



Project Summary

Adsorption and Desorption of Hexachlorobiphenyl

D.M. DiToro, L.M. Horzempa, and M.C. Casey

The experimental and theoretical results that lead to the development model for the analysis of adsorption and desorption of hexachlorobiphenyl from suspended and sedimented particles are discussed.

The reversibility of the adsorption reaction between dissolved organic chemicals and naturally occurring soils, sediments, and suspended particles is of fundamental importance in the understanding of the fate of these chemicals in the environment. The issue of reversibility becomes critical if the adsorption-desorption behavior of a chemical is to be expressed quantitatively within the framework of mass balance equations. In the formulations used to date, with a notable exception to be discussed below, the formulations used to express the adsorption and desorption reactions assume reversible behavior, that is, at equilibrium, the same isotherm applies for adsorption and desorption.

The difficulty with this assumption is that for many organic chemicals and many naturally occurring adsorbents, laboratory adsorption and subsequent desorption experiments demonstrate only partially reversible behavior.

In the experiment described in Part A of the final report, this nonsingular behavior was confirmed and, using various experimental procedures, it was found to persist, which suggests that it is necessary to account for this behavior in a quantitative and consistent way.

In Part B of the final report, a framework, is presented within which this nonsingular behavior can be analyzed in a manner that can be easily incorporated into mass balance calculations.

This Project Summary was developed by EPA's Environmental Research

Laboratory, Duluth, MN, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The purpose of the final report, summarized herein, is to present the experimental and theoretical results that lead to the development model for the analysis of adsorption and desorption of hexachlorobiphenyl from suspended and sedimented particles. In contrast to the desorption reaction, a large body of information already exists for the adsorption reaction. Several authors have reported relationships that relate the extent of adsorption of organic chemicals to their characteristics such as aqueous solubility and adsorbent properties such as specific surface area and organic carbon content.

This is not the case, however, for the desorption reaction. The available information, to be discussed in more detail below, indicates that for a great many organic adsorbent systems the desorption reaction is not completely or even moderately reversible. As a consequence, the assumption of reversible behavior is neither justified nor realistic, and it is not possible to directly apply the large body of adsorption theory and data to describe desorption since, for nonreversible systems, it is not the same reaction.

This is unfortunate since it is not clear how to incorporate nonreversible behavior into modeling frameworks that have been, and are being, developed by EPA and other groups for the computation of the fate of toxic chemicals in natural waters. If the adsorption were either completely reversible, or completely

irreversible so that no desorption occurred, then it would be straightforward to include such behavior in a fate model. What has been found experimentally, however, is that some desorption takes place. The amount is variable and depends on the details of the situation, such as the mass of adsorbent and the adsorbate-adsorbent pair involved.

The use of a desorption "partition coefficient" in a way that is analogous to the use of the adsorption partition coefficient in fate computations, is not a solution to the problem since the actual quantity of chemical desorbed when exposed to lower aqueous concentration is not directly related to only the desorption partition coefficient but also to the quantity of chemical previously adsorbed. As it happens, for the desorption model described below, the desorption partition coefficient does have a specific meaning, which the model clarifies, but it cannot be used directly in fate computations. Without a specific model for nonreversible desorption, it is not surprising that this mechanism has not been explicitly included in fate computations.

The nonreversible behavior of adsorption and desorption can have important consequences for the fate of chemicals in natural waters. As inputs of toxic chemicals are reduced, the desorption of already existing toxic chemical from suspended solids and sediments will constitute the major inputs of dissolved toxicants into the water column. The magnitude and extent of this reaction can control the environmental distribution and the exposure level for the biota. If the quantity of chemical desorbed is much less than the quantity initially adsorbed then assuming completely reversible behavior can significantly overestimate the dissolved chemical in the water column. This overestimate may translate into an underestimation of the impact of remedial measures such as discharge reductions via treatment of effluents. Hence, a quantitative understanding of the factors that influence the behavior of the desorption reaction is an essential component for understanding the fate of toxic chemicals in natural waters and the consequences of remedial actions.

Summary

As part of the effort at Manhattan College to formulate and test mathematical models of the fate of PCB's in the Great Lakes, a series of experiments have been conducted using tritiated hexachlorobiphenyl (abbreviated as HCB) as the adsorbate and natural sediments and

inorganic clays as the adsorbents. The experiments concentrated on the desorption behavior as well as conventional adsorption tests. Nonreversible desorption occurred, and an effort was made to formulate a model which explained the data.

It was assumed that the adsorbed HCB was made up of two components: an exchangeable component which readily and reversibly desorbs and readsorbs depending upon aqueous phase concentration, and a second component, which was termed nonexchangeable, which resisted desorption until very low (or possibly zero) aqueous concentrations. This idea is often used to explain nonreversible behavior in qualitative terms, e.g., physical versus chemical adsorption. Methods were developed for calculating the quantity of the exchangeable and nonexchangeable components from the experimental adsorption and desorption data. This is the unique feature of the model since it gives quantitative estimates of the magnitudes of these components. An analysis of the individual behavior suggested that each was describable in terms of (distinct) linear isotherms. This regular behavior, for both natural sediments and inorganic clays, represents a significant simplification and codification of a large quantity of adsorption and desorption data in terms of distinct partition coefficients for the exchangeable and nonexchangeable components. Subsequent consecutive adsorption experiments confirmed the distinct behavior of the two components and supported the validity of the model.

The fact that two distinct isotherms are found for the adsorption and desorption data indicates that the desorption is not completely reversible. Consider a single pair of points corresponding to a single adsorption-desorption experiment. If it is assumed that continued desorption cycles follow a straight line, then the intersection of this line and the ordinate defines the particulate concentration which is nonexchangeable (since it remains on the particles even at zero aqueous concentration). Once the nonexchangeable component concentration, r_o , has been found, the differences between this concentration and that found at adsorption and desorption equilibria must be the exchangeable component since two components are assumed to be present. The fact that it responded to the decrease in aqueous concentration that occurred from adsorption to desorption equilibrium supports its exchangeability. Note that two exchangeable component data points result: at adsorption equi-

librium, $r_{x,a}$ and that desorption equilibrium, $r_{x,d}$. These correspond to the two aqueous concentrations c_a and c_d , respectively. If this analysis is repeated for the remaining two adsorption-desorption data pairs, the result is six pairs of exchangeable component-aqueous concentration data.

The validity of this analysis depends upon the observation that all the exchangeable component data conform to a single isotherm. The same isotherm applies to all exchangeable component data, regardless of whether they correspond to the quantity of exchangeable component that is present at adsorption, $r_{x,a}$ in equilibrium with aqueous concentration, c_a , or at desorption, $r_{x,d}$, in equilibrium with aqueous concentration, c_d . That is, the exchangeable component is behaving in accordance with classical reversible adsorption-desorption theory.

The three nonexchangeable component concentrations calculated from the data analysis also have been found to follow one isotherm. They are a linear function of the adsorption aqueous concentration.

Part B of the final report contains additional results of the isotherm analysis for HCB and a full discussion of the development of the proposed adsorption-desorption model. Part A of the final report presents further data and the results of experimental modifications designed to eliminate experimental artifacts as the cause of the nonreversible behavior.

A second focus of the experiments conducted with HCB was the effect of the mass of adsorbent on the partition coefficients. It had been observed from an analysis of published data that adsorption partition coefficients decrease as adsorbent mass increases. This phenomenon was investigated for HCB adsorption and also for desorption. It was found to occur for both reactions. If the data is interpreted in terms of exchangeable and nonexchangeable components, the nonexchangeable partition coefficient is essentially independent of adsorbent mass, whereas the exchangeable partition coefficient is inversely proportional to adsorbent mass. The adsorption and desorption partition coefficients are seen to decrease as adsorbent mass, m , increases. Note that the extent of irreversibility increases as mass increases. That is, the desorption partition coefficient becomes increasingly larger than the adsorption partition coefficient as adsorbent mass increases. The exchangeable partition coefficient is seen to be inversely proportional to mass whereas the nonexchangeable partition coefficient is independent of mass. This

suggests a definition of an exchangeable distribution coefficient: $v_x = \pi_x m$ which is also mass independent.

The variation of these mass-independent parameters as functions of sediment properties has been examined. The details, together with additional data and a more complete description of the adsorbent mass effects are given in Parts A and B of the final report.

The result of this combined experimental and modeling program is a quantitative framework within which it is possible to predict the adsorption, and more significantly, the desorption behavior of hexachlorobiphenyl as a function of adsorbent mass and its characteristics.

The importance of the interaction between modeling analysis and experimental design in such an investigation cannot be overemphasized. The exchangeable-nonexchangeable model was formulated as a consequence of the need to organize, synthesize, and understand the experimental data. Once the hypothesis was formulated in quantitative terms, it was possible to design experiments to test the model predictions and elucidate the relevant features. The dual capability to do the experiments and formulate the models within a cooperating group is essential if progress is to be made in formulating and testing rational, quantitative descriptions of complex phenomena such as the desorption reaction.

Implications for Receiving Water Fate Models

The use of models for the computation of toxic chemicals exposure levels in natural waters is currently an important component of rational toxic chemical regulation and control. The development of EXAMS by EPA models for PCB, radionuclides and toxic heavy metals in the Great Lakes by Manhattan College, and other investigations, are currently in progress. These models have a common approach in dealing with the adsorption-desorption reaction.

The mass balance equations are written in terms of total chemical, c_T , with the transport and kinetic terms suitably modified with the fraction of chemical in the dissolved, f_d , or particulate f_p , form depending on whether the terms in the equation apply to particulate or dissolved phases. As an example, consider a two-layer segmentation representing the water column of depth H_1 , and an active sediment layer of depth H_2 . These interact via vertical mixing of the aqueous phases, with mass transfer coefficient K_L and settling and resuspension of the

particulate phases, with velocities w_a and w_{rs} respectively. The governing mass balance equations are:

$$H_1 \frac{dc_{T1}}{dt} = K_L(f_{d2}c_{T2} - f_{d1}c_{T1}) - w_a f_{p1}c_{T1} + w_{rs} f_{p2}c_{T2} + W \quad (1)$$

$$H_2 \frac{dc_{T2}}{dt} = K_L(f_{d1}c_{T1} - f_{d2}c_{T2}) + w_a f_{p1}c_{T1} - w_{rs} f_{p2}c_{T2} \quad (2)$$

where c_{T1} and c_{T2} are the total chemical concentrations in the water column and sediment layers respectively, and W is the input mass loading rate ($M/L^2/T$). Note that the central roles of the dissolved f_{d1} and f_{d2} are particulate (f_{p1} and f_{p2}) fractions in the water column and sediment segments, respectively. They directly affect the magnitudes of the mass transfer coefficients and, therefore, the fate of the chemical. A more complex fate computation would include terms for outflow, the various appropriate decay mechanisms, and sedimentation losses. However, the principle is still the same. Once the total concentration is computed, the dissolved water column concentration is given by: $c_{d1} = f_{d1}c_{T1}$, with analogous expressions for the particulate concentration. Again, the particulate and dissolved fractions play a central role, and these fractions are a direct result of the adsorption-desorption model employed.

For completely reversible adsorption-desorption and a linear isotherm, the dissolved and particulate fractions are given by:

$$f_d = \frac{1}{1 + m\pi} \quad (3)$$

$$f_p = \frac{m\pi}{1 + m\pi} \quad (4)$$

where π is the reversible partition coefficient and m is the adsorbent concentrations. The subscripts 1 and 2 in equations (1) and (2) refer to evaluating these fractions using the appropriate adsorbent concentration in segments 1 and 2.

For the HCBC exchangeable-nonexchangeable component model of adsorption-desorption, these fractions depend upon the model parameters: π_o , the partition coefficient for the nonexchangeable component; and v_x , the distribution coefficient for the exchangeable component; and the maximum dissolved aqueous concentration to which the particle has

been exposed: c_{md} . This latter concentration sets the magnitude of the nonexchangeable component. It can be shown that the dissolved and particulate fractions are given by the expressions:

$$f_d = \frac{1}{1 + v_x + m\pi_o(c_{md}/c_d)} \quad (5)$$

$$f_p = \frac{v_x + m\pi_o(c_{md}/c_d)}{1 + v_x + m\pi_o(c_{md}/c_d)} \quad (6)$$

where c_d is the current dissolved aqueous phase concentration. The conventional expression, assuming reversible behavior is also shown. There is a significant difference between the conventional reversible formulation and the exchangeable - nonexchangeable model. The particulate fraction is always a substantial portion of the total chemical concentration, even at low suspended solids concentrations that are characteristic of most receiving waters (10-100 mg/l). This suggests that fate computations using the exchangeable-nonexchangeable model will give quite different results which emphasize the importance of particle transport.

D. M. Di Toro, L. M. Horzempa, and M. C. Casey are with Manhattan College, Bronx, NY 10471.

W. R. Richardson is the EPA Project Officer (see below).

The complete report, entitled "Adsorption and Desorption of Hexachlorobiphenyl: A. Experimental Results and Discussions; B. Analysis of Exchangeable and Nonexchangeable Components," (Order No. PB 83-261 677; Cost: \$25.00, subject to change) will be available only from:

*National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650*

The EPA Project Officer can be contacted at:

*Large Lakes Research Station
Environmental Research Laboratory-Duluth
U.S. Environmental Protection Agency
9311 Groh Road
Grosse Ile, MI 48138*

☆ U.S. GOVERNMENT PRINTING OFFICE 1983-659-017/7236

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Official Business
Penalty for Private Use \$300

• •

• •