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Design of Laboratory Systems for Controlling the Activity of Moderately Volatile Organic Compounds

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The theory for transfer from gas to a liquid is developed. The effects of association of HCB with humate and other competing processes (head space losses, adsorption to food, organisms, sediment)are included.

Experimental data from the use of the apparatus in actual bioaccumulation experiments are discussed.

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Corvallis Environmental Research Laboratory

United States Environmental Protection Agency

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Abstract

The gas-phase transfer of hexachlorobenzene (HCB) from the solid to the chambers used for sediment-water bioaccumulation tests was investigated.

The physical properties of HCB found in the literature are summarized. Significant discrepencies were found among different methods. The values determined in this study were (with standard deviation in parentheses): vapor pressure of HCB at 295 K: 1.37 (0.02) mPa; saturation concentration of HCB in air at 295 K: 0.554 (0.007) nmol/L; the delivery rate of HCB with apparatus: 0.26 pmol/s; saturation concentration of HCB in water at 295 K: 18 (1) nmol/L; saturation concentration of HCB in water with 1 mg/L humate at 295 K: 21 (1) nmol/L; saturation concentration of HCB in water with 50 mg/L humate at 295 K: 62 (2) nmol/L; transfer rate constant for HCB between gas and water in apparatus: 5.8×10^{-6} (0.7×10^{-6}) s^{-1}. The chief sources in uncertainty in these data were due to variations in temperature, and the possible incomplete equilibration of the solid with the gas. These items are discussed in detail.

The theory for transfer from gas to a liquid is developed. The effects of association of HCB with humate and other competing processes (head space losses, adsorption to food, organisms, sediment) are included.

Experimental data from the use of the apparatus in actual bioaccumulation experiments are discussed.

1. OVERVIEW

The accumulation of organic pollutants by aquatic organisms is of concern when considering regulatory criteria and disposal options. Not only must the source of chemical to the organism be considered (e.g., sediments, pore water, overlying water), but also the environmental impact (e.g., lethal and sublethal effects within an ecosystem, and the "route back to man" and effect on human health).

Carefully controlled laboratory exposure experiments are necessary to study biological effects and accumulation of organic chemicals as a function of dose, concentration, and mode of exposure. A fundamental problem in designing these experiments involves dosing with target compound in such a way that the chemical activity of the compound can be controlled in each of the important compartments of the experiment. There are many ways of introducing organic chemicals to biological exposure experiments, whether they be batch or flow-through in design.

Typically, the target compound is introduced to the aqueous phase in a pulse-mode or with sequential aliquots over the course of the experiment, via contaminated sediments if they are present, or through contaminated food added at discreet time intervals. Contaminant exposure levels are difficult to control, because chemical equilibration between food, sediment, water, and other possible important phases can be slow in many cases. The target compound of interest may also volatilize, be degraded, or be bioaccumulated to such an extent that concentration of chemical may be depleted with time in other compartments of the experiment. Finally, measured aqueous phase concentrations of hydrophobic organic compounds may not reflect the dissolved phase activity due to

interactions with colloidal or humic-type organic matter (Means and Wijayaratne, 1982; McCarthy et al., 1985; Brownawell and Farrington, 1986).

One way to achieve a known and constant dissolved phase activity of a neutral organic compound is to bubble continuously a solution with a gas stream of controlled concentration. This method of dosing is also attractive due to the fact that oxygen aeration is performed without loss of volatilization of target compound from the system. In this report, the theory of gas-liquid transport of moderately volatile organic compounds is presented and discussed in terms of the practical experimental variables that must be considered when designing experiments. Gas-water transfer of one model hydrophobic organic compound, hexachlorobenzene (HCB), is examined in detail and results from fundmental experiments are interpreted in terms of the theoretical models developed.

HCB has several properties which make it an excellent model compound for this study: (i) the hydrophobicity of HCB indicated by its high octanol-water partition coefficient and relativley low water solubility is representative of a large range of pesticides and other xenobiotic organic compounds, (ii) HCB is highly resistant to biological or chemical degradation, simplifying experimental procedures for long term experiments and interpretation of bioaccumulation studies, (iii) the high analytical sensitivity afforded by capillary gas chromatography with electron capture detection for HCB allows low level aqueous phase measurements despite the low solubility of HCB, (iv) the moderately high Henry's Law constant of HCB is somewhat higher than most chlorinated hydrocarbons and pesticides, which facilitates the air-water exchange of HCB in gas bubbling experiments, and (v) HCB is a stable, ubiquitous, environmental

contaminant which has been widely used as a pesticide, and is also a stable by-product in the synthesis of many chlorinated solvents and pesticides (Versar Inc., 1986). HCB is a suspected carcinogen and an EPA priority pollutant. Biological effect and chemical transport data are needed to understand better the transport and fate of this compound in aquatic environments.

Outline of the report. The objectives of this report are to define clearly physical transport models for air-water transfer of any volatile organic compound, to discuss the physical meaning of the kinetic models in terms of experimental design, and to discuss critically some aspects of the results obtained in gas-bubbling experiments performed with HCB as a model compound.

The report is divided into the following sections: a review of the physical properties of HCB; the theory of exchange of solutes at air-water interfaces; an interpretation of experiments in which HCB was transferred from the solid phase to the liquid phase via the gas phase; and a summary of results and recommendations for future study.

The basic physical properties which control the behavior of HCB in biological exposure experiments are reviewed critically. This section provides the background for the physical chemical parameters which are required to model air-water exchange and biological uptake, provides a basis for comparing the physical-chemical property estimates derived from this work, and also provides insight into the quality of critical chemical property data that exist for low-solubilty, low-vapor pressure organic compounds of environmental significance.

Physical transport models for volatile chemicals are developed in a general way by considering a microscopic view of mass transfer across an

air-water interface. The two-film diffusive transfer model is discussed to provide a physically intuitive understanding of the factors that affect transfer. A mathematical model to describe the time dependent water concentration of HCB, or other volatile species, is developed in two steps: (i) the transfer of HCB between water and individual rising bubbles; and (ii) the increase in the concentration of HCB in the liquid. Also considered in the theoretical section of this report is the effect that an association of HCB with a solute such as sodium humate will have on both air-water equilibrium and transfer kinetics. Finally, the effect of competing chemical or biological processes on air-water exchange is discussed, with particular emphasis on the effect of headspace losses.

The experimental section is organized to answer several questions which are suggested from the theoretical sections as important in modelling air-water exchange of HCB and properly designing biological exposure experiments for this compound:

i. the vapor pressure and the concentration of HCB in air in equilibrium with the solid, and the rate of delivery of HCB through a particular experimental set-up;

ii. the solubility of HCB in water and its rate of uptake in water from an HCB-saturated gas;

iii. the effect of humic material suspended in the aqueous phase on the total amount of HCB in the aqueous phase;

iv. the effect of humic material suspended in the aqueous phase on the exchange rate of HCB between the aqueous and gaseous phases.

Theoretical and experimental results are discussed in the last section of the report. The advantages of the gas phase transfer of HCB to water were discussed earlier. The major disadvantage lies in the relative values of gas solubility, water solubility and tendency to adsorb: it is difficult to supply enough HCB through the gas phase to buffer a system that is in contact with a large mass of sediments. Contaminated or uncontaminated, the sediments represent a large source or sink of HCB relative to the source or sink that it is possible to achieve through the gas phase. The gas phase equilibration method is perhaps more suitable in the study of biological uptake of HCB in solutions containing relatively low concentrations of suspended particles rather than those containing bulk sediments.

Recommendations for experimental design and future study are then discussed.

2. HEXACHLOROBENZENE - PHYSICAL PROPERTIES

Reliable information on physical properties are required for accurate estimates of the equilibrium distributions and transport rates of organic compounds, such as HCB, in aquatic systems. For example, sorption of neutral hydrophobic organic compounds to natural sediments and soils can be well predicted from the water solubility or octanol-water partition coefficient, K_{ow}, of the compound (Karickhoff et al., 1979; Schwarzenbach and Westall, 1981). Predictive models for bioconcentration of neutral organic compounds by aquatic organisms have also been based on solubility and K_{ow} correlations (Chiou et al., 1977; Mackay, 1982). The rate and degree of air-water exchange for volatile species depends on the Henry's Law constant. In this part of the report is presented a review of reported K_{ow}'s, aqueous soubilities, vapor pressures, and Henry's Law constants for HCB (Table 2.1), and a discussion of the quality of these data.

Octanol-water partition coefficients

K_{ow} determinations are generally performed by analysis of the aqueous phase after equilibration with octanol, usually with the equilibration and separation being made in a centrifuge tube. Table 2.1 shows reasonable agreement among the four K_{ow} determinations performed by this method, with an average log K_{ow} value of 5.36 ± 0.13. The generator column method used by Miller et al. (1984) gave a log K_{ow} value of 5.47, consistent with the batch equillibration methods.

Careful examination of the literature reveals large standard errors associated with log K_{ow} measurements greater than 5.0, and particularly

Table 2.1. Physical properties of hexachlorobenzene.

Log K_{ow} (°C if given)	method	reference
5.44	batch equilibration	Briggs (1981)
5.50	" "	Chiou et al. (1982)
5.31 (25)	" "	Watarai et al. (1982)
5.20 (20-25)	" "	Platford et al. (1982)
5.47	generator column	Miller et al. (1984)
6.52	reverse phase HPLC	McDuffie (1981)
5.75	" "	Garst and Wilson (1984)
6.71	" "	Rapaport and Eisenrich (1984)
6.86	" "	Burkhard et al. (1985)
6.53	calculated from fragments	Yalkowsky et al. (1979)
Water solubility (°C if given)		
5.0 µg/L (25)	shake flask	Yalkowsky et al. (1979)
5.0, 4.9 (20)	" "	Chiou et al. (1982)
5.2-14 (20)	" "	Hashimoto et al. (1982)
47.0	generator column	Miller et al. (1984)
5.4 (20)	micro-column method	Hashimoto et al. (1982)
Vapor pressure (°C) mm Hg / mPa		
(15) 0.40×10^{-5} / 0.53	gas saturation	Farmer et al. (1980)
(20) 1.09×10^{-5} / 1.43	" "	Verschueren (1983)
(25) 1.91×10^{-5} / 2.51	" "	Farmer et al. (1980)
(35) 6.40×10^{-5} / 8.42	" "	Farmer et al. (1980)
(25) 2.25×10^{-5} / 2.96	gc estimate on Apolane-87	Bidleman (1984)
(25) 2.92×10^{-5} / 3.84	gc estimate on BP-1	Bidleman (1984)
Henry's Law constant - H/RT (cm^3 water/cm^3 air)		
(23) 0.054	gas stripping	Atlas et al. (1982)
(23) 0.029	gas saturation	Atlas et al. (1983)
(20) 0.034	calculation assumes vapor pressure of 1.09×10^{-5} mm Hg and water solubility of 5.0 ug/L	
(25) 0.059	calculation assumes vapor pressure of 1.91×10^{-5} mm Hg and water solubility of 5.0 ug/L	

Molar Mass = 284.8 g/mole

for compounds having log K_{ow}'s greater than 6.0. This scatter is due to the difficulty of measuring very low concentrations of chemicals in the aqueous phase, and to the presence of micro-emulsions of octanol which can be present in the aqueous phase. It is not uncommon for the range of reported octanol-water partition coefficients to span more than an order of magnitude for the more highly chlorinated biphenyls (Bromawell, 1986), for instance.

There has been considerable effort in recent years to develop reverse-phase HPLC methods for estimating the K_{ow} of organic compounds (e.g., Weber et al., 1986; Chiu et al., 1986). These methods have the advantage that phase separations are complete, detectable concentrations are readily achieved, analysis time is rapid, and multicomponent determinations are easily performed. In this approach, log K_{ow} is correlated with retention time, retention volume, or capacity factor of a set of "calibration" standards. An inherent problem arises in choosing the correct value of log K_{ow} for compounds having large enough K_{ow}'s to comprise a good calibration range. RP-HPLC approaches also assume that the mechanism of association of large hydrophobic solutes with chemically-bonded reverse-phases is similar to solute-solvent interactions in octanol. The four log K_{ow} estimates listed in Table 2.1 for the RP-HPLC method have a large standard error (± 0.49 log units) and have an average K_{ow} which is greater than one log unit above that determined by the equilibration methods.

Estimation methods based on the additivity of molecular fragments to the total log K_{ow} are often used when experimental values are absent or uncertain. Yalkowsky et al. (1979) have reported a log K_{ow} of 6.53 for HCB calculated by the method of Nys and Rekker (1974). This deviation from

experimentally determined values may be due to non-additivity of chlorine fragment contributions in this approach.

The variation of K_{ow} with temperature for HCB cannot be determined accurately from these literature values, but is not expected to be to greater than the errors associated with the experimentally determined values given in Table 2.1. Leo et al. (1971) report an average temperature dependence of approximately 2%/degree in K_{ow} for a wide range of organic compounds.

Aqueous solubility

Solubility determinations of low solubility compounds (< 100 μg/L) are fraught with many of the same experimental difficulties that are discussed above for octanol-water experiments. In the traditional shake-flask method, solubility determinations of solids may be influenced by slow dissolution kinetics, or the presence of small crystals or micro-aggregates suspended in the aqueous phase. Filtration of the aqueous phase is often performed to minimize contamination from undissolved compound, but unfortunately it is rarely specified whether adsorption of dissolved compound to the filter or filtration apparatus was taken into account. The impact of adsorption can be minimized by saturating all filtration apparatus surfaces before sampling. Hashimoto (1982) reported that membrane filters adsorbed considerably more refiltered HCB than did glass fiber filters. An increased number of workers are measuring solubilities of low solubility compounds with generator column methods adapted from May et al. (1978). In these methods, the passing aqueous phase equilibrates with a large surface area of coated sand or glass beads, and all post column surfaces are saturated before sampling begins.

There is reasonable agreement among the solubility measurements given in Table 2.1 with the notable exception of the value of 47.0 μg/L reported by Miller et al. (1984), who used the generator column method. However, Hashimoto (1982) measured a solubility for HCB by a micro-column method of 5.4 μg/L which is in good agreement with those solubilities determined by the shake-flask method.

It is difficult to estimate what effect temperature has on the solubility of HCB. Several large polycyclic aromatic hydrocarbons have a positive solubility dependence on temperature, with solubilities increasing 4-8%/degree (Wauchope and Getzen, 1972; May et al., 1978). However, p-dichlorobenzene's solubility decreases with increasing temperature over a range of environmentally relevant temperatures (Wauchope and Getzen, 1972). It is not easy to predict temperature effects on solubility, without experimental data, because the heats of solution are not constant with temperature. The solubility data in Table 2.1 suggest that the temperature dependence of HCB solubility is not great between 20 and 25°C.

Vapor pressure

The few direct measurements of the vapor pressure of HCB which have been made near room temperature have employed the gas saturation method. This technique is similar to the generator column approaches used for solubility measurements. The vapor pressure of HCB is seen to have a greater dependence on temperature than does solubility, increasing by about 15-30%/degree.

Bidleman (1984) has estimated the vapor pressures of many chlorinated hydrocarbons by a capillary gas chromatography method in which the retention times at several temperatures are correlated to retention times of

hydrocarbons with known vapor pressures on nonpolar columns. Because the GC method estimates the vapor pressure of the supercooled liquid, the data listed in Table 2.1 have been converted to vapor pressures of solid HCB by correcting for the heat of fusion by the following equation:

$$\log (P_s/P_l) = - \Delta S_m(T_m - T)/2.303\ RT \qquad (2.1)$$

where ΔS_m is the entropy of melting, given by Miller et al. (1984) as 44.8 J mol^{-1} K^{-1} for HCB, T_m and T are the melting (230°C) and ambient temperatures, in Kelvin, P_s and P_l are the solid and supercooled liquid vapor pressures at temperature T, and R is the ideal gas constant (8.314 J mol^{-1} K^{-1}). The GC determinations agree with experimentally determined values within the uncertainties of the estimation method.

Henry's Law constant

The Henry's Law constant relates the concentration of a solute in the liquid phase to its concentration or vapor pressure in the gas phase. (The constant is defined in Equations 3.2 and 3.5 in the next part of the report). Table 2.1 lists two experimental determinations of H/RT, and two values calculated from the vapor pressure and solubility data in Table 2.1. It might be fortuitous that the four values agree within a factor of two, given the uncertainties in experimental data and the unknown dependence of solubility with temperature. The extent to which H depends on temperature cannot be ascertained at this point.

3. THEORY

Introduction

Continuous contact of an aqueous solution with bubbles of a gas stream containing a known concentration of an organic compound, such as HCB, can be an effective way to maintain a known and constant activity of that compound dissolved in solution. This method is especially attractive for ecotoxicological studies where aeration is also necessary to supply oxygen to the system. Solving the equations for the transfer of HCB (or other neutral organic compounds) from incoming gas to aqueous solution allows for the understanding and optimization of experimental design, such that near saturation conditions in the aqueous phase can be obtained, and possible effects of competing transfer rates can be evaluated.

This part of the report contains (i) a brief discussion of general theory describing the transport of volatile gases or organic compounds across air-water interfaces; (ii) the analytical solution for the transfer of chemical species between a bubble and water, from which the change of water concentration as a function of time is derived; and (iii) a discussion of competing rate processes which may affect the concentration of HCB in solution, with particular emphasis on predicting the effect of a loss of HCB from solution into the headspace of experimental systems. Further information on the air-water transfer of volatile compounds in environmental systems can be found in the review by Thomas(1982).

Henry's Law: Equilibrium of a solute between liquid and gas phases.

A moderately volatile solute such as hexachlorobenzene will distribute itself between closed liquid and gas phases according to the

reaction

$$C_l = C_g \qquad H' \tag{3.1}$$

where C_l represents the concentration of the solute in the liquid phase (mol/L), C_g represents the concentration of the solute in the gas phase (mol/L), and H' is the dimensionless Henry's Law constant. The mass action equation corresponding to Reaction 3.1 is

$$H' = \frac{C_g}{C_l} \tag{3.2}$$

Occasionally the activity of the solute in the vapor phase is expressed in terms of partial pressure instead of concentration. Although the dimensionless Henry's constant given above will be used throughout this report, the relationship in terms of pressure is given below for reference. The conversion between units of concentration and partial pressure can be made by way of the ideal gas law,

$$p\,V = N\,R\,T \tag{3.3}$$

where ρ is the partial pressure (kPa), V is the volume (dm^3), N is the number of moles, R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K). The concentration is then related to the partial pressure by

$$C_g = \frac{N}{V} = \frac{p}{RT}, \tag{3.4}$$

and the Henry's Law constant (mol dm^{-3} kPa^{-1}) in terms of partial pressure is

$$H = \frac{p}{C_l} = H'\,RT \tag{3.5}$$

Other forms of the Henry's constant are found, but they will not be used in this report.

Rate of transfer at gas-liquid interfaces: the film model.

One of the goals of the transport model is to describe the concentration of the solute in one phase or the other as a function of time. The differential equation that leads to that function is developed below.

The rate of transfer of a solute from the liquid phase to the gas phase, or from the gas phase to the liqiuid phase, depends in a complex way on many factors such as mixing of the gas phase, mixing of the liquid phase, the affinity of the solute for the gas phase and the liquid phase, and the diffusivity of the solute in both phases. Often very simple conceptual models are used with operational parameters to relate observed rates of transfer to observed experimental conditions such as rate of mixing, molecular diffusivity and Henry's Law constant of compound being transferred.

Two such models (Morel, 1983) are (i) the surface renewal model and (ii) the film model. In this study, we have little basis for selecting one model or the other, since very few of the factors listed above were varied. In particular, the transfer of only one compound was considered. Thus almost any model in which flux is directly proportional to concentration difference between the two phases would be acceptable. In this study the commonly used film model has been used as the basis for the transfer equations. However, it is important to bear in mind that other conceptual models could lead to the same final equations.

According to the film model (Figure 3.1), the completely mixed bulk gas phase and completely mixed bulk liquid phase are separated from each other by a stagnant gas film and a stagnant liquid film. For both films

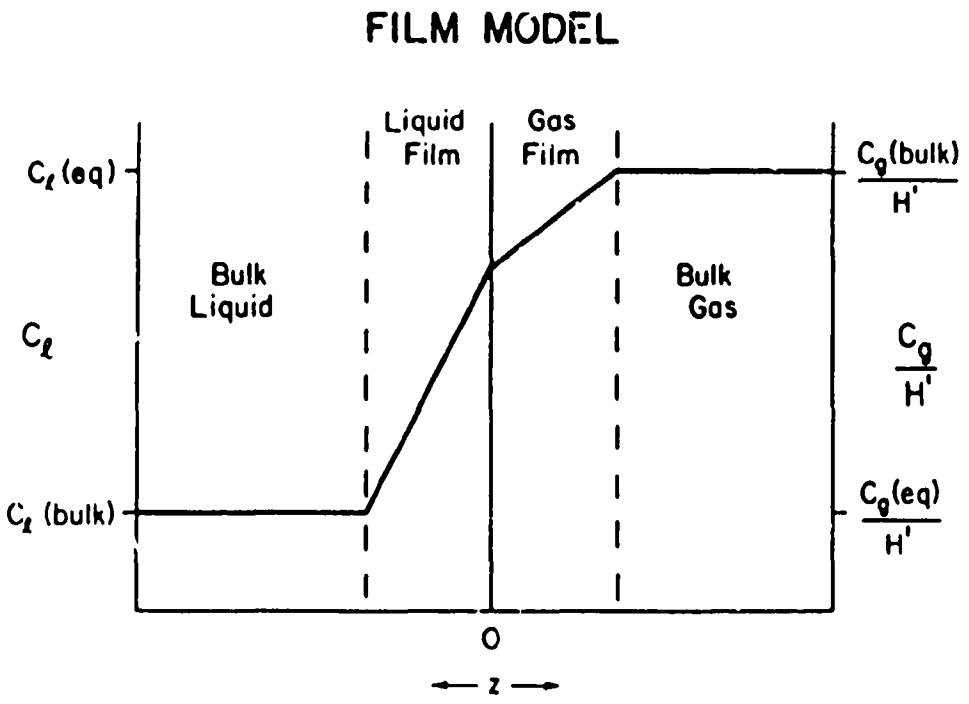

Figure 3.1. The film model. The gas phase concentrations are plotted in terms of the equivalent liquid phase concentration to allow easy comparison betwen scales. In the figure, the solute is moving from the bulk of the gas phase to the bulk of the liquid phase. If the concentration in the liquid phase does not change, the concentration in the gas phase will approach $C_g(eq)$, as in a bubble leaving solution in equilibrium with the liquid. If the concentration in the gas phase does not change, the concentration in the liquid phase will approach $C_l(eq)$, as in a liquid eventually equilibrating with an inflowing gas stream.

the flux through the film is equal to a mass transfer coefficient times the concentration difference across the film:

$$J_l = \frac{1}{A}\frac{dN}{dt} = k_l \ (C_l - C_l^{z=0}) \tag{3.6}$$

$$J_g = \frac{1}{A}\frac{dN}{dt} = - k_g \ (C_g - C_g^{z=0}) \tag{3.7}$$

where J_i is the flux (mol dm^2 s^{-1}) across film i, A is the interfacial area (dm^2), N is the number of moles, t is time (s), k_i is the heterogeneous mass transfer coefficient for film i (dm s^{-1}), C_i is the bulk concentration in phase i, and $C_i^{z=0}$ is the concentration in phase i at the interface. Flux out of the liquid into the gas is defined as positive, and flux into the liquid from the gas is defined as negative. The concentration of the solute in the liquid phase and the gas phase at the interface (z=0) are assumed to be at equilibrium, related by Henry's Law (Equation 3.2).

At steady state the flux through the gas film is equal to the flux through the liquid film; this net flux is denoted by J:

$$J = J_l(\text{steady state}) = J_g(\text{steady state}) \tag{3.8}$$

A combination of Equations 3.2, 3.6-3.8 yields this overall steady state flux in terms of the bulk concentrations,

$$J = k \ (C_l - C_l(eq)), \tag{3.9}$$

where k (dm s^{-1}) is the effective mass transfer coefficient

$$\frac{1}{k} = \frac{1}{k_l} + \frac{1}{k_g H'} \tag{3.10}$$

and $C_l(eq)$ is defined as the liquid phase concentration that would be in equilibrium with the *bulk* gas phase concentration,

$$C_l(eq) = \frac{C_g}{H'} \tag{3.11}$$

Note that the effective mass transfer coefficient, k, depends on the Henry's law Constant, as well as k_l and k_g. It is not the objective of this study to examine transport in terms of these parameters as they appear in Equation 3.10. Nonetheless, the equation is still important in allowing us to consider the effects of mixing in the gas phase and the liquid phase and to address questions such as, will stirring of the liquid phase affect transfer rate? In the next section the application of the film model to environmental and laboratory systems is discussed.

Finally the flux in Equation 3.9 can be transformed into an equation in change in concentration in the liquid phase, by multiplying the flux (Equation 3.9) by interfacial area A (dm^2) and dividing by the liquid volume V_l (dm^3):

$$\frac{d\,C_l}{d\,t} = \frac{k\,A}{V_l}\,(C_l - C_l(eq)) \tag{3.12}$$

Equation 3.12 is the fundamental equation for first order change in concentration. As mentioned in the introduction to this section, this equation can be derived by considerations other than those of the film model; the form of the equation remains the same, but the interpretation of the constant k is different.

Transport across air-water interfaces in laboratory and field environments

The exchange of gases or neutral organic compounds between air and water can be represented as a first order process with the net flux across the interface described by Equation 3.9. The mass transfer coefficient k is dependent on the diffusivity and Henry's Law constant of the compound, and the mixing conditions of the experiment.

Several methods have been used to estimate the mass transfer coefficients of individual chemicals under different environmental and laboratory conditions. Most commonly, a two-film model has been used (Liss and Slater, 1974). It is assumed that the bulk phases are well mixed and the main resistance to transport is due to molecular diffusion processes in both gas and liquid interfacial layers. When the overall mass transfer coefficient is written on a liquid-phase basis, as in Equation 3.9, the relationship between k and the individual liquid and gas phase mass transfer coefficients (k_l and k_g, repectively) is given by Equation 3.10.

The values of k_l are much lower than k_g due to slower rates of molecular diffusion in liquids. Measured ratios of k_l/k_g are in the range of 0.003 to 0.02 in the environment (Liss and Slater, 1974; Mackay et al., 1979). Estimates of k_l and k_g have been reported by Smith et al. (1981) for several polycyclic hydrocarbons (PAH), under a range of mixing conditions in laboratory experiments. From those values it is possible to estimate approximate values of mass transfer coefficients which can be expected for HCB. This estimate is made by setting the ratio of transfer coefficients of two compounds equal to the reciprocal of the ratio of the square roots of their molar masses (Liss and Slater, 1974).

Table 3.1 shows the estimates of mass transfer coefficients of HCB for laboratory conditions (from the data of Smith et al., 1981), and for typical open ocean conditions (Liss and Slater, 1974). The mass transfer coefficients increase greatly when the solution is mixed, with the value for the open ocean falling in the range of the stirred experimental vessels.

The ratio k_l/k_g is seen to be in the range 0.03 to 0.003 for environmental and field systems. According to Equation 3.10, the mass transfer will be controlled by the liquid film when $H' \gg k_l/k_g$ and by the gas film when $H' \ll k_l/k_g$. Thus for compounds with $H' > 0.1$, liquid film control is anticipated, and for compounds with $H' < 0.001$, gas film control.

The value of H' reported for HCB is 0.029 (Atlas et al., 1984); it has been estimated from solubility vapor pressure measurements to be 0.031 in the experimental section of this report. Thus transfer of HCB is likely to be controlled primarily, but not exclusively, by the liquid film. It can be seen from Table 3.1 that most of the resistance to HCB transfer is in the liquid phase, with a variable contribution from the gas phase depending of mixing in each phase. This indicates that increasing mixing in the liquid phase will generally promote transfer of HCB. However, it is important to note that the effect of gas phase resistance cannot be ignored when trying to estimate k for HCB, as it can for chemicals with greater values of H'.

In the following discussions of laboratory experiments, only one compound, hence only one value of H', is being considered. Therefore differentiation between gas film and liquid film control is not so important, since Equation 3.12 is generally valid. However, part of the

Table 3.1 Extrapolated values of k_g, k_l, and k for HCB under different mixing conditions based on laboratory volatilization experiments of Smith et al. (1981). $k(HCB) = k(PAH)(MW_{PAH}/MW_{HCB})^{1/2}$. k is calculated by Equation 3.10. Mass transfer coefficients predicted for open ocean conditions are based on k_g and k_l values of H_2O and CO_2, respectively, in a similar manner (Liss and Slater, 1974).

Experimental Conditions	k_g	k_l (μm / s)	k	k_l/k_g
stagnant (no mixing)	190	1.0	0.86	0.0052
stirred at 100 rpm	620	9.5	6.4	0.015
stirred at 200 rpm	890	26	13	0.029
stirred at 200 rpm + 3-4 m/s wind	6300	28	25	0.0045
open ocean (typical conditions)	2100	22	16	0.010

study involves the association of HCB with humic material; the association with humic material is operationally equivalent to altering H' of HCB, if all chemical reactions are fast compared to transport. In this case, differentiation of film control becomes important again. Furthermore, it should be clear that changing the mixing conditions (e.g., changing the shape of the vessel or gas flow rate) will affect k.

Transfer Rate From Gas Bubbles to Solution

Equation 3.12 is a valid approximation for many gas-liquid interfaces. To solve the transport equation for transfer of HCB from bubbles to solution, in terms of experimental variables, it is useful to write the equation for transfer between the water column and a single bubble as it rises through the water column. Reformulation of Equation 3.12 in terms of the gas phase concentration in a bubble gives:

$$\frac{dC_b(t)}{dt} = -\frac{k_b A_b}{V_b H'} (C_b(t) - C_b(eq)) \qquad (3.13)$$

where $C_b(t)$ (mol/L) is the time-varying concentration in the bubble, k_b (dm/s) is the effective mass transfer coefficient across the bubble-water interface (as given in Equation 3.10), A_b (dm^2) is the area of the bubble-water interface, V_b (L) is the volume of the bubble, and $C_b(eq)$ (mol/L) is the gas phase concentration that would be in equilibrium with the bulk water concentration:

$$C_b(eq) = C_1 H' \qquad (3.14)$$

This equilibrium concentration is assumed to be constant over the lifetime of one bubble, that is, the change in concentration in the water is slow compared to that in the bubble.

Equation 3.13 can be solved for the concentration in the bubble as it leaves the solution by separating variables and integrating over the lifetime of a bubble, t_b (s):

$$(C_b(t_b) - C_b(eq)) = (C_b(t=0) - C_b(eq)) \exp\left(-\frac{k_b A_b t_b}{V_b H'}\right) \qquad (3.15)$$

where $C_b(t=0)$ is the concentration of the solute in the inflowing gas stream. It can be seen that for residence time of the bubble t_b

sufficiently long compared to $k_b A_b/(V_b\ H')$, the bubble leaves the solution in equilibrium with the water.

Equation 3.15 can be rearranged to express the degree of approach to equilibrium more quantitatively in terms of the parameter f, defined as the actual change in the concentration in the bubble from entry to exit, divided by the change in concentration if the bubble were to leave the solution at equilibrium:

$$f = \frac{C_b(t=0) - C_b(t_b)}{C_b(t=0) - C_b(eq)} = 1 - \exp\left(-\frac{k_b A_b t_b}{V_b\ H'}\right) \qquad (3.16)$$

Change in liquid-phase concentration.

The quantity that is measured in these experiments is the change in concentration of the solute in the liquid. To calculate this change, two time scales are involved: the timescale of a single bubble, discussed above, and the timescale for the equilibration of the liquid with the inflowing gas stream, to be discussed here.

The discussion that follows is valid for a completely mixed liquid phase. At any time t during the course of the equilibration of the liquid with the inflowing gas stream, the rate of change in the concentration of HCB in the liquid phase is simply the change in concentration in the gas stream from entry to exit, multiplied by the volumetric flow rate of the gas, Q_g (L/s), divided by the volume of liquid V_l (L):

$$\frac{dC_l(t)}{dt} = \frac{Q_g}{V_l} \left(C_b(t=0) - C_b(t_b)\right) \tag{3.17}$$

The bubble phase concentrations in Equation 3.17 can be transformed to liquid phase concentations through Equations 3.11, 3.14, and 3.15 to yield the differential equation in terms of $C_l(t)$ alone:

$$\frac{dC_l(t)}{dt} = - k' \left(C_l(t) - C_l(eq)\right) \tag{3.18}$$

where the effective rate constant, k' (s^{-1}),

$$k' = \frac{Q_g H'}{V_l} \left(1 - \exp\left(- \frac{k_b A_b t_b}{V_b H'} \right) \right)$$

$$= g \quad f \tag{3.19}$$

is composed of two factors: $g = Q_g H'/V_l$, which is related to the rate of supply of the solute through the gas stream to the liquid, and f, related to the degree of equilibration of a single bubble with the solution (Equation 3.16).

Finally Equation 3.18 can be integrated to yield the concentration in the liquid as a function of time:

$$(C_l(t) - C_l(eq)) = (C_l(t=0) - C_l(eq)) \exp(-k' t) \qquad (3.20)$$

where $C_l(eq)$ is the concentration in the liquid that would be in equilibrium with the bulk concentration in the inflowing gas, as described in Equation 3.11.

It can be seen from Equation 3.20 that the aqueous concentration increases with time and assymptotically approaches $C_l(eq)$, with a time constant given by Equation 3.19. The rate at which $C_l(t)$ approaches $C_l(eq)$ can be increased by increasing gas flow rate, increasing t_b or the effective height of the water column, increasing k_b (possibly by increasing mixing), increasing A_b/V_b by decreasing the bubble size, or by decreasing the volume of water, V_l. The rate of equilibration will also increase with H' by an amount dependent on the other variables as given by Equations 3.19 and 3.10.

One important limiting case exists when $f = 1$, and the bubbles leave the solution in equilibrium. When this is the case, $k' = H'Q_g/V_l$, and the Henry's constant can be determined experimentally from the rate.

Association with Humic Matter

In the presence of humic matter the solubility of HCB is observed to exceed that in the absence of humic matter. Similar observations have been reported by Chiou et al. (1986), and Callaway et al. (1984). This apparent enhancement of the solubility can be interpreted through two different mechanisms: (i) the association of HCB with humic material in solution, or (ii) the modification of the properties of the solvent. The fact that the effect is observed at relatively low concentrations of humate tends to favor the first mechanism, but a contribution from the second cannot be ruled out. To a first approximation both mechanisms can be represented by the same linear model, and the distinction between mechanisms is not necessary. The simple linear model will be developed here in terms of the association mechanism.

In assessing the interaction of HCB with humic material, it is necessary first to distiguish between the concentration of free HCB, C_l, the concentration of HCB associated with humic material, C_a, and the total HCB concentration in solution, C_T,

$$C_T = C_l + C_a \tag{3.21}$$

According to the association mechanism, the operational mass action equation for the binding of HCB to humate is

$$C_l \; C_h \; K_h = C_a \tag{3.22}$$

where K_h is the operational stability constant (L mg^{-1}) and C_h is the humate concentration in mg L^{-1}. The mathematical form of the association mechanism presented above is identical to that of the partition mechanism, which has been used to describe the distribution of nonpolar hydrophobic compounds between sediments and water. Here the term

association is preferred to partition, since partition implies the distribution between two three-dimensional phases.

If the solution concentration of free HCB is established at the saturation value by contact with the saturated vapor, and if the total humate concentration is in great excess over the total HCB concentration, then the operational stability constant can be determined from the total HCB concentration and the free HCB concentration (determined in the absence of humate) through a combination of Equations 3.21 and 3.22:

$$K_h = \frac{C_T - C_1}{C_1 \; C_h} \tag{3.23}$$

Thus the apparent association constant can be determined from the concentration of HCB in solutions, with and without humic matter, by maintaining the solutions in equilibrium with a constant gas-phase activity of HCB. In addition to this equilibrium effect of humate, humate will also affect the rate of transfer of HCB as expressed in Equation 3.19, by altering the apparent Henry's constant. This effect is described below.

The simplest model of kinetics for transfer of HCB to the humate solution involves three assumptions, in addition to those of the film model: (i) association-dissociation kinetics of the humate-HCB complex are infinitely fast compared to transport kinetics; (ii) the liquid film transport coefficient of the humate-HCB complex is identical to that of the free HCB; and (iii) the humate is in great excess over the HCB and uniformly distributed, not accumulating significantly at the air-water interface. (One might expect that humic materials would accumulate at the interface; the impact of an enrichment of humic materials at the interface is discussed with the results.) Under the three assumptions listed

above, the two-film model with humate is of the same mathematical form as the model without humate, with two replacements: the free HCB concentration C_1 is replaced by the total HCB concentration C_T, and the conventional Henry's constant H' is replaced by an effective Henry's constant H'', defined

$$H'' = \frac{C_g}{C_T} \tag{3.24}$$

This effective Henry's constant is related to the conventional Henry's constant through the association constant and humate concentration by combining Equations 3.2, 3.21, 3.22, and 3.24:

$$H'' = \frac{H'}{(1 + K_h C_h)} \tag{3.25}$$

Thus, the effective Henry's constant varies with humate concentration and binding intensity. Furthermore, the equilibrium and kinetics of HCB transfer in the presence of humate is analogous to that in the absence of humate, with the effective Henry's constant replacing the true constant. The question then becomes, how do the kinetic constants depend on the Henry's constant?

In Equation 3.19 it was shown that the constant k' is composed of two factors: g, which is the rate constant if each bubble left the solution at equilibrium, and f, the fraction of equilibrium approached by each bubble. For very small values of H', the factor g obviously becomes very small. The value of k_b in Equation 3.10 approaches $k_g H'$, and the value of f approaches $1-\exp(k_g A_b t_b/V_b)$ in Equation 3.16. Thus the apparent rate constant for equilibration with the incoming gas is very small, but proportional to H'. The physical interpretation of this

situation is that the distribution of HCB to the liquid phase is favored. The equilibration of the liquid with the incoming gas is relatively slow, being ultimately limited by the rate of supply of the solute through the gas stream. This condition is true regardless of whether the bubbles leave the solution stripped of the solute or the bubbles leave partially full due to short residence time compared to the gas-film limited transport.

For large values of H', the factor g is large, but f becomes very small. In the limit of very large H', the two effects cancel each other, and the observed rate constant becomes independent of H'. The physical interpretation of this situation is that distribution of HCB to the gas phase is favored. Transfer is liquid film controlled, and the concentration of HCB in a bubble is virtually unchanged during the course of the bubble's rise through the solution. The tendency of a larger Henry's Law constant to decrease the amount of solute required to saturate the solution, and to speed equilibration, is offset by the tendency of the increased Henry's coefficient to decrease the driving force across the liquid film, and to retard equilibration.

Thus we expect the effect of complexation of HCB by humate to have no effect or to decrease the overall rate constant, i.e., the rate at which the total concentration of HCB in solution approaches its equilibrium value.

Competing processes.

The equations above describe the transfer kinetics of HCB from gas to water in the absence of other sources or sinks for HCB. Additional reactions which might be important in controlling $C_l(t)$ include volatilization of HCB from water to the headspace of the experimental apparatus, exchange with container walls, sediments, dissolved organic matter, organisms, or food, and any other reactions which might affect HCB concentration in solution. Once equilibrium conditions exist in the experimental vessel, introduction of clean food, organisms, or sediments that are not in equilibrium with dissolved HCB will decrease the dissolved concentration, if the amount of HCB exchanged to that phase is significant compared to the total amount in solution. If an equilibrium partition coefficient, K_p (L/kg) is used to describe partitioning into a solid phase, then the effect of HCB uptake on C_l can be neglected only when $m K_p << V_l$, where m (kg) is the dry weight of the solid phase. To maintain a constant, saturated concentration of HCB in solution, the mass of such solids per unit volume of solution should be kept below $1/K_p$.

Experiments in which $C_l(t)$ does not approach equilibrium with incoming vapor, $C_l(eq)$, in the absence of non-equilibrium phases in the vessel suggest a loss of HCB out of the system across the air-water interface, into the headspace of the apparatus. This loss can be significant if the headspace gas is mixed with outside air of C_g lower than that exiting the water column. Alternatively, HCB could be injected into the headspace by aerosol formation as bubbles burst at the air-water interface. If we ignore this latter possibility, the effect of a headspace loss on the overall air-water exchange kinetics can be included easily in the model developed previously.

The flux of HCB out of the liquid at the free headspace surface can be described by an equation simlar to Equation 3.9

$$\frac{1}{A_s}\frac{dN}{dt} = k_s\,(C_1(t) - C_1(eq,s)) \qquad (3.26)$$

where k_s is the mass transfer coefficient at the water-headspace interface of area A_s, and $C_1(eq,s)$ is the concentration in the liquid that would be in equilibrium with the concentration in the gas of the headspace, assumed to be constant.

From Equation 3.26 and a similar equation for the flux at the bubble-liquid interface, the differential equation for the time dependent concentration of HCB in water can be developed:

$$\frac{dC_1(t)}{dt} = -\frac{k_s A_s}{V_1}(C_1(t) - C_1(eq,s)) - k'\,(C_1(t) - C_1(eq,b)) \qquad (3.27)$$

The steady state concentration in the liquid phase ($C_1(ss)$) is found by setting the derivative equal to zero and rearranging terms:

$$C_1(ss) = \frac{k_s A_s C_1(eq,s) + k' V_1 C_1(eq,b)}{k_s A_s + k' V_1} \qquad (3.28)$$

It is seen from Equation 3.28 that the effects of headspace loss are minimized when the A_s/V_1 is minimized, when k'/k_s is maximized (increasing Q, A_b/V_b, and t_b), or when $C_1(eq,s)$ approaches $C_1(eq,b)$.

Representative calculations with Equation 3.28 illustrate the possible importance of volatilization losses across the headspace. It is assumed that k' is 6×10^{-6} s^{-1} (data from these experiments with round bottom flasks), k_s is 1.4×10^{-3} cm/s (5.0 cm/hr) (extrapolation of data from Southworth, 1979), V_1 equals one liter, A_s is 100 cm^2,

and C(eq,s) is zero, i.e., we assume that the headspace is so rapidly mixed with clean air that the concentration at the surface is effectively zero. The resulting C_1(ss) is equal to 0.041 C(eq,b); headspace losses are seen to be very important.

If k' and k_s are maintained constant, C_1(ss) is a linear function of C(eq,s). If C(eq,s) = C(eq,b)/2, that is, the head space gas were a half-half mixture of clean air and gas stream, the value of C(ss) would be equal to 0.52 C_1(eq,b). If A_s were decreased to 1.0 cm^2 and the assumptions in the above two examples were maintained, C_1(ss) would be equal to 0.81 and 0.90 C_1(eq,b), respectively.

It is obvious that it is necessary to decrease the mixing of clean air into the headspace to minimize effectively this potential loss mechanism.

Summary

The rate laws which describe air-water transfer of neutral organic compounds, such as HCB, in gas bubbling experiments have been developed. The time-dependent aqueous phase concentration, $C_1(t)$, of a volatile compound is given by:

$$(C_1(t) - C_1(eq)) = (C_1(t=0) - C_1(eq)) \exp(-k't)$$

C_1 approaches $C_1(eq)$, the equilibrium concentration with respect to the incoming vapor concentration, with a time constant k'. The constant k' can be described in terms of experimental parameters and provides insight into the controlling factors which should be considered when optimizing gas bubbling experiments

$$k' = \frac{Q_g H'}{V_1} \left(1 - \exp\left(- \frac{k_b A_b t_b}{V_b H'} \right) \right)$$

The overall rate of tranfer can be increased with increasing the flow rate of bubbles (Q_g), by decreasing the volume of water (V_1), or by using a compound with a higher Henry's Law constant (H'). The extent to which a rising bubble approaches equilibrium with the aqueous phase before it leaves the solution is indicated by the exponential term in this equation. If rising bubbles do not leave the water at equilibrium, then the overall rate constant, k', can be increased by increasing the surface to volume ratio of the bubbles (A_b/V_b), by making the bubbles smaller, by increasing the pathlength or contact time of the bubbles in the water (t_b), by decreasing the Henry's Law constant (however this will not increase the overall rate of transfer) by choice of the compound or changing solution chemistry, and by increasing the air-water mass transfer coefficient, k_b, by increased mixing of the aqueous phase. When the

exponent in this equation becomes sufficiently negative and bubbles leave in equilibrium with the water, then k' cannot be increased by further control of these latter variables.

Equations to describe the aqueous concentration of HCB in gas bubbling experiments can be complicated by additional sources or sinks of HCB. Exchange of HCB with container walls, sediments, organisms, and food may affect C_1 when the total capacity of these phases approaches that of the total volume of water. The mass of non-equilibrium phases per volume of water introduced to experiments should be minimized.

Volatilization across the air-water interface into the headspace can provide an important loss mechanism for HCB when the vapor in the headspace is allowed to mix with even a small amount of clean air. Equations are developed which show that in a steady-state situation headspace losses are minimized when the interfacial area at the headspace is small, when the headspace concentration of HCB approaches equilibrium with the water (low mixing with clean air), and generally when k' is optimized, as described above. Mixing of clean air into the headspace can be minimized by keeping the interfacial area of the effluent gas flow low, or by bubbling the outflow through a water trap to prevent back diffusion of clean air.

4. EXPERIMENTS

A series of experiments were performed to characterize the transfer of hexachlorobenzene from the solid phase, through the gas phase to the liquid aqueous phase. The experiments involved both the addition of HCB to the liquid and stripping of HCB from the liquid.

These experiments are outlined in Table 4.1. All of the experiments were variations on the same basic design. Gas was bubbled through a liquid; during the contact between the gas and the liquid, solutes are exchanged between the two phases. The liquids used were ethyl acetate, which extracts HCB from the vapor phase with high efficiency, and water, with and without suspended humic material. The objectives of the experiments were to determine:

i. the vapor pressure and the concentration of HCB in air in equilibrium with the solid, and the rate of delivery of HCB through a particular experimental set-up;

ii. the solubility of HCB in water and its rate of uptake in water from an HCB-saturated gas;

iii. the effect of humic material suspended in the aqueous phase on the total amount of HCB in the aqueous phase;

iv. the effect of humic material suspended in the aqueous phase on the exchange rate of HCB between the aqueous and gaseous phases.

The source of the humic materials used in these experiments was humic acid from Aldrich. Malcolm and MacCarthy (1986) have discussed limitations on the use of this material in research on soils and water. Humic materials were added to samples through a spike of a well mixed solution containing 1 g/L of humic acid. No attempt was made to separate soluble and insoluble material in the concentrated solution.

Table 4.1. Description of Experiments

Experiment	Gas	Liquid	Solute
1. Uptake	Air/HCB	Ethyl Acetate	HCB
2. Uptake	Air/HCB	0.010 M NaCl	HCB
3a.Uptake	Air/HCB	0.010 M NaCl + 1.0 mg/L Na Humate	HCB
3b.Uptake	Air/HCB	0.010 M NaCl + 50. mg/L Na Humate	HCB

Description of Experiments.

The experimental apparatus for the transfer of HCB from the solid to the liquid is shown in Figure 4.1. Compressed air pressure was set at 40 kPa (5 psi) over atmospheric pressure. The air was passed through a drying column and a molecular sieve to remove trace impurities, and flow was regulated by a needle valve.

The needle valve was placed downstream of the molecular sieve to reduce re-equilibration time after an adjustment of the valve, and upstream of the HCB column to avoid the potential of pressure build-up, and explosion, in the HCB column. The flow rate was measured with a bubble flow meter attached to the exit port of the system. After an adjustment of the needle valve, time was allowed for the system pressure to re-equilibrate. Flow was measured at several times during the course of an experiment and found to be relatively constant.

From the needle valve, the air was equilibrated with water and passed through a 25 x 2.5 cm column filled with 0.5 cm diameter glass beads coated with solid HCB. (In the experiments with ethylacetate, the water equilibration step was bypassed.) The beads were coated by preparing a slurry of 2 g HCB in enough diethyl ether to cover the beads; when the slurry became thick, the beads were transferred to a tray, no more than 1 layer of beads deep for final drying.

The gas stream was then bubbled into the sample liquid through a glass frit of porosity 40-60 μm. The sample liquid was contained in a three-liter round bottom flask. The gas leaving the sample vessel was passed through a water trap to limit back diffusion of HCB-free air into the vessel. The gas passing out of the water trap was passed through Tenax resin to trap HCB.

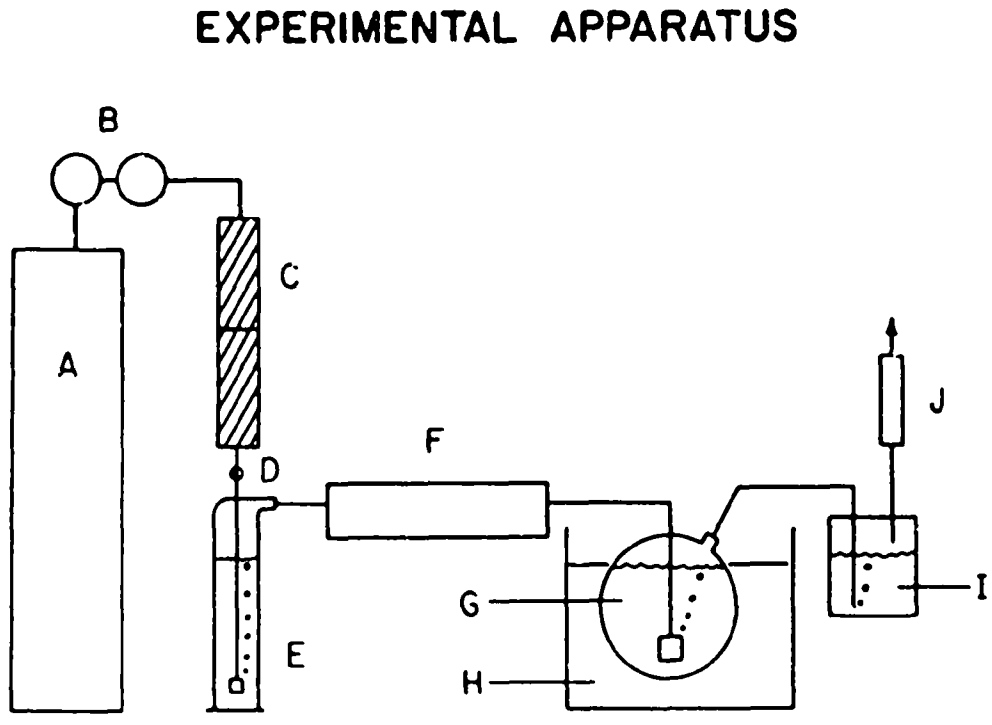

Figure 4.1. Apparatus for transferring HCB from the solid phase to the liquid phase via the gas phase. A. compressed air; B. regulator set at 35 kPa; C. gas purification column (drying agent and molecular sieve); D. needle valve; E. vessel to presaturate air with water vapor; F. column with solid HCB on glass beads; G. vessel containing sample liquid; H. constant temperature bath; I. water trap; J. Tenax resin trap.

The entire apparatus was operated in a fume hood. The three-liter flask was maintained at 295 K in a water bath. The column with HCB was not placed in the water bath, due to its limited resistance to corrosion and leaks. However, for further studies, a thermostatted column for the HCB is highly recommended due to the strong dependence of HCB vapor pressure on temperature (Table 2.1).

The liquid in the round bottom flask was sampled with a glass pipet through a ground-glass stoppered sampling port. The volume of liquid withdrawn for analysis was replaced by an equal volume of HCB-free solvent. A correction for this dilution was made in the data analysis (vide infra).

Three factors appeared to be important in minimizing losses of HCB to the walls of the vessel and the headspace: (i) minimizing headspace in the sample flask by filling the flask close to capacity; (ii) minimizing loss of HCB across the solution-headspace interface by use of a water trap on the exit port of the sample flask; and (iii) minimizing the glass surface to solution volume ratio through use of a round-bottom flask. No experiments were conducted to quantify the effects of these three measures, but performance of the system seemed to improve as the measures were introduced.

Analysis for HCB by Gas Chromatography.

The standards for the calibrations were made up in three different media: (i) toluene, (ii) 0.001 M $NaHCO_3$, and (iii) 0.001 M $NaHCO_3$, 20 mg/L sodium humate.

Laboratory standard solutions of pentachlorobenzene (PeCB), which is the internal standard, and HCB were prepared from the pure solids (Supelco, 99%) by adding a known mass of the compounds to a 25 mL volumetric flask and filling to the mark with toluene. The concentration of the laboratory standard HCB was 3.10 ug/mL and PeCB 16.20 ug/mL.

The nonaqueous calibration standards were prepared by adding a known volume of the laboratory standards to a 40 mL glass bottle with a Teflon lined screw cap containing 3 mL of toluene. Aluminum foil was placed over the mouth of the bottle to prevent the sample from contacting the Teflon cap liner. The volume of HCB was varied and the volume of PeCB was held constant. The solutions were placed on a vortex mixer for 90 seconds, then added by pipette to crimp-top autosampler vials.

The aqueous calibration standards were prepared by adding a known volume of the laboratory standards to a 40 mL glass bottle with a Teflon lined screw cap containing 20 mL of the aqueous solution. Aluminum foil was placed over the mouth of the bottle to prevent the sample from contacting the teflon lining. The solutions were placed on a vortex mixer for 90 seconds, 3 mL of toluene were added, the solutions mixed for another 90 seconds, then the phases allowed to separate. Three (in some cases only two) aliquots of the toluene phase were removed by pipette and placed in separate crimp-top autosampler vials; the separate subsamples allowed for replication of the gas chromatography step of the analysis. There were no replicates of the extraction procedure in these

calibrations. Samples were extracted and analyzed by the same procedure described above for the standards.

The samples were run on a Perkin-Elmer Model Sigma 2000 gas chromatograph with an electron capture detector, programmable temperature vaporizing injector, Model LCI 100 integrator, and Model AS-2000 autosampler. A Perkin-Elmer bonded methylsilicone column (10 m x 0.25 mm) was used isothermally at 180 °C, with split injection at 275 °C. Each calibration involved solutions with standards of five different concentrations; two or three replicate injections of each standard were made. Peak height and peak area for both HCB and PeCB were recorded. Peak height was used for quantitation. Relative standard deviation was 4% for replicate injections. Some of the samples early in the program were analyzed by a similar procedure on a different gas chromatograph.

Results and discussion.

The raw data obtained from all of these experiments are time series of concentrations in the sample vessel. The raw data for Experiments 1 - 3 are presented in Tables 4.2 - 4.4.

The data for time and concentration were interpreted in terms of two adjustable parameters in the model developed in Section 4 of this report: the saturation concentration, C(eq), and the rate constant, k'. The equations that were actually used in the determination of these constants, corrected for sampling volume, are presented in Table 4.5.

The values of C(eq) and k' determined by this method are presented in Table 4.6. The fundamental constants that have been derived from these results are summarized in Table 4.7. It can be seen that the fundamental constants determined in this study agree well with those of Atlas et al. (1984), discussed in Part 2 of this report.

In the following section, the results presented in Table 4.7 are discussed in detail, including the determination of: (i) the vapor pressure and vapor phase saturation concentration of HCB through uptake experiments with an organic liquid; (ii) the saturation concentration of HCB in water and Henry's constant through vapor phase uptake experiments; (iii) the degree of equilibration of a bubble as it passes through solution; (iv) the association of HCB with dissolved organic matter (equilibrium and kinetics) through saturation concentration and gas-liquid exchange kinetics. The values of apparent Henry's constants, degree of equilibration, and association constants are summarized in Table 4.8.

Table 4.2. Data from Experiment 1. Transfer of HCB from air to ethylacetate.

Time (hr)	C(HCB)(μg/L)	Standard Deviation[a]
16.67	1.24	.05
17.83	1.45	.05
18.83	1.91	.06
19.75	1.67	.23
23.08	2.14	.27
24.00	2.19	.28
24.83	2.33	.29
40.25	3.74	.43
44.50	3.86	.15
48.35	4.45	.17

[a] Calculated by propagation of error from slope and intercept of calibration curve and replicate injections of sample (cf. Peters, Hayes, Hieftje, 1976)

Table 4.3. Data from Experiment 2. Transfer of HCB from air to 0.01 M NaCl.

Time (hr)	C(HCB)(μg/L)	Standard Deviation[a]
18.1	1.53	0.24
23.7	1.85	0.29
25.5	2.72	0.46
26.5	2.27	0.38
41.6	2.78	0.47
43.5	2.62	0.44
45.7	2.59	0.44
47.4	2.70	0.43
49.3	2.49	0.39
65.4	3.48	0.59
67.4	3.75	0.60
71.0	3.69	0.59
73.3	3.66	0.59
90.7	4.26	0.69
95.0	4.29	0.69
99.2	4.14	0.67
185.4	5.08	0.83
189.7	5.24	0.85
192.6	4.86	0.79
209.6	4.95	0.80
212.7	4.65	0.75
214.4	4.36	0.71
233.7	4.74	0.77
239.0	4.53	0.76
240.4	4.07	0.68
256.0	3.99	0.66
259.4	4.16	0.69
262.4	4.07	0.68
280.5	4.69	0.78
280.5	4.83	0.80
280.5	4.56	1.09
287.3	4.70	0.78
303.2	3.72	0.62
309.0	3.53	0.56
327.0	3.70	0.59
353.4	3.84	0.62
449.6	3.77	0.60
449.6	4.12	0.66
495.6	4.28	0.69
495.6	4.32	0.70

[a] Calculated by propagation of error from slope and intercept of calibration curve and replicate injections of sample (cf. Peters, Hayes, Hieftje, 1976)

Table 4.4. Data from Experiment 3.[a]

Transfer of HCB from air to 0.01 M NaCl with 1.0 mg/L humic matter

Time (hr)	Concentration (μg/L)
0.0	0.00
27.0	3.00
93.7	6.20
142.2	6.64
195.0	5.64
267.7	5.39
307.0	5.34
359.5	5.44
431.5	5.40
475.5	6.26
526.5	5.99
629.0	5.07

Transfer of HCB from air to 0.01 M NaCl with 50.0 mg/L humic matter

Time (hr)	Concentration (μg/L)
0.0	0.00
20.5	4.61
45.7	5.04
113.7	11.00
138.6	11.16
163.1	13.46
187.6	13.55
204.8	14.35
276.8	14.69
329.7	15.73
348.4	16.72
469.3	16.47

[a] Standard deviation estimated at 0.7 μg/L for all determinations.

Table 4.5. Equations used to define models. The object function, of which the weighted sum of squares was minimized, was $Y(i) = C(i) - C^{exp}(i)$. The function $C(i)$ is given below; the values of $C^{exp}(i)$ are given in Tables 4.2-4.5.

A. Experiment 1. Determination of C_g by uptake of HCB in ethylacetate.

$$C_l(i) = C_g Q_g t(i) - \sum_{j=1}^{i} \frac{V_a}{V_l} C_l(j-1)$$

where:

$C_l(i)$, $t(i)$	time series of concentrations in the liquid phase;
$C_g = 0.554$ nmol/L	concentration in gas phase (Table 4.6)
$Q_g = 0.463$ mL/s,	gas flow rate
$V_l = 3.00$ L,	volume of liquid in sample vessel
$V_a = 0.100$ L,	volume of sample withdrawn for analysis (and replaced with HCB-free ethyl acetate)

B. Experiments 2, and 3. Determination of $C_l(eq)$ and k' (kinetic model) for uptake of HCB in aqueous solutions.

$$C_l(i) = C_l(eq) + [C_l(i-1)[1-V_a/V_l] - C_l(eq)] \exp(-k'[t(i)-t(i-1)])$$

where:

$C_l(i)$, $t(i)$	time series of concentrations in the liquid phase;
$Q_g = 0.463$ mL/s,	gas flow rate
$V_l = 2.90$ L,	volume of liquid in sample vessel
$V_a = 0.100$ L,	volume of sample withdrawn for analysis (and replaced with HCB-free aqueous solution)

Table 4.6. Optimal values of parameters C(eq) and k' found for model.[a]

Experiment	k' [s^{-1}]	(SD)[b]	C(eq) [nmol/L]	(SD)[b]
1. Uptake HCB Ethyl Acetate			0.554[c]	(0.007)[c]
2. Uptake HCB Water	5.8E-6	(0.7E-6)	18	(1)
3a. Uptake HCB Water Humate 1 mg/L	8.7E-6	(2.8E-6)	21	(1)
3b. Uptake HCB Water Humate 50 mg/L	2.5E-6	(0.2E-6)	62	(2)

[a] Values in table determined by weighted nonlinear least squares analysis of experimental concentration vs. time data, corrected for sampling volume, according to equations in Table 4.5.

[b] Standard Deviation determined from propagation of error through weighted nonlinear least squares

[c] In this case the concentration of HCB in air.

Table 4.7. Summary of Results[a,b]

Vapor pressure of HCB at 295 K

1.37 (0.02) mPa

Saturation concentration of HCB in air at 295 K

0.554 (0.007) nmol/L

Delivery rate of HCB with apparatus

0.26 pmol/s

Saturation concentration of HCB in water at 295 K

18 (1) nmol/L

Saturation concentration of HCB in water with 1 mg/L humate at 295 K

21 (1) nmol/L

Saturation concentration of HCB in water with 50 mg/L humate at 295 K

62 (2) nmol/L

Transfer rate constant for HCB between gas and water in apparatus

5.8×10^{-6} (0.7×10^{-6}) s^{-1}

[a] The numbers in parentheses are the standard deviation determined from propagation of error through weighted nonlinear least squares.

[b] In this table, the results that are discussed in detail in the text summarized for convenience. Several important qualifications on the accuracy and precision of these values are discussed in the text; these values should not be cited or used without a full appreciation of these qualifications.

Table 4.8. Results of Uptake Experiments[a]

Experiment	H''	SD	f[b]	SD	K_h [L / mg]	SD
2. Uptake HCB Water	0.031	0.03	1.2	0.2		
3a. Uptake HCB Water Humate (1 mg/L)	0.026	0.01	2.0	0.8	0.17	0.17
3b. Uptake HCB Water Humate (50 mg/L)	0.0089	0.0005	1.7	0.3	0.05	0.01

[a] Values in table calculated from values in Table 4.6 and equations discussed in text. The values are:

H'' the (effective) Henry's constant (Equation 3.24);

f the fractional approach to equilibrium of a bubble (Equation 4.4);

K_h the effective association constant of HCB with humate (Equation 3.23).

[b] As discussed in the text, values of f *significantly* greater than one are physically unreasonable, indicating error in the data or insufficiency of the model.

Vapor pressure and gas phase concentration at saturation. The first quantity to be determined is the vapor pressure and gas phase saturation concentration of HCB. For this determination, Experiment 1 was conducted: air was passed over solid HCB and then through ethylacetate. If (i) the vapor is in equibrium with the solid, and (ii) all of the HCB is extracted from the bubbles during their passage through ethylacetate, then the saturation concentration can be calculated from the rate of change of concentration of HCB in the ethylacetate:

$$\frac{dC_1}{dt} = \frac{Q_g C_g}{V_1} \tag{4.1}$$

and the vapor pressure from the ideal gas law:

$$p = C_g R T \tag{4.2}$$

The validity of the assumptions (i) and (ii) above have been supported qualitatively by other experiments in which the gas flow rate was varied, and the linearity of the increase in concentration of HCB in ethylacetate with time. The vapor pressure found from Equations 4.2 was 1.37 mPa, which agrees well with other determinations (Table 2.1).

These data indicate that HCB can be delivered at unit activity at the rate of

$$\frac{dN}{dt} = C_g Q_g = 0.26 \text{ pmol s}^{-1} \tag{4.3}$$

A major sorce of uncertainty in the number reported for this concentration is in the control of the temperature of the column with the solid HCB, since it was not thermostatted.

Solubility and Henry's Constant. The next step is to calculate the water solubility and the dimensionless Henry's Law constant. The water solubility found from Experiment 2 (Table 4.6), was combined with the gas solubility from Experiment 1 to yield the Henry's Law constant. The value of H' found from these data and Equation 3.2 was 0.031 (0.003). This value is within the range of those reported in the literature. The relative standard deviation is calculated to be approximately 10%.

Kinetics. The uptake of HCB by aqueous solutions is shown as a function of time in Figure 4.2. The experimental data and the model, which is defined in Tables 4.5 and 4.6, are shown. The effect of sampling on the concentration is quite evident.

The kinetic constant k' is composed of two factors, one of which is related to the degree to which a bubble approaches equilibrium with the liquid during its passage through the water column. This approach to equilibrium can be quantified in terms of the quantity f, defined in Equation 3.16 as the actual change in the concentration of the bubble from entry to exit, divided by the change if the bubble left at equilibrium:

$$f = \frac{C_b(t=0) - C_b(t_b)}{C_b(t=0) - C_b(eq)} = 1 - \exp\left(-\frac{k_b A_b t_b}{H' V_b}\right) = \frac{V_l k'}{H' Q_g} \qquad (4.4)$$

For Experiment 2 the value of f calculated from V_l, k', H', and Q_g is 1.3 (0.3). A value of f greater than one is physically unreasonable, indicating that the extraction of HCB from a bubble exceeds that predicted if the bubble leaves the solution at equilibrium. Therefore we interpret this value of f to mean that the bubbles leave the solution very close to equilibrium with the solution. An alternative interpretation, involving the a priori assumption of equilibrium between bubbles and solution, is examined at the end of this section.

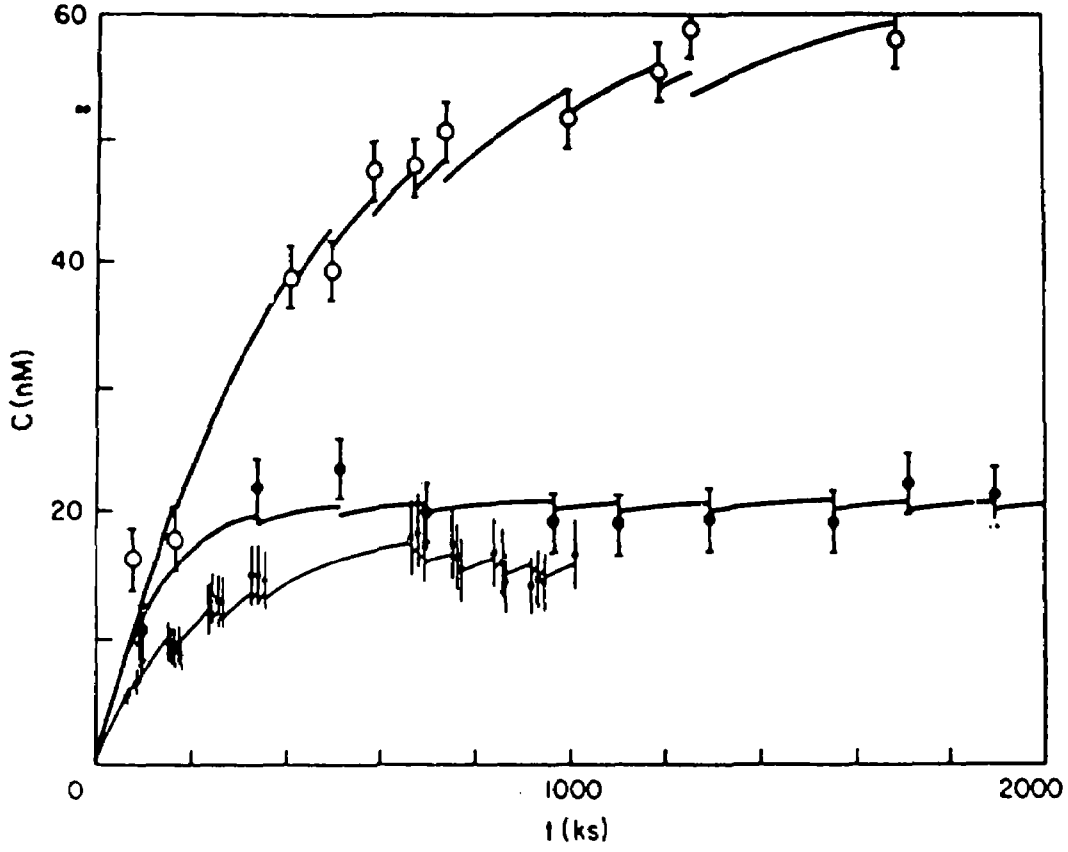

Figure 4.2. Uptake of HCB by 0.01 M NaCl (.) ; by 0.01 M NaCl with 1 mg/L humate (•); by 0.01 M NaCl with 50 mg/L humate (σ); and the kinetic model (solid lines). Data points with error bars (standard deviation of mean) are shown. The solid lines are the model calculations. The experimental conditions and equations of the model are given in Table 4.5; the adjustable parameter values used in the model are given in Table 4.6. The discontinuities in the calculated concentrations are due to the volume removed for analysis.

Association with Humate. Experiment 3 allows the association of HCB with humate to be assessed. The experimental data and the model for the uptake of HCB in solutions containing humate are shown in Figure 4.2. From these data both the equilibrium association constant of HCB with humate and the uptake rate can be found.

From the values of C(eq) from in Table 4.6 and Equation 3.23, the operational contants of K_h = 0.17 and 0.05 L mg^{-1} are determined for the 1 mg/L and 50 mg/L solutions, respectively. Only 14% of the HCB is bound in the first solution and 70% in the second. Considering the low degree of binding the lack of agreement between these two parameters is not too disturbing; the data show that binding of HCB by this humic material is significant only at relatively high concentrations of humate.

According to the arguments presented in Part 3, the effect of humates on transfer kinetics can be assessed by using an effective Henry's constant (Equation 3.25) in the kinetics equations, Equations 3.20 and 3.19. From this approach it is expected that complexation by humates will have no effect or decrease the rate constant. A decrease appears to be apparent in the data presented in Table 4.6.

However, when the value of f is calculated (Table 4.8), it is again significantly greater than one, the maximum physically reasonable value. This value of f suggests that the extraction of HCB from a bubble exceeds the equilibrium concentration in the water. Two alternatives to this physically unreasonable situation seem most plausible: (i) the assumption in the model are incorrect, or (ii) on account of experimental error, the values of f are not significantly different from one, and the bubbles are actually very close to equilibrium with the solution.

One of the assumptions in the model was that HCB was homogeneously distributed through the solution. However it is known tht humic material is enriched at the air-water interface. If the humic material in these tests was selectively accumulated at the bubble-water interface, the association of HCB would occur to a higher degree than in the bulk of solution, and the extraction from the bubble would occur at a rate faster than predicted on the basis of bulk concentrations. A quantitative model of this process can be worked out, but the limited amount of data available and the number of unknown parameters makes this pursuit of little benefit at this time.

Equilibrium Assumption. The values of f in Table 4.8 are all greater than one, the maximum physically reasonable value under the assumptions of the model. Another way of interpreting these values of f is that the initial uptake of HCB by the solution is too rapid to be consistent with the relatively low plateau concentration attained with time. Among the many possible explanations of this apparent inconsistency, two appear to be most plausible: (i) the vapor phase concentration varies with time due to temperature fluctuations, and (ii) the bubbles really do leave the vessel at equilibrium with the liquid, and the anomalously high values of f are simply a result of covariance among the two adjustable parameters, C(eq) and k'. If the first explanation is correct, the interpretation of the data given above is as good as can be done with the data, and no further work is necessary. If the second explanation is correct, the data could be interpreted in terms of an equilibrium model, in which the factor f is set equal to 1 and the only adjustable parameter is C(eq).

The equations for this equilibrium model are presented in Table 4.9, the values of the adjustable parameters in Table 4.10, and the function superimposed on the data in Figure 4.3. It is seen that for the aqueous solution (no humates) the equilibrium model fits the data about as satisfactorily as the kinetic model, and the factor f has a plausible value. For both of the humate solutions, the value of C(eq) is unreasonably high, in an attempt to match the high initial uptake rate.

Thus our tentative conclusions are: (i) the equilibrium model is satifactory for the solution without humate; (ii) the kinetic model is necessary to describe uptake in the presence of humic material. Callaway et al. (1984) reached similar conclusions in a study of more volatile compounds. The uptake rate in the presence of humic material is faster than predicted on the basis of the equilibrium model with adjusted Henry's constant, suggesting the enhancement of uptake due to an enrichment of humic material at the air-water interface. The validity of these conclusions is subject to uncertainty about the effects of small variations in tempertature.

Table 4.9. Equation used to define equilibrium model. The object function, of which the weighted sum of squares was minimized, was $Y(i) = C(i) - C^{exp}(i)$. The function $C(i)$ is given below; the values of $C^{exp}(i)$ are given in Tables 4.3-4.4.

Experiments 2, and 3. Determination of $C_l(eq)$ (equilibrium model) for uptake of HCB in aqueous solutions.

$$C_l(i) = C_l(eq) + [C_l(i-1)[1-V_a/V_l] - C_l(eq)] \exp\left(- \frac{Q_g C_l(eq)}{V_l C_g} [t(i)-t(i-1)]\right)$$

where:

$C_l(i)$, $t(i)$	time series of concentrations in the liquid phase;
Q_g = 0.463 mL/s,	gas flow rate
C_g = 0.554 nmol/L	concentration of HCB in gas phase
V_l = 2.90 L,	volume of liquid in sample vessel
V_a = 0.100 L,	volume of sample withdrawn for analysis (and replaced with HCB-free aqueous solution)

Table 4.10. Optimal values of parameters $C_1(eq)$ found for equilibrium model.[a]

Experiment	C(eq) [nmol/L]	(SD)[b]
2. Uptake HCB Water	20	1
3a. Uptake HCB Water Humate 1 mg/L	22	1
3b. Uptake HCB Water Humate 50 mg/L	91	4

[a] Values in table determined by weighted nonlinear least squares analysis of experimental concentration vs. time data, corrected for sampling volume, according to equations in Table 4.9.

[b] Standard Deviation determined from propagation of error through weighted nonlinear least squares