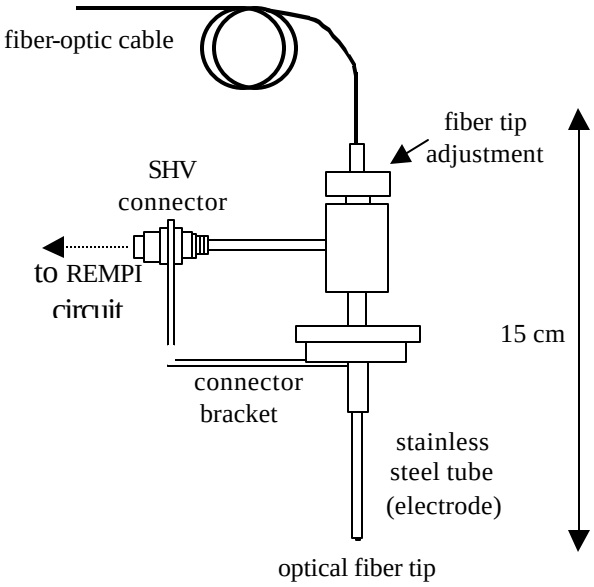

Figure 1. Diagram of optical coaxial fiber/electrode REMPI probe.

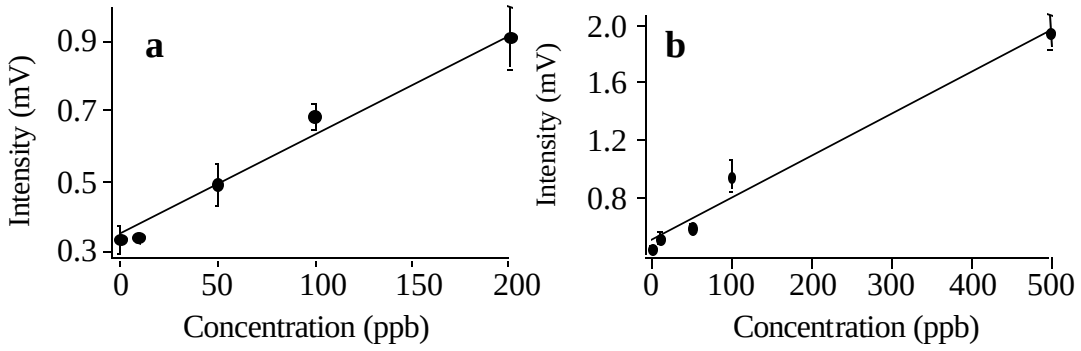

Figure. 2. Calibration of (a) toluene and (b) benzene. For both calibrations a 600 micron diameter optical fiber was used. Each point represents the average of five measurements with error bars showing ±1 sample standard deviation using 15 mJ/pulse.

- USC and LLNL performed mixture studies of benzene, toluene, and m-xylene using visible excitation and showed feasibility for selective excitation.
- USC performed a chemometric analysis on the mixture data showing selectivity of individual species within the mixture.
- USC used a new measurement cell to measure less than 2 ppb of toluene using only 3 mJ/pulse with an excitation optical fiber

- USC compared various core diameter optical fibers with the coaxial fiber/electrode REMPI probe in terms of sensitivity and optimal probe voltage.
- Boise State has begun construction of the soil column for *in-situ* REMPI measurements (Figure 3).
- LLNL has started the design of a cone pentrometer incorporating the fiber-optic REMPI probe.
- A white paper was drafted proposing a field demonstration in Spring 2002 at the Savannah River Laboratory.

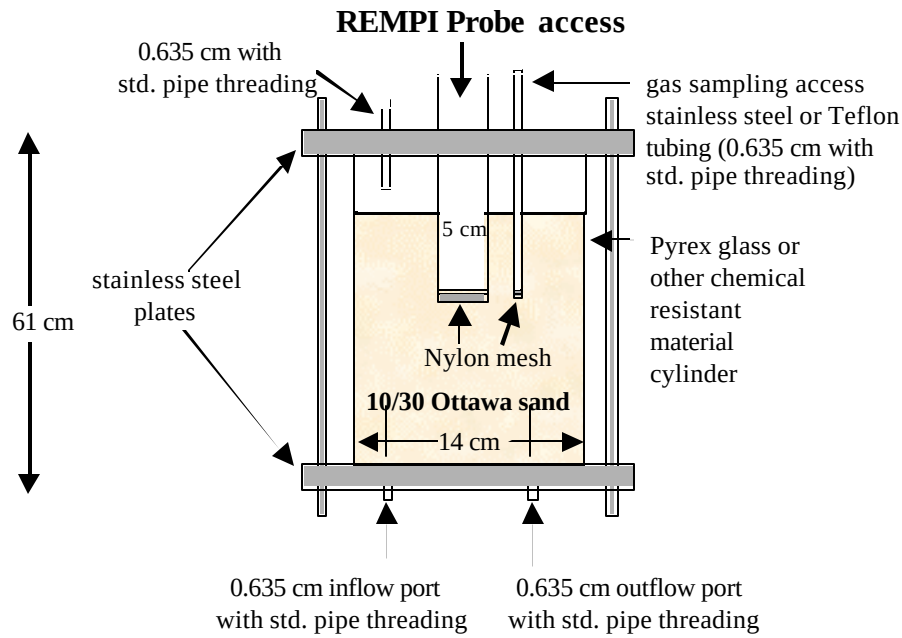

Figure. 3. Diagram of the soil column for in-situ REMPI measurements.

Planned Activities: <u>next 12 months (Year 3)</u>

- USC will measure chlorinated contaminants and optimize 1+1 and 2+2 experiments.
- LLNL will begin designing and testing the cone penetrometer compataible REMPI cell.
- Mixture studies of aromatic and chlorinated contaminants will be completed.
- The coaxial fiber/electrode REMPI probe will be tested in the soil column.
- Tests on the cone-penetrometer compatible REMPI probe and the field test will be completed.

Publications:

David M. Gold, Rosemarie C. Chinni, Bill W. Colston Jr., Steve B. Brown, S. Michael Angel, and John T. Chang. "A Miniature Fiber-Optic Resonance-Enhanced Multiphoton Ionization (REMPI) Probe With No Focusing Optics." *Submitted to Applied Spectroscopy Summer 2001*.

S. Michael Angel, Rosemarie C. Chinni, Brian M. Cullum, Slade K. Shealy, David M. Gold, David Le Sage, Steve B. Brown., Bill W. Colston Jr. "*In-Situ* Resonance-Enhanced Multiphoton Ionization (REMPI) Measurements Using an Optical Fiber Probe." Resonance Ionization Spectroscopy 2000. Proceedings of the Tenth International Symposium, Knoxville, TN, Oct. 2000.

Brian M. Cullum, and S. Michael Angel, "Fiber-Optic Resonance Enhanced Multiphoton Ionization Probe for *In-situ* Detection of Aromatic Contamination," *Appl. Spectrosc*. **53**, 1646 (1999).

Brian M. Cullum and S. Michael Angel, "Development of a fiber optic REMPI probe for environmental contaminants," *SPIE Proceedings*, Vol. **3534-06**, Boston, MA (1998).

Conferences:

David M. Gold, Rosemarie C. Chinni, S. Michael Angel, Steve B. Brown., Bill W. Colston Jr. "*In-Situ* Detection of Volatile Pollutants Using Resonance-Enhanced Multiphoton Ionization (REMPI) Spectroscopy." ACS, Chicago, IL, Aug 2001.

S. Michael Angel, Rosemarie C. Chinni, Brian M. Cullum, Slade K. Shealy, David M. Gold, David Le Sage, Steve B. Brown., Bill W. Colston Jr. "*In-Situ* Resonance-Enhanced Multiphoton Ionization (REMPI) Measurements Using an Optical Fiber Probe." Resonance Ionization Spectroscopy 2000. Invited Plenary Lecture at the Tenth International Symposium, Knoxville, TN, Oct. 2000.

Rosemarie C. Chinni, David M. Gold, David Le Sage, Steve B. Brown., Bill W. Colston Jr, S. Michael Angel. "A Miniature Fiber-Optic Resonance-Enhanced Multiphoton Ionization (REMPI) Probe With No Focusing Optics." Pittcon (The Pittsburgh Conference), New Orleans, LA, March 2001.

Rosemarie C. Chinni, Brian M. Cullum, Slade K. Shealy, Bill W. Colston Jr., David M. Gold, Steve B. Brown, David Le Sage, S. Michael Angel. "Fiber-Optic Resonance-Enhanced Multiphoton Ionization (REMPI) Analyses of Volatile Organic Compounds Using Visible Excitation." Paper #SE06-03, The International Society for Optical Engineering (SPIE Opto Southeat), Charlotte, NC, Sept. 2000

Rosemarie C. Chinni, Brian M. Cullum, Slade K. Shealy, Bill W. Colston Jr., David M. Gold, Steve B. Brown, David Le Sage, S. Michael Angel. "Resonance-Enhanced Multiphoton Ionization (REMPI) Measurements Using Visible Excitation and a Compact Integrated Fiber-Optic Probe." Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) Nashville, TN, Sept 2000