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Characterization of parameters in mechanistic models: A case study of a PCB fate and transport model

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Abstract

As a first step in a Bayesian analysis of PCB fate and transport in the upper Hudson River, a joint probability density function for parameters in a simulation model is created. The density function describes the joint probabilities of the following parameters: the anaerobic dechlorination rate constant, the volatilization rate constant, the aerobic biodegradation rate constant, the sedimentation rate, and the contaminated sediment depth. Difficulties in forming this probability density function are shown to result from problems with extrapolating data from the laboratory to the field, non-stationarity and aggregation, extrapolating information and analyses from other sites, and bias due to study design. These difficulties result in a density function characterized by high variances, and imply that predictions from this simulation model, and similarly large fate-and-transport models, are apt to be highly uncertain. Bayesian analysis is proposed as a rigorous mathematical technique for including observational data in density function generation in order to reduce prediction uncertainty. © 1997 Elsevier Science B.V.

Keywords: Bayes theorem; Polychlorinated biphenyl; Fate and transport models; Hudson River; Parameter estimation

1. Introduction

It is common practice to use a combination of expert judgment and experimental evidence to select parameter values for application of a mechanistic (process-oriented) environmental simulation model. Optimization is infrequently applied with site-specific data for parameter estimation, and error estimates to reflect parameter uncertainty are rarer still. The emphasis on judgment and selection (as opposed to observation and optimization) has probably developed for a number of reasons including: (1) the lack of observational data for optimal estimation of more than a few parameters, and (2) the belief that the model equations are correct so that parameters are measurable and transferable.

Classical optimization techniques can be used with site-specific observational data to yield point and interval estimates for parameters; however, classical (or frequentist) statistical inference is ill-suited for incorporation of collateral information into the parameter estimation algorithm. In contrast, Bayesian inference provides a framework for combining all information in a probabilistic expression of knowl-

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edge concerning parameters. Indeed, Bayesian inference is quite consistent with current modeling practice, but with Bayes' theorem replacing the current ad hoc information pooling approach used by modelers.

To apply Bayes' theorem, the modeler must first express existing knowledge about parameters in probabilistic terms. This expression, called the 'prior probability', represents all information on the parameters available before new data are obtained. If no additional data are to be acquired, then the prior probability is a complete characterization of knowledge (and uncertainty) concerning a parameter; clearly, the prior probability conveys more information than does a single point value (selected under current modeling practice).

In this paper, we describe how scientific knowledge, expert judgment, experimental evidence, and observational data can be used to characterize probability distributions for parameters for a contaminant fate and transport model. This is undertaken for a mechanistic model of polychlorinated biphenyl (PCB) in the upper Hudson River which is briefly described in the next section; details of the complete modeling study are presented elsewhere (Steinberg, 1993; Steinberg et al., 1996). Following the description of the model, we describe how extant information was used to define the parameter probability distributions. The paper concludes with a discussion of parameter estimation and specification of functional relationships in mechanistic models.

2. The PCB fate and transport model

PCBs were introduced into the upper Hudson River of New York State as a consequence of waste discharges from General Electric manufacturing plants in Fort Edward and Hudson Falls, NY (Schroeder and Barnes, 1983). The discharged PCBs were in the form of Aroclors, complex chemical mixtures of the 209 different possible PCB congeners. Due to the hydrophobicity of PCBs most of the chemical sorbed to river sediments. This material has migrated downstream, contaminating the Hudson River sediments with PCB from Fort Edward to New York Harbor and serving as a source of PCB loading to the water column.

A simulation model for PCB fate and transport in the Hudson River from Fort Edward south to Waterford, NY was developed (see Steinberg et al., 1996) from the advection–dispersion-reaction equation. In Steinberg et al. (1996) the development of the model is discussed in detail and it is shown that simulation results vary depending on the method used to fit the model parameters. The maximum likelihood method produced the best fits to the data, but the paper shows that the Bayesian method of parameter estimation will produce better fits to new data (i.e. data not used in the calibration).

Steinberg et al. (1996) made a number of simplifying assumptions in deriving the simulation model from the advection–dispersion-reaction equation. These assumptions were driven primarily by the lack of observational data to support more complex model formulation. One of the most important simplifications was in the sedimentation and resuspension terms. Data to parameterize a model with flow-specific resuspension rates have not been collected in the upper Hudson River (see Zimmie, 1985). In light of this difficulty, resuspension was parameterized using a constant resuspension rate which represents the mean behavior of sediment in the upper Hudson River over time. The sedimentation rate was inferred by imposing a mass balance in each segment.

The simulation model developed in Steinberg et al. (1996) consists of two coupled differential equations, Eq. (1) and Eq. (2). Eq. (1) simulates c_a, the PCB concentration in the water column, and Eq. (2) models c_b, the PCB concentration in the sediments. In addition to transport terms (1), Eq. (1) includes a first order reaction term for volatilization and aerobic biodegradation in the water column (2), a term for increases in c_a due to resuspension of bottom sediments (3), and a term for loss of PCB mass due to sedimentation from the water column (4). Symbols in Eq. (1) include: u, the water velocity; D, the longitudinal dispersion coefficient; k_{vol}, the volatilization rate constant; k_o, the aerobic biodegradation rate constant; F_w, the fraction of PCB which is dissolved; v_r, the sediment resuspension velocity; z, the water column depth; and v_s the sediment sedimentation velocity. Changes in the concentration of PCB in the bottom sediment, c_b, are modeled with a term for concentration increase due to sedimentation of PCB-contaminated particles from the water column (1), and a term for concentration decrease due to anaerobic dechlorination and resuspension of PCB-contaminated sediment (2). The sedimentation velocity is modeled as the complement to the resuspension velocity. Its value is set as required to ensure that the flux of material resuspended is compensated by an equal flux onto the bed. In this way, no net scour or fill at any cross-section is simulated [1]. Symbols in Eq. (2) include: ζ, the thickness of the contaminated sediment layer and k_a, the anaerobic dechlorination rate constant.

$$\frac{\partial c_a}{\partial t} = \overbrace{-u\frac{\partial c_a}{\partial x} + \frac{\partial}{\partial x}\left(D\frac{\partial c_a}{\partial x}\right)}^{1} - \overbrace{(k_{vol} + k_o)F_w c_a}^{2} + \overbrace{\frac{v_r}{z}c_b}^{3} - \overbrace{\frac{v_s}{z}(1 - F_w)c_a}^{4} \tag{1}$$

$$\frac{\partial c_b}{\partial t} = \overbrace{\frac{v_s}{\zeta}(1 - F_w)c_a}^{1} - \overbrace{(\frac{v_r}{\zeta} + k_a)c_b}^{2} \tag{2}$$

Calculation of the simulation model inputs are detailed in Steinberg et al. (1996). In brief:

1. river velocity was calculated from the equation of continuity using flow rates reported by the United States Geological Survey (USGS) and assuming rectangular channels with width measured from USGS topographic maps;
2. the longitudinal dispersion coefficient was calculated using Fischer's equation;
3. F_w was calculated assuming equilibrium partitioning, with the partition coefficient calculated from K_{ow} estimates of Hawker and Connell (1988), Karickhoff's K_{oc}–K_{ow} relationship ($\log_{10} K_{oc} = \log_{10} K_{ow} - 0.21$), and the observed fraction organic carbon found in upper Hudson River sediment;
4. boundary PCB concentrations in the water column were available from measurements of PCBs taken by the USGS;
5. initial PCB concentrations in the sediment were available for 1976 from the USEPA.

3. Parameter estimation

It was assumed that several of the parameters in the model were uncertain and should be characterized by probability density functions. Steinberg et al. (1996) combined these density functions into a single prior probability density function in a Bayesian analysis for parameter estimation. Here, we focus on the interpretation of available information to define the individual parameter probabilities. From Eqs. (1) and (2), the following uncertain model terms are discussed and estimated below: anaerobic dechlorination rate constant (k_a), aerobic biodegradation rate constant (k_o), volatilization rate constant (k_{vol}), resuspension velocity (v_r), and the thickness of the contaminated sediment layer (ζ).

3.1. *The anaerobic dechlorination rate constant*

Laboratory research and field studies have shown that PCB molecules are dechlorinated by bacteria under anaerobic conditions. For example, Brown et al. (1987a); Brown et al. (1987b) evaluated chromatograms of upper Hudson River sediment in the anaerobic zone and found that the distribution of congener concentrations was inconsistent with Aroclor 1242. Assuming this Aroclor was the primary Aroclor discharged into the river, Brown et al. concluded that the discrepancy was due to dechlorination by anaerobic bacteria. The effect of the dechlorination, Brown et al. hypothesized, was to reduce the relative concentration of the more highly chlorinated congeners, and to increase the concentration of those which are less chlorinated. Laboratory evidence for dechlorination was reported by Quensen et al. (1990). In these experiments, the more highly chlorinated congeners of Aroclor 1242, 1248, 1254, and 1260 were dechlorinated, while most di- and tri-chlorinated congeners increased in concentration over the

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[1] This approach is suggested by the results of Lane and Borland (1954), Culbertson and Dawdy (1964), Colby (1964), and Andrews (1979), each of whom reported cycles of fill and scour and little net deposition or fill over the time period studied.

24 week incubation period. Similar results were reported by Abramowicz et al. (1993) in a study of Aroclor 1242, 1254, and 1260 in Hudson river sediments.

These investigations are useful in establishing the important factors which control the dechlorination process, and in quantifying changes in PCB concentration due to dechlorination over time. However, they do not propose detailed kinetic models of the process or provide process parameters. In the absence of this guidance from microbiology, a simple pseudo-first order reaction rate was chosen for this analysis. This is equivalent to assuming Michaelis–Menten enzyme kinetics when the substrate concentration is much less than K_m, the saturation constant. Descriptions of more complex kinetics which, for example, account for the loss of microbial enzyme activity or for the presence of growth and energy substrates, have not yet been developed for PCB dechlorination.

The probability density function for the rate constant k_a which characterizes the loss of mass due to the dechlorination process under the assumption of a first order reaction must be estimated from the available data. Laboratory studies were used to define this density function, since no naturally-occurring PCB dechlorination rates measured in actual rivers have been reported in the literature. Four published laboratory studies were reviewed, each simulating different environmental conditions. The anaerobic dechlorination rate constant was calculated from each study, and then adjusted to reflect the PCB congener combination believed to have been originally discharged into the Hudson River (38% Aroclor 1016 and 62% Aroclor 1242 (Bopp, 1979)). Table 1 shows the calculated half-lives.

Table 1
Rate constants computed from anaerobic laboratory experiments

Author	Rate constant (s^{-1})	Half-life (d)
Chen et al. (1988)	3.3×10^{-8}	243
Rhee et al. (1989)	3.2×10^{-8}	251
Quensen et al. (1990)	1.4×10^{-8}	573
Rhee et al. (1993)		
120 ppm	4.6×10^{-9}	1740
300 ppm	4.6×10^{-9}	1740
500 ppm	8.3×10^{-9}	966
800 ppm	4.0×10^{-9}	2000

The wide range of half-lives in Table 1 is difficult to reconcile. It emphasizes the need for a probability density function for the rate constant, since a modeler would clearly be uncertain if asked to choose a point estimate on the basis of these data. Some of the variability in the rates is surely due to the different conditions under which the experiments were conducted. Table 2 summarizes some of the important parameters of the experiments and their variability across experiments. Possibly important differences in parameters include the use of enriched versus unenriched bacteria, the amount of agitation the bacteria were subject to, the sediment origins, the gaseous environment maintained, the total PCB concentration, and the particular congener mix which the bacteria were dechlorinating. Table 2 also shows conditions which would be expected in the Hudson River.

The differences in environmental conditions shown in Table 2 lend uncertainty to the extrapolation of the laboratory data to the field. For some conditions, it is possible to guess what the impact of the difference on the rate is. For example, the 25°C temperature probably permits faster dechlorination rates than would be seen under the colder conditions that exist in the sediment during the winter.

The impacts of other differences are much harder to guess. Continuous stirring to simulate a continuously stirred reactor equalizes the concentration of PCB throughout the reactor, and allows uniform contact between the PCB-contaminated sediment and the bacteria, but does not simulate the heterogeneous concentrations which exist in the upper Hudson River. Use of enriched bacteria selects for those bacteria which are capable of degrading PCB, and therefore the population of PCB-degrading bacteria is probably higher in the laboratory experiments than in the Hudson River. Chen et al. (1988) showed the gaseous environment to be important, but it is not known what gases predominate in the sediment environment of the upper Hudson River.

Another important variable is the particular mix of congeners in the sediment. Experiments show that different congeners are degraded at very different rates. Rhee et al. (1993) showed that different starting concentrations of Aroclor 1242 underwent varying degrees of dechlorination during the same time period.

Table 2
Comparison of environmental conditions for anaerobic biodegradation

Environmental condition	Upper Hudson River	Chen et al. (1988)	Rhee et al. (1989)	Quensen et al. (1990)	Rhee et al. (1993)
Bacterial characteristics	naturally occurring	enriched bacteria	enriched bacteria	unenriched	unenriched
Temperature	0–30°C	25°C	25°C	25°C	room temperature
Sediment stability	disturbed during flood flows	stirred vigorously and continuously	not clear: treatment may include mechanical agitation	no agitation reported	no agitation reported
Geochemistry	naturally occurring	Hudson River sediments	Hudson River sediments	Hudson River sediments	Owasco Lake, NY sediments
Gaseous environment	not known	CO_2/H_2	N_2	N_2–CO_2	N_2
Total PCB concentration	0–1500 ppm	30 ppm	707 ppm	500 ppm	120–800 ppm
Congener mix	originally Aroclor 1242/1016; current conditions not known	naturally occurring	naturally occurring	Aroclor 1242	Aroclor 1242

A disturbing pattern in the data is the tendency for the degradation to become slower over time. One possible hypothesis is that below certain concentrations of congeners, very little degradation occurs. Thus, the rates calculated from the experiments may be relevant only for a narrow range of concentrations.

Using all the laboratory data and all the knowledge about differences in laboratory and field conditions, and recognizing the heterogeneity and nonstationarity of the field conditions, the following estimates are made:

1. 25% chance that the half-life is less than 1700 days;
2. 25% chance the half-life is between 1700 and 3000 days;
3. 50% chance the half-life is greater than 3000 days;

Let t_a denote the half-life in days for PCB in the sediment due to anaerobic dechlorination. A log–normal distribution for t_a approximately fitting the specifications above is: LN(4320, 4444^2). This distribution produces a 0.1% probability that t_a is less than 240 days and a 3.5% probability that t_a is less than 570 days. The corresponding distribution for the anaerobic first order rate constant k_a is log–normal with a mean of $0.00034/d$ and a variance of $1.34 \times 10^{-7}/d^2$. A plot of the probability density function for k_a appears in Fig. 1.

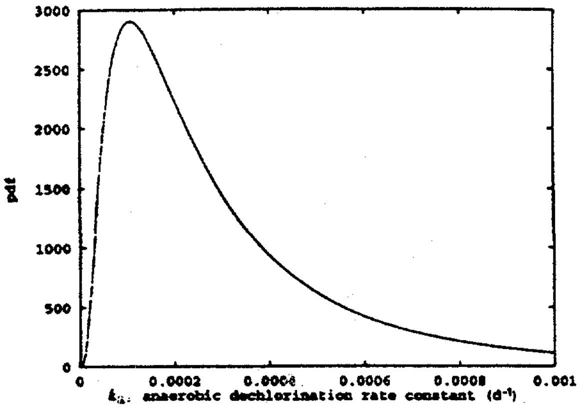

Fig. 1. Prior probability density function for the anaerobic dechlorination rate constant.

3.2. *Aerobic biodegradation rate constant*

Aerobic biodegradation of PCBs has been observed in the laboratory (Bedard et al., 1986; Bedard et al., 1987; Furukawa et al., 1978) and in situ under artificial stimulation in the upper Hudson River (Harkness et al., 1993). As is the case of dechlorination by anaerobes, no detailed kinetic model for the aerobic degradation of PCBs has been proposed. In the absence of such a model, we have chosen to use a simple pseudo-first order reaction to model the aerobic degradation of dissolved PCBs in the water column of the Hudson River.

The prior density for the rate constant is determined from laboratory data gathered by Furukawa et al. (1978), Bedard et al. (1986), and Bedard et al. (1987). In these experiments, aerobic bacteria extracted from aquatic sediments were used to degrade various mixtures of PCB congeners. As was the case for anaerobic dechlorination, the half-lives calculated from these experiments span more than one order of magnitude. Table 3 shows the calculated rate constants and half-lives after adjustment for the Aroclor 1016/1242 mixture of congeners. Some of the variability in the rate constants may be explained by the differing environmental conditions under which the experiments were performed. These are summarized in Table 4, which also shows the environmental conditions which are expected to predominate in the natural environment of the Hudson River.

The problems in extrapolating the laboratory aerobic biodegradation rate constant to the upper Hudson River are similar to those for extrapolating laboratory anaerobic biodegradation rates. Each of the differences in Table 4 adds uncertainty to the extrapolation. While for some conditions, it is possible to guess what the impact of the difference, for other conditions, there are not enough data to understand how the degradation rate will be effected.

Temperature: The 25°C temperature probably en-

Table 3
Rate constants computed from aerobic laboratory experiments

Author	Rate constant (s^{-1})	half-life (h)
Furukawa et al. (1978)		
Acinetobacter	3.2×10^{-4}	0.60
Alcaligenes	3.3×10^{-4}	0.58
Bedard et al. (1986)	8.4×10^{-6}	22.9
Bedard et al. (1987)	1.6×10^{-5}	12.0

courages biodegradation at a higher rate than would be found in the cooler waters of the river.

PCB concentration: In the work of Furukawa et al. (1978), the rate decreased as the experiment proceeded, implying that as the concentration of PCB decreases, the biodegradation rate may decrease. Hence the less concentrated PCB in the water column (0.1 ppb versus 10 to 20 ppm in the laboratory) may be subject to degradation at a much slower rate than that observed in the laboratory.

Bacterial strain and concentration: The experiments exposed PCB to enriched bacteria grown on biphenyl; the field contains many more species of bacteria and concentrations of the particular strains tested are likely to be much smaller than those created in the laboratory experiments. It is unlikely that the concentrations of PCB-degrading bacteria are as high in the water column as they were in the reactors.

Congener mix: The particular combination of congeners in the mix could effect the rate of biodegradation. Bedard et al. (1986) showed that 4,4′-dichlorobiphenyl had different degradation rates depending on the mixture of congeners it is found in. The mixture of congeners in the upper Hudson River is heterogeneous and probably non-stationary, implying that the aerobic biodegradation rate may be variable in time and space as well.

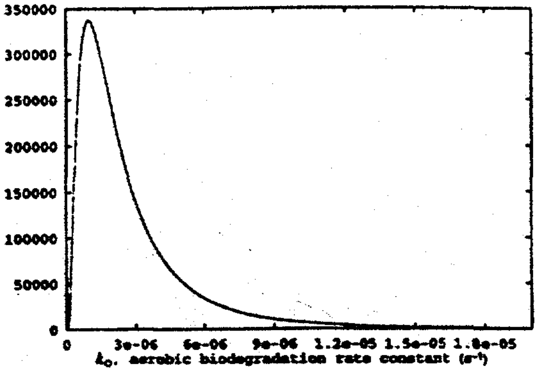

Fig. 2. Prior probability density function for the aerobic biodegradation rate constant.

Considering the smaller expected bacterial populations, cooler prevailing temperatures, and lower PCB concentrations in the upper Hudson River when compared to the laboratory environment, it is assumed that the half-lives shown in Table 4 are considerably shorter than the half-lives in the upper Hudson River. After weighing all the data, the large variability between the computed rate constants, and our knowledge of the two environments, the following estimates are made:

1. 95% chance that the half-life is greater than 24 h;
2. 50% chance that the half-life is less than 96 h.

A log-normal distribution for the half-life (in hours) approximately fitting these specifications is LN(136, 19140). This corresponds to a log–normal distribution for the aerobic biodegradation rate constant k_o with expectation 0.012 h^{-1} and variance 0.00011 h^{-2}. The probability density function for k_o is graphed in Fig. 2.

3.3. Volatilization rate constant

Using Whitman's two-film theory of volatilization, and assuming liquid film control (Mackay et al. (1983)), the volatilization rate may be modeled as

$$\frac{\partial c_a}{\partial t} = -\frac{K_l}{z} c_d = k_{vol} c_d \tag{3}$$

Table 4
Comparison of environmental conditions for aerobic biodegradation

Environmental condition	Upper Hudson River	Furukawa et al. (1978)	Bedard et al. (1986)	Bedard et al. (1987)
Bacterial species	not known	enriched *Alcaligenes* and *Acinetobacter*	enriched *Alcaligenes*	enriched *Alcaligenes*
Bacterial concentration	not known	*Alcaligenes*: 2.9×10^9 ml^{-1}; *Acinetobacter* 4.4×10^8 ml^{-1}	3.8×10^9 ml^{-1}	3.8×10^9 ml^{-1}
Temperature	0-30°C	not given	30°C	30°C
Total PCB concentration	0-10 ppb	10 ppm	20 ppm	10 ppm
Congener mix	originally 1242/1016; current condition not known	individual congeners	mixture of congeners	Aroclor 1242

Table 5
Distributions for volatilization parameters

Parameter	Distribution
Molecular weight, M (g/mol)	N(250, 918)
Velocity, u (m/s)	LN(1.5, 0.58)
Depth, z (m)	LN(3.7, 0.81)
Temperature, T (°C)	LN(10, 95)

where c_d is the dissolved contaminant concentration, z is the water column depth, and K_1, the liquid film transfer coefficient, can be approximated by

$$K_1 = \left(\frac{32}{M}\right)^{0.25} \frac{(D_L u)^{0.5}}{z^{0.5}} \tag{4}$$

where M is the molecular weight, D_L is the oxygen diffusivity, and u is the stream velocity (Mills et al., 1985; O'Connor and Dobbins, 1958).

Using the formulation in Eq. (4) and dividing by z, a prior density function for k_{vol} can be calculated. The first step is to create first and second moments for each of the parameters in the equation (Table 5) based on knowledge of the upper Hudson River environment and the molecular weight of congeners found in Aroclors 1016 and 1242. The exception is that for M, the molecular weight. In the case of M, the mean is so far removed from zero and the variance is so small, that the probability in the left tail at values of M less than zero is negligible.

The mean of the prior distribution for k_{vol} is found by solving Eq. (4) with the mean values of the parameters given in Table 5. The mean value thus calculated is 3.88×10^{-6} s^{-1}.

The variance of the prior distribution is found using first order error analysis:

$$V(k_{vol}) = \sum_{i=1}^{4} \sum_{j=1}^{4} \left(\frac{\partial k_{vol}}{\partial x_i}\right)\bigg|_m \left(\frac{\partial k_{vol}}{\partial x_j}\right)\bigg|_m \operatorname{cov}(x_i, x_j) \tag{5}$$

where $\mathbf{x} = [M, T, u \text{ and } z]$ and $|_m$ represents the partial derivative evaluated at the mean value of $\mathbf{x}$. Assuming a diagonal variance–covariance matrix for $\mathbf{x}$, Eq. (5) yields a variance of 3.24×10^{-11} s^{-2}.

The two moments are now used to parameterize a log–normal distribution for the volatilization rate constant:

$$k_{vol} \sim \mathrm{LN}(3.88 \times 10^{-6}\ \mathrm{s}^{-1}, 3.24 \times 10^{-11}\ \mathrm{s}^{-2}) \tag{6}$$

The probability density function for k_{vol} is plotted in Fig. 3.

3.4. Resuspension and sedimentation velocity

Sorbed PCBs are transported between the water column and the benthic sediment via resuspension and sedimentation. No field studies measuring the rates of these processes have been reported for the upper Hudson River. However, field studies have been conducted at other sites. The data from these studies are used to construct a prior distribution for the resuspension velocity in the upper Hudson River.

In the simulation model, the resuspension velocity represents the rate of sediment loss from the river bottom in units of L/T. For example, a resuspension rate of 1 m/yr means that resuspension is responsible for removing 1 m from the top of the sediment bed each year. Under the assumption of scour and fill equilibrium discussed above, this resuspended material is replaced with the same amount of sedimenting material, so the bed elevation at any point in space remains constant.

Colby (1964) recorded gross resuspension of four feet in the Colorado River over four months in the spring and summer, and two feet of gross resuspension in the same amount of time in the Elkhorn River in Nebraska. Both these rivers, however, had sediment concentrations one to two orders of magnitude higher than those observed during the spring and summer in the upper Hudson River.

Culbertson and Dawdy (1964) studied scour and fill in the Rio Grande River. During the spring

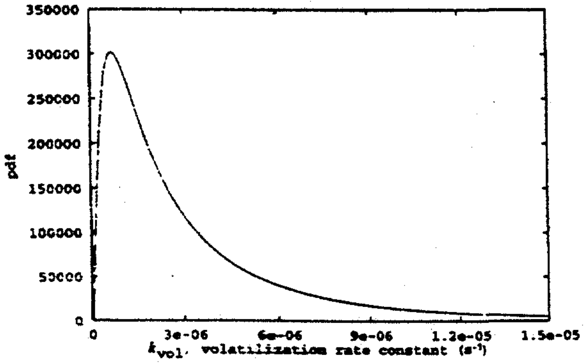

Fig. 3. Prior probability density function for the volatilization rate constant.

high-flow season, between zero and two feet of bed material was removed (and subsequently replaced by sedimentation) at the thirteen cross-sections studied. Once again, the suspended sediment concentrations recorded during this period were two orders of magnitude higher than those found in the upper Hudson River during the spring and summer.

The study of Andrews (1979) analyzed scour and fill data from the East Fork River in Wyoming. In the cross-sections Andrews studied the amount of scour recorded in each cross-section varied from three-quarters of a foot to two feet over a sixty-four day period in the spring. No suspended sediment data are given in the study.

Analyses of suspended sediment concentrations and correlations with flow have indicated that resuspension at Fort Edward does not occur until a flow of 283–340 m^3 is reached, and that resuspension at Waterford requires minimum flows of 538 m^3 (Zimmie, 1985). These flows are typically reached several times each year. With these data and the results of the studies by Colby, Culbertson and Dawdy, and Andrews, the prior distribution for the resuspension velocity in meters per year is defined as:

$$v_r \sim \mathrm{LN}(0.46\ \mathrm{m/yr}, 0.40\ \mathrm{m^2/yr^2}) \qquad (7)$$

This distribution is derived such that the conditions

$$P(v_r < 0.05\ \mathrm{m/yr}) = 0.05 \qquad P(v_r < 1\ \mathrm{m/yr}) = 0.90$$

are met. The probability density function for v_r is plotted in Fig. 4.

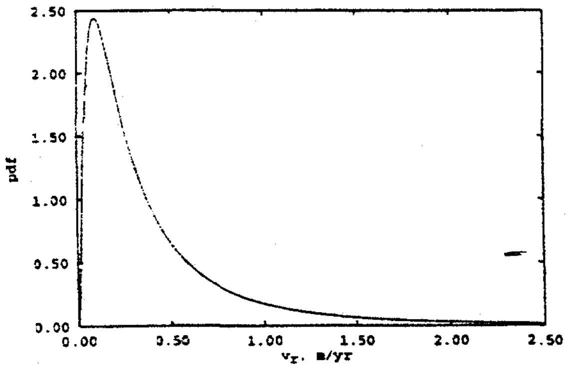

Fig. 4. Prior probability density function for the resuspension velocity.

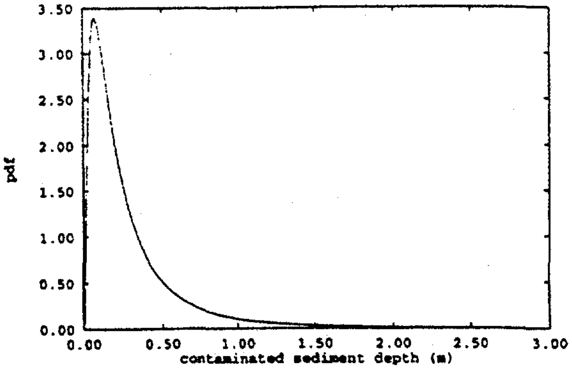

Fig. 5. Prior probability density function for the contaminated sediment depth.

3.5. Contaminated sediment depth

The contaminated sediment depth, ζ, is an artifact of the model specification. It enters the model in Eq. (2) as the depth over which the mass of PCB is averaged in order to convert PCB mass to PCB concentration. This value should reflect the depths used to calculate the initial condition PCB concentrations (PCB concentrations taken from cores drilled during 1976–1978), and those used to calculate the 'observed' PCB concentrations. These values are not the same for all the cores — they varied from 5 cm to 300 cm, depending on the depth of the core, and the depth to which PCB mass was detected. ζ also represents contaminated sediment depths for averaging of the mass at locations where no core samples were taken and where the depth of, or even the existence of, PCB is uncertain.

The uncertainty in the sediment depth is reflected in the chosen prior probability density function which assumes a 25% probability that it is less than 0.1 m and a 5% probability that the sediment depth is greater than 1 m. This distribution represents, in part, additional knowledge that cores were taken at location thought most likely to have high PCB concentrations. This implies that many locations would have contaminated sediment depths significantly less than those observed in the cores. A log–normal distribution with expectation 0.317 m and variance 0.167 m^2 fits the specifications above. The probability density function is plotted in Fig. 5.

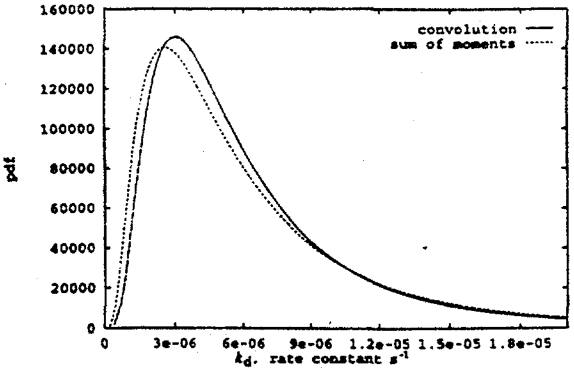

Fig. 6. Probability density functions for k_d calculated using convolution and the summation of moments.

3.6. *Combining the volatilization and aerobic biodegradation rate constants*

From Eq. (1) it is clear that the aerobic biodegradation rate constant and the volatilization rate individually will not be identifiable in the model. However, their *sum* is an identifiable quantity. The prior density function for the combined aerobic biodegradation rate constant and the volatilization rate constant is constructed from a log–normal distribution with expectation created by adding the expectations of the two rate constants and variance created by adding the two variances. The true distribution, given the two prior density functions, would be obtained by convoluting the density functions, but it was expected that the addition of moments would provide a nearly identical distribution. This assumption was checked by actually performing the convolution; the resulting two probability density functions are shown in Fig. 6 and are nearly coincident.

4. Discussion

There are formal, established methods (see Morgan and Henrion, 1990) for judgmental probability elicitation from experts; these methods are apt to be useful for uncertain model parameters in some cases. However, in this study we chose to assume a typical mechanistic modeling scenario in which scientific experts for each uncertain term are not readily available, so the modeler must rely on the existing literature for parameter estimates. Our observation of this exercise is that modelers tend to make quick, *ad hoc* choices. Indeed, there is often little discussion of parameter selection and little justification for choice in the literature on mechanistic surface water quality models. As the preceding section illustrates, the use of simple point estimates for parameter values may necessitate that the investigator ignores considerable amounts of conflicting data in an effort to limit parameter estimation to a single value.

A generally-held perspective is that most model parameters have physical meaning and thus can be measured directly. However, direct measurements of the quantities of interest are often unavailable, as was the case in the Hudson River study. Furthermore, this perspective assumes that the model equations represent truth. The preceding discussion illustrates, however, that at least two types of model-specification errors, aggregation error and assumptions of stationarity, may be unavoidable in model development. In these cases, where the equations are approximations to actual behavior, it is probably not reasonable to insert a measured parameter into a model without adjustment (tuning). Thus, despite modeler claims, the presence of so-called 'tuning' parameters in a model is apt to be a positive attribute, since tuning allows the modeler the opportunity to adjust for, or correct, the approximations or errors in the model equations.

Notwithstanding modeler bias against tuning parameters, there is general acknowledgment among modelers that lab-to-field differences and field-to-field differences are important in the extrapolation of scientific inferences. Ironically, these differences imply that adjustment, or tuning, is apt to be necessary when extrapolating to a field site of interest. If this is so, then how scientific knowledge is used to make this adjustment to point estimates and to uncertainties is an important modeling step and should be thoroughly documented.

For example, the differences in experimental conditions for anaerobic dechlorination studies identified in Table 2 are undoubtedly responsible for some of the variability in the half-lives presented in Table 1. This variability (in Table 1) is substantial, and it illustrates the need for scientific judgment in the interpretation and application of laboratory studies. Furthermore, extrapolation of these estimates to reflect natural environmental conditions is apt to involve additional uncertainty because relationships between environmental conditions and natural processes are complex and poorly understood. Explanation of the use of this limited scientific information for model parameter estimation should be part of model documentation and justification.

Other factors contribute to the difficulty in model parameterization, as identified in the examples that we discuss above. These factors include:

- nonstationarity and aggregation, which affected the estimate of the volatilization rate,
- extrapolation of information and analyses from other sites, which was instrumental in the determination of sedimentation/resuspension velocity,
- bias due to study design (location of sampling sites), which appeared to be important in the estimation of the contaminated sediment depth.

All of these factors are likely to increase uncertainty in the point estimates of parameters, and thus explanations relating each scientific analysis to the resulting parameter estimate should be provided to improve model applications. Beyond that, the inevitable problems with point estimates underscore the need to include uncertainty in the analysis.

5. Conclusions

Two primary conclusions result from our work, one concerned with a key weakness of current modeling approaches and the other concerned with a promising solution to this weakness. The parameterization difficulties that are the focus of this paper highlight a problem with many existing water quality models. Gaps in scientific understanding and limited data contribute to the fact that the predictions from large mechanistic water quality models are apt to be highly uncertain. As a consequence of this scientific uncertainty, management recommendations and scientific inferences based on these models may have relatively little scientific support. If decision makers are to have confidence in science-supported management, then better, more rigorous methods are needed to extract and combine information from scientific studies for simulation modeling.

A promising solution to this problem is to use Bayesian analysis for pooling information about model parameters and for expressing parameter uncertainty. As we demonstrate in this paper, Bayesian inference leads to probabilistic characterization of uncertainties, both data-based and judgmental. In a full Bayesian analysis (see Steinberg et al., 1996), these probabilities are combined and a complete expression of uncertainty results. While there are difficulties that remain to be resolved (as discussed above and in Steinberg et al., 1996), Bayes' theorem still appears to offer the best chance for a logical, rigorous analysis that characterizes the uncertainty in water quality models when these models must be parameterized with limited information obtained or extrapolated from several sources.

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