NCER STAR GRANT ANNUAL REPORT

Date of Report:	**3 October, 2003**
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 was 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* were to develop new data and modeling approaches 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 were: (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:

The project effort was accomplished primarily by a post-doctoral associate (Dr. Isam Sabbah), who was supported at approximately 55% time on this project between October 1, 2001 and June 15, 2002, with the remainder of his time supported by external funding in relation to other on-going projects. 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).

The project involved two principal areas of effort: (1) the development and application of new computer models for considering the combined effects of sorption and diffusion on rates of contaminant desorption from sediments, including the coupling of such effects with aqueous processes of biodegradation; and (2) laboratory evaluation of selected Baltimore harbor sediments in regard to both their carbon content (and carbon type) as well as their sorption characteristics with respect to a probe nonpolar organic chemical (phenanthrene) in order to begin to assess the potential importance of sorption nonlinearity and competition in urban sediments. In the sub-sections below, we very briefly describe our accomplishments to date in each of these two areas.

Modeling. Modeling was conducted in order to better understand the role of nonlinear and nonequilibrium adsorption on long-term desorption and biodegradation. Numerical computer models were developed (based on modifications of models used in prior work) 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, long-term desorption was considered for a "virtual" sediment-water-contaminant system which involved a diffusion-limited nonlinear sorption isotherm and which was subjected to simulated conditions of either short or longer-term periods of sorptive chemical uptake from solution. Simulated desorption data under the various uptake conditions (short and long-term uptake) were then interpreted with "best-fit" parameterizations of a diffusion rate model, using alternative assumptions about the equilibrium isotherm. Good fits of short-term rate data were possible in all cases, but models based on erroneous isotherms (as based on uptake experiments characterized by premature termination or insufficient range of concentration) were shown to cause severe errors in the prediction of long-term desorptive mass fluxes and rates of biodegradation. Results also illustrated how short-term sorption experiments can seem to be at equilibrium, yet lead to adsorption/desorption results that would be misinterpreted as "hysteretic," despite the intrinsic reversibility of the synthetic system. Some initial modeling was also conducted to illustrate how the desorptive fluxes could be integrated with fluid-phase biodegradation rates. The results of these modeling exercises have been presented at several conferences and a draft manuscript has been prepared for future publication, preferably in the journal *Environmental Engineering Science*.

The developed computer code has been carefully verified and documented in accordance with the QA/QC requirements of the project and will be the basis for modeling in Phase II of the work, in which the competitive aspects of sorption and biodegradation will also be considered. (See Future Work.).

Laboratory Experimentation. Laboratory experimentation on this project was originally envisioned to include 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 (Ms. Thanh Nguyen, funded primarily through separate NSF funding) implemented the Gustafsson *et al.* technique in our laboratory and conducted an evaluation of the method with regard to its ability to discern soot and char samples. Because early results were not encouraging, we expanded that study and now have a very complete dataset relating to the method, with a paper of results in press (Nguyen et, 2003 – see Publications). Regrettably, these results indicate that the method will not be able to provide unambiguous results about black carbon (and especially char) in soils and sediments. In the second year of the project we obtained field samples of Baltimore harbor sediments and conducted sorption equilibrium tests using nonpolar organic chemical probes. Three samples of the Baltimore harbor sediments were collected as part of other on-going research at the University of Maryland Chesapeake Bay Laboratory and kindly provided to us by Dr. J. Baker. (These samples were collected using a ship-deployed grab sampler that scoops up surface sediment from the top 10 to 20 centimeters. Once obtained, the sediment was thoroughly mixed, placed in glass jars and frozen.) In our laboratory, these sediments were air-dried and sieved through 250 mesh prior to analysis. The fraction of organic carbon content and the black carbon were determined using methods described elsewhere (Nguyen et al., 2003), and preliminary phenanthrene sorption results obtained using methods developed in our laboratory. For the sediment sample studied most extensively (from the Middle Branch of the Patapsco River), the two point sorption of phenanthrene showed log K_{oc} in the range of 4.4 to 4.7, which is slightly higher than would be expected for "normal" sediment organic matter (log K_{oc} = 4.2); however, the difference was far below the order-of-magnitude differences sometimes observed with sediments containing similarly high fractions of soot carbon. (11% of the total carbon in the sample was nominally identified as "soot carbon.") Additional studies with these and other sediments are required in order to more fully investigate the potential importance of sorption nonlinearity and sorption competition in urban sediments, but unfortunately could not be completed within the time and budget of Phase I. (See "Future Activities.")

Publications/Presentations:

Nguyen, T.H., W.P Ball, and R.A. Brown, 2002. "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.

Sabbah, I., E.J. Bouwer, and W.P. Ball, 2002."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.

Ball, W.P., I. Sabbah, and M.R. Paraskewich, Jr., "Sorbed-Phase Remediation under Diffusion-Limited Conditions: The Role of Equilibrium Driving Forces and Initial Conditions," invited presentation, San Francisco, CA, Dec. 6-10; *Eos*, *Transactions, American Geophysical Union,* <u>83</u>(47), Fall Meeting Supplement, Abstracts, H21E-08, 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, San Francisco, CA, Dec. 6-10; *Eos*, *Transactions, American Geophysical Union,* <u>83</u>(47), Fall Meeting Supplement, Abstracts, H22A-0874, 2002.

Ball, W.P., I. Sabbah, and E.J. Bouwer, 2003."Sorption of Hydrophobic Organic Chemicals by Soils, Sediments, and Rocks—The Role of Thermally Altered Carbon", co-sponsored by CHSUE and NSF Industry/University Cooperative Research Program, Johns Hopkins University, Baltimore, MD, June 2, 2003.

Sabbah, I., E.J. Bouwer, and W.P. Ball, 2003."Diffusion as a Source of Confusion," presentation at International Conference on PAH and BTEX Contamination, co-sponsored by CHSUE and NSF Industry/University Cooperative Research Program, Johns Hopkins University, Baltimore, MD, June 2, 2003.

Bouwer, E.J., I. Sabbah, P.C. D'Adamo and W.P. Ball, 2003. "Bioavailability of Aromatic Hydrocarbons in Saturated Porous Media: The Effects of Contaminant Aging And Mass Transfer," presentation at International Conference on PAH and BTEX Contamination, co-sponsored by CHSUE and NSF Industry/University Cooperative Research Program, Johns Hopkins University, Baltimore, MD, June 2, 2003.

Ball, W.P., I. Sabbah, and E.J. Bouwer, "Co-Contaminant Effects on Risk Assessment and Remediation Activities in Urban Settings," presentation at the ORD/HSRC/OSWER Meeting on Superfund Research, August 26-27, Cincinnati, OH, 2003.

Nguyen, T.H., I. Sabbah, and W.P. Ball, "Precise Measures of Sorption Non-Linearity for Hydrophobic Organic Chemicals with Diesel Soot," presentation at the 226th ACS National Meeting, NY, NY, *Preprints of Extended Abstracts*, <u>43</u>(2), paper no. ENVR-120, 2003..

Sabbah I., E.J. Bouwer, and W.P. Ball, "Misinterpretations of Desorption Results in Diffusively Limited Systems Owing to Deficiencies in Equilibrium Isotherm Determination," in preparation for submission to *Environmental Engineering Science*, 2003.

Future Activities:

A Phase II study to build upon the findings of this project is now underway, also under the auspices of the Urban Center Hazardous Substances Research Center. At the time of this writing, this project is still being staffed, but some of the intended future activities are briefly described below.

<u>*Modeling*</u>. Future modeling efforts will apply numerical models to evaluate the sensitivity of overall degradation rates to the presence of co-contaminants, with consideration of adsorption, diffusion, and biodegradation effects. Toward this end, we intend to survey selected Superfund sites in the region and conduct literature review in order to select appropriate waste mixtures and model parameter values. 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 under conditions of both batch experimentation and flow through porous media. In addition to direct effects on biodegradation rates, competing co-solutes are expected to lead to more linear sorption during both sorption and desorption. The precise nature of these sorption effects is expected to be complex, however, owing to the fact that concentrations of all chemicals will also be affected by processes of intrasorbent diffusion and biodegradation.

<u>*Laboratory Experimentation*</u>. We also intend to continue our investigation of the sorption of non-polar organic chemicals probes with selected samples of urban sediments and soils. Our emphasis will be on the characterization of the black carbon content and the overall role of competitive adsorption processes on observed sorption isotherms. Sediments from EPA regions I, II, and III will be sought, with emphasis on integrating the results of this project to other on-going HSRC research. 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