NCER STAR GRANT ANNUAL REPORT

Date of Report: 30 August, 2002
EPA Agreement Number: R828771-0-01
Center Name/Institution of Director: Center for Hazardous Substances in Urban Environments, Johns Hopkins University
Identifier Used by Center for Project: RP #4
Title of Project: Co-Contaminant Effects on Risk Assessment and Remediation Activities Involving Urban Sediments and Soils
Investigator(s) and Institution(s): William P. Ball, Johns Hopkins University; Edward J. Bouwer, Johns Hopkins University
Type of Research: Basic Research (Laboratory and Modeling)
Project Period: October 1, 2001 to September 30, 2003

Background/Objectives of Research:

Contaminated sites typically involve complex mixtures of contaminants, the fate of which is affected by both biochemical interactions that impact microbial attenuation (e.g., cometabolic effects, competitive inhibition and toxicity), as well as competitive adsorption on solid phases that can complicate mass transfer rates during desorption. Because sediment- or soil-bound contaminants are usually not bioavailable (from either a remediation or biotoxicity viewpoint), successful prediction and assessment of fate and transport require a full accounting and integration of the sorption effects. The solid phases from which desorption must be considered include sediments, surface soils and subsurface geologic materials, all of which can contain substantial quantities of thermally altered or "black" carbon, such as the chars, soot, and coals that are ubiquitous to urban environments. Such black carbon materials will tend to both strengthen the sorption effect and to add complexity to our modeling approaches, and especially so under conditions of contamination by multiple chemicals in mixtures.

With the above as background, the *overall goal* of this research is to evaluate the need and develop the means to achieve improved modeling of the transport and fate of organic chemical contaminants, as applied to risk assessment and management for contaminated sediments and soils. *Objectives* are to develop new data and modeling approaches that can be applied toward better predictions of the combined effects of both sorption and biodegradation on organic contaminants, with a focus on solid phases typical of urban environments and on chemical fate in the presence of complex organic contaminant mixtures. Specific sub-objectives of the work are: (1) to apply modeling simulations to evaluate the impact of nonlinear and competitive sorption on rates of desorption; (2) to experimentally evaluate sources and mechanisms of nonlinear and competitive sorption in environmentally relevant solids; and (3) to develop and evaluate alternative (mechanistically based) approaches for quantifying overall rates of desorption and biodegradation in contaminated soil/water environments that include complex mixtures of contaminants.

Progress Summary/Accomplishments:

Our proposed experimental approach for this project is based on a combination of computer modeling and laboratory evaluation. In the sub-sections below, we very briefly describe our progress in each of these two areas.

<u>*Modeling*</u>. Modeling has been conducted in order to better understand the role of nonlinear adsorption on long-term desorption and biodegradation. This effort has been accomplished primarily by a post-doctoral associate who has worked approximately 50% time on this project since his arrival at JHU in late October of 2001 (Isam Sabbah). Dr. Sabbah came to JHU from a research position with the Regional Research & Development Center of the Galilee Society and has degrees in both chemical engineering (B.S.) and environmental engineering (M.Sc., Ph.D.), all from the Israel Institute of Technology (Technion). On this project, he made progress on the development of numerical computer models to simulate the combined effects of nonlinear adsorption isotherms and diffusion limitations on rates of contaminant desorption under hypothetical scenarios of sorption "loading" and desorption, assuming sorbing particles that are modeled after those previously studied in our laboratory (e.g., sediments from Bozeman, Montana and CFB Borden in Canada). More specifically, "known" nonlinear equilibrium isotherm information and intraparticle diffusion rate constants for these materials have been used to conduct alternative model simulations of long-term contaminant desorption and bioavailability, as based on model formulations and parameterizations that

might be obtained from both short-term and longer-term sorption uptake experiments. We have explored the extent to which sorption nonlinearity and a failure to experimentally evaluate truly long-term equilibrium can lead to inaccurate estimate of rate parameters and subsequently inaccurate predictions of biodegradation and desorption. The results obtained to date have shown that desorptive mass flux can be extremely sensitive to the "perceived" reality of the sorption isotherm. Since desorptive mass flux is an important determinant of contaminant persistence at waste sites, very careful experimentation will be required to fully understand long-term and non-linear contaminant distribution. The computer code that has been written will be the basis for future work in which competitive sorption is introduced. (See "Future Activities.")

Laboratory Experimentation. In regard to laboratory experimentation, our proposed approach focused on the application of a previously published method (Gustafsson *et al.*, 1997; *Environ. Sci. & Technol,* 31:203-209) to estimate black carbon (BC) content of field samples, including harbor sediments, brownfield soils, and other sites of contamination in urban settings and to obtain screening–level sorption equilibrium and rate data using nonpolar organic chemical probes. Toward this end, a doctoral student (Thanh Nguyen) has fully implemented the Gustafsson *et al.* approach in our laboratory and has been conducting an evaluation of the method with regard to its ability to discern soot and char samples. Because early results were not encouraging, we have had to expand that study. We now have a very complete dataset relating to the method. Regrettably, these results cause us to believe that the method will not be able to provide unambiguous results about black carbon (and especially char) in soils and sediments. We presented this work to colleagues at an international conference (see "Publications/Presentations") and have a manuscript in progress. Nonetheless, we intend to proceed with an evaluation of sorption properties on some selected field samples in the second year of the project. Given our results with the BC method, however, these sorption results will now be viewed as examples for our modeling exercise, with less emphasis on integrating the BC measurement into the modeling approach. (See "Future Activities.")

Publications/Presentations:

Nguyen, T.H., W.P Ball, and R.A. Brown, "Preliminary Investigation of Thermal Treatment for Quantification of Black Carbon in Environmental Samples," poster presentation, Proceedings of the 20th Anniversary Conference of the International Humic Substances Society, pp 302-305, Boston MA, July 21-26, 2002. (A related manuscript is in preparation.)

Nguyen, T.H., W.P Ball, and R.A. Brown, "Investigation of Thermal Treatment for Quantification of Black Carbon in Environmental Samples," poster presentation at the Gordon Research Conference on Environmental Sciences: Water, Holderness, NH, June 23-27, 2002.

Sabbah, I., E.J. Bouwer, and W.P. Ball, "Diffusion as a Source of Confusion: Complications and Misconceptions in the Interpretation of Desorption Data," poster presentation at the Gordon Research Conference on Environmental Sciences: Water, Holderness, NH, June 23-27, 2002. (A related manuscript is in preparation.)

Future Activities:

Modeling. Future modeling efforts will apply postulated numerical models to evaluate the sensitivity of overall degradation rates to both biochemical issues and nonlinear adsorption effects. We intend to survey selected Superfund sites in the region in order to select some waste mixtures and model parameterizations. Using these selected conditions as case studies, we intend to apply our models toward estimating the magnitude of effect that co-contaminants may have on both desorption and degradation. In addition to direct effects on biodegradation rates, competing co-solutes are expected to lead to more linear sorption during both sorption and desorption. These effects are too complex to understand without modeling, however, owing to the fact that concentrations are also controlled by processes of intrasorbent diffusion.

Laboratory Experimentation. We also intend to obtain field samples of harbor sediments and Superfund site soils and, if constraints of personnel time and budget permit, to conduct screening–level sorption equilibrium and rate tests using nonpolar organic chemical probes. In this work, our emphasis will be on testing for sorption nonlinearity and competition. The results of this work will allow us to better relate our continuing modeling sensitivity exercises to actual case scenarios.

Supplemental Keywords: toxic chemicals, chlorinated organic chemicals, sorption, biodegradation, competitive adsorption, cleanup, restoration, hydrogeology

Relevant Web Sites:

http://www.jhu.edu/hsrc
http://www.jhu.edu/~dogee/people/faculty/ball.html
http://www.jhu.edu/~dogee/people/faculty/bouwer.html