TIME VARIABLE MODEL OF THE FATE OF DDE AND LINDANE IN A QUARRY

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Abstract — A time variable model has been used to analyze a field scale experiment in which a flooded limestone quarry was dosed with equal quantities of Lindane and DDE. The water column and sediment chemical concentrations were monitored for one year after the initial dosing. The markedly different physical-chemical characteristics of the test chemicals provided an interesting contrast for model application.

A simplified time variable model of partitioning chemicals is cast in the form of analytical solutions for the total, dissolved and particulate concentrations of chemical in completely mixed, interactive, water column and sediment compartments. The model formulation incorporates chemical decay and transport mechanisms of particulate and diffusive exchange between water column and sediment. The Lindane and DDE model calibrations based on data from the first year after dosing are presented. A preliminary verification of the model, obtained by projecting DDE levels in the water and sediment five years after initial dosing, when the quarry was revisited, is also shown. The model results underscore the significance of chemical partitioning on chemical fate and highlight the importance and utility of a modeling framework which incorporates realistic mechanisms of water column and sediment interaction.

Keywords — Partitioning Fate Calibration Lindane DDE

INTRODUCTION

The evaluation of the fate of chemicals in the environment requires the use of a modeling framework which incorporates various idealizations of the transport and reaction mechanisms that are thought to be important. The validity of such models can only be established by careful calibrations and verifications using field data sets. A number of applications of this type have been reported [1] which illustrate to various degrees that realistic simulations of observed chemical behavior are possible. However, rigorous tests are not yet available. The major problems are the lack of reliable estimates of chemical mass discharge rates and independent measurements of transport and reaction rates. Controlled field scale experiments provide a useful source of these data. The purpose of this paper is to present an analysis of such an experiment.

An abandoned, flooded limestone quarry provided the setting for the field scale experiment which is the basis of the investigation described herein [2]. The time history of
Spike releases of DDE and Lindane were monitored in the biotic and abiotic sectors of the quarry water column and sediment for a period of approximately one year after the initial release. The experiment was performed under relatively controlled environmental conditions which were not subject to complicating factors such as a variable inflow, outflow, or loading history. The time variable nature of the experiment was a desirable feature since it enhances the importance of certain model parameters which are of lesser significance in steady state situations.

CHRONOLOGICAL REVIEW AND DATA PRESENTATION

The quarry experiment was initiated during May of 1972. Pre-dosing levels of DDE and Lindane were measured and found to be negligible. A known mass of each chemical was uniformly distributed over the surface of the quarry on June 27, 1972 and on the following day, samples were collected for analysis of post release initial conditions in the water column, sediment and biota. Subsequent samples were collected on Days 5, 10, 21, 42 and at progressively longer time intervals over the course of the next year. The water column and sediment were usually sampled at various depths.

An intense rainfall occurred on the day after chemical addition, resulting in a significant influx of particles to the epilimnion of the thermally stratified quarry. Sedimentation trap data indicated that 2920 kg of solids entered the quarry and settled from the water between days 0 to 21. As will be shown, settling of these particles had a significant effect on the fate of both DDE and Lindane, chemicals with markedly different adsorptive characteristics.

As shown on Figure 1, the chronological plot of water column DDE concentration, the initial input of 2.77 g of DDE resulted in a depth averaged concentration on Day 1 of about 44 ng/L. This concentration was reduced to less than 10 ng/L by Day 10 and then gradually decreased to 1 ng/L by Day 100. A DDE concentration of about 1 ng/L persisted for the duration of the monitoring effort, although an increase to 3 ng/L was reported on Day 360, at the termination of the monitoring program.

The lower graphs in Figure 1 illustrate vertical profiles of DDE in the water column on selected days. Some vertical stratification is exhibited on Day 1, with average concentrations of 50 ng/L to a depth of 9 m and 10 to 20 ng/L at depths of 12 and 15 m. Although the fall overturn did not occur until Day 144, a relatively homogenous vertical concentration profile was established by Day 21, and persisted for the duration of the study.

Sediment DDE data for the upper 1.5 cm of bottom sediment (µg DDE/kg wet sediment) are summarized in the upper panel of Figure 2. The sediment DDE concentration on Day 1 was quite low, but increased sharply to about 20 µg/kg by Day 5 and this concentration persisted for about 50 days. Although the results are variable, the average concentration increased to about 30 µg/kg for the next three sampling dates and then decreased to about 20 µg/kg on Day 241, the final day for which sediment data are available. As shown in the lower graphs, sediment samples from depths of 0 to 1.5, 1.5 to 3.5 and 3.5 to 5.5 cm showed that DDE penetration was for the most part limited to the upper 1.5 cm sediment layer.

Several distinctly different characteristics were observed in the temporal distributions of water column and sediment Lindane concentrations, (Figures 3 and 4). Significantly higher water column concentrations of Lindane were observed throughout the study, with the minimum concentration approaching 10 ng/L, an order of magnitude higher than the corresponding DDE concentration, at the end of the study. The wide ranges in the water column concentrations preceding the fall overturn (Day 144) reflect the vertical gradient of chemical between the epilimnion and hypolimnion of the stratified water body. The ranges are reduced after Day 144, when the water body was mixed by the fall overturn.

The vertical gradient of Lindane in the water column is more clearly illustrated in the four lower graphs of Figure 3. The concentration near the surface on Day 1 was more than 300 ng/L, while at a depth of 15 m it was less than 10 ng/L. Vertical profiles on Days 21 and 81 also exhibited order of magnitude differences between the upper and lower layer average Lindane concentrations, in contrast to the DDE profiles which were nearly uniform at these same times. On Day 173, however, which followed the fall overturn, the physical mixing of the water body established a uniform vertical concentration profile in the water column.

Sediment Lindane data are shown in Fig-

Fig. 1. Temporal variation of DDE in water.
ure 4. With the exception of a sediment concentration of 7 μg/kg on Day 1, the sediment Lindane concentration averaged 1 to 2 μg/kg, an order of magnitude lower than sediment DDE levels. Lindane penetrated to the deeper sediment layer of 3.5 to 5.5 cm, and did not exhibit a pronounced vertical gradient. This is in contrast to the DDE results which were an order of magnitude higher in the surface layer, but at generally negligible levels at sediment depths greater than 1.5 cm.

Estimates of the mass of both DDE and Lindane associated with the water column, sediment, quarry walls, water surface film, fish, microcrustaceans and plankton were made [2]. Essentially, all of the chemical which was recovered was in the water column and sediment and only a relatively small fraction was associated with the remaining compartments, which can, therefore, be neglected in the analysis of the fate of Lindane and DDE.

DESCRIPTION OF MODELING FRAMEWORK

The principal features of the modeling framework [3] are illustrated in Figure 5. An instantaneous release of chemical, M₁, is discharged to a completely mixed receiving water of volume V, and depth H, where it undergoes dilution by the freshwater inflow, Q. The chemical is partitioned between the dissolved and particulate phases in the water column and sediment which have suspended solids concentrations of m₁.
and $m_2$, respectively. Chemical is transferred between the water column and sediment layer by settling and resuspension of contaminated particles and via diffusive exchange between the dissolved phases in the water and sediment. The chemical may also undergo first order decay in the water column and sediment or it may be removed from the system by sedimentation.

The solution for an instantaneous release of chemical of mass $M_T$ is required. The initial water column concentration is simply $c_{W0}(t) = M_T/V_0$. The analytical solution for the time variable water column and sediment concentrations can be readily obtained [4]. The notation and general solutions (Eqsns. 1–8) are listed in Tables 1 and 2. Equations 2A and 2B may be evaluated in time to obtain the total chemical concentrations in the water and sediment, $c_{W}(t)$ and $c_{S}(t)$, which result from initial conditions in the water column and sediment.

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**Table 1. Definitions**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Water Column</th>
<th>Sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical/Biological</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Loading (g)</td>
<td>$M_T$</td>
<td>$K_2$</td>
</tr>
<tr>
<td>Sum of hydrolysis, oxidation, biodegradation, photolysis, volatilization rates (d)$^{-1}$</td>
<td>$K_1$</td>
<td></td>
</tr>
<tr>
<td>Partition coefficients (L/kg)</td>
<td>$r_1$</td>
<td>$r_2$</td>
</tr>
<tr>
<td>Physical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solids Concentration (mg/L)</td>
<td>$m_1$</td>
<td>$m_2$</td>
</tr>
<tr>
<td>Depth (m)</td>
<td>$H_1$</td>
<td>$H_2$</td>
</tr>
<tr>
<td>Volume (m$^3$)</td>
<td>$V_1$</td>
<td>$V_2$</td>
</tr>
<tr>
<td>Flow Rate (m$^3$/d)</td>
<td>$Q_1$</td>
<td>$Q_2$</td>
</tr>
<tr>
<td>Detention Time (d)</td>
<td>$t_{det} = V_1/Q_1$</td>
<td></td>
</tr>
<tr>
<td>Settling Velocity (m/d)</td>
<td>$w_s$</td>
<td>$w_s$</td>
</tr>
<tr>
<td>Resuspension Velocity (m/d)</td>
<td>$w_r$</td>
<td>$w_r$</td>
</tr>
<tr>
<td>Diffusion Exchange Coefficient (cm$^2$/d)</td>
<td>$K_L$</td>
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<tr>
<td>Sedimentation Velocity (mm/yr)</td>
<td>$K_s = w_s/H_2$</td>
<td></td>
</tr>
<tr>
<td>Sedimentation Rate Coefficient, (d$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentrations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total = Dissolved + Particulate (µg/L)</td>
<td>$c_{W} = c_W + c_S$</td>
<td>$c_{S} = c_W + c_S$</td>
</tr>
<tr>
<td>Particulate chemical ratio (µg chemical/g solids)</td>
<td>$r_1 = c_S/m_1$</td>
<td>$r_2 = c_S/m_2$</td>
</tr>
<tr>
<td>Chemical Phase Fractions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particulate: $f_1 = \frac{\text{mm/µg}}{1 + \text{mm/µg}}$</td>
<td>$f_1$</td>
<td>$f_2$</td>
</tr>
<tr>
<td>Dissolved: $f_2 = \frac{\text{µg/µg}}{1 + \text{µg/µg}}$</td>
<td>$f_3$</td>
<td>$f_3$</td>
</tr>
</tbody>
</table>

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**Fig. 5.** Schematic of model framework.
The differential equations which control the water column and sediment response are:

**Water Column**

\[
\frac{dc_1}{dt} = -K_1 c_1 - \frac{c_2}{n} - \frac{c_3}{n_3} + \frac{c_4}{n_4} + \frac{c_5}{n_5} - \frac{W_c}{n} c_1 + \frac{W_t}{n} c_T + \frac{W_s}{n} \tag{1A}
\]

\[
\frac{dc_2}{dt} = -K_2 c_2 + \frac{c_1}{n_1} - \frac{c_3}{n_3} + \frac{c_4}{n_4} + \frac{c_5}{n_5} - \frac{W_c}{n} c_2 + \frac{W_t}{n} c_T - \frac{W_s}{n} c_T \tag{1B}
\]

The analytical solutions are given by

**Water Column**

\[
c_1(t) = c_1(0) \left[ \frac{e^{-K t}}{1 - e^{-K t}} \right] + c_2(0) \frac{e^{-K_T t}}{1 + K_T t} \tag{2A}
\]

\[
c_2(t) = c_2(0) \left[ \frac{e^{-K_T t}}{1 + K_T t} \right] + c_1(0) \frac{e^{-K t}}{1 - e^{-K t}} \tag{2B}
\]

where \(c_1(0)\) and \(c_2(0)\) are evaluated using the positive and negative terms respectively of the following expression:

\[
\frac{c_2}{n} = \frac{c_1}{n} \left[ 1 \pm \left( 1 - 4s_1(K_1 + 1/t_1) + (K_1 + K_2 + K_3) \right) \right] \frac{t_2}{t_1} \tag{3}
\]

Here,

\[
s_1 = \frac{c_1}{n} + \frac{c_2}{n_2} \tag{4}
\]

\[
s_2 = \frac{c_2}{n} + \left[ \left( c_1 + c_2 \right)/n_2 \right] \tag{5}
\]

\[
s_3 = s_1 + s_2 \tag{6}
\]

and \(s_4 = s_1 + 1/t_1\). The sediment capacity factor is given by

\[
\beta = \frac{m_1}{m_2} \frac{f_2}{f_1} \tag{7}
\]

As shown elsewhere \(4\) the ratio of the steady state particulate chemical concentrations in the sediment and water, \(s/\beta t_1\), may be expressed as:

\[
\frac{s_2}{s_1} = \frac{w_0 (m_2/\beta t_1) f_2 + \beta (s_1/\beta t_1) f_1}{w_0 + m_2 + \beta (s_1/\beta t_1) f_1 + \beta (s_1/\beta t_1) f_2} \tag{8}
\]

Approximate forms for the roots of the quadratic Equation 3 have been found \(4\) and these greatly simplify the solution:

\[
c_1(t) = c_1(0) \left[ \frac{s_1 e^{-K t}}{s_1 + s_2} + \frac{s_2 e^{-K_T t}}{s_1 + s_2} \right] \tag{11}
\]

\[
+ c_2(0) \frac{e^{-K_T t}}{1 + K_T t} \tag{12}
\]

\[
c_2(t) = c_2(0) \left[ \frac{s_1 e^{-K t}}{s_1 + s_2} + \frac{s_2 e^{-K_T t}}{s_1 + s_2} \right] \tag{13}
\]

\[
+ c_1(0) \frac{e^{-K t}}{1 - e^{-K t}} \tag{14}
\]

where \(K_T = K_1 + \beta (s_2/t_1) (K_2 + K_3)\). The detention time of the quarry is very long and \(s_1 = s_2\). Using these approximate roots, the solutions become:

Two important features of general interest can be seen in these simplifications. The concentrations are determined by two terms: \(s_1\), which is the sum of the water column decay and sediment transfer fluxes; and \(s_2\), which is the analogous sum of sediment decay and water transfer fluxes. The "fast" decay rate, \(s_1\), is simply the sum of \(s_1\) and \(s_2\) and represents the rate at which water column and sediment concentrations initially equilibrate. The "slow" decay rate, \(s_2\), is a fraction \((s_2/s_1 + s_2)\) of the total equivalent removal rate, \(K_T\), which is the parameter that controls the steady state water column concentration, \(c_1(\infty)\), if the mass input rate were constant, \(W_T\). That is:

\[
c_1(\infty) = (W_T/Q)(1 + K_T t_1) \tag{15}
\]

Thus, a straightforward calculation of \(s_2\) gives immediately the half life \((= 0.693/s_2)\) to be expected as a function of the relevant physical and chemical properties.

**MODEL PARAMETERS**

Based on a review of long-term climatological records, it was found that the difference between average annual precipitation \((-100\ \text{cm/yr})\) and evaporation \((-85\ \text{cm/yr})\) in the vicinity of the quarry, 15 cm, is insignificant in comparison to the overall depth of water in the quarry \((H_1 = 13.9\ \text{m})\). It is, therefore, reasonable to assume constant geometry and no net inflow. The quarry itself was represented as a completely mixed water column and sediment layer. The depth of the active sediment layer is estimated from observed chemical penetration into the sediment. DDE was observed to penetrate, at most, the upper 1.5 cm of sediment while Lindane penetrated to a depth of at least 5.5 cm (Figs. 2 and 4). Thus, chemical specific sediment layer depths of \(H_2 = 1.5\ \text{cm}\) and \(5.5\ \text{cm}\) were used to characterize DDE and Lindane respectively. The use of different sediment layer depths is necessitated by the simplified representation of diffusive exchange and the assumption of a completely mixed sediment layer incorporated in the modeling framework.

The mass loadings of interest are the chemical and solids flux rates to the quarry. The chemical inputs of DDE and Lindane were accurately measured. Sedimentation trap data was used to estimate the mass of sediment which entered the quarry between Days 0 and 21. The analysis of particulate transport in the quarry is complicated by the lack of field measurements of the suspended solids concentrations in the water column and sediment, \(m_1\) and \(m_2\), respectively. Sediment trap and secochi depth data were used as the basis for characterizing the temporal variation of \(m_1\). Empirical correlations with secochi depth measurements indicated that pre-rainstorm suspended solids levels were about 5 mg/L. Assuming the added material settled out of the water between days 0 to 10, from the temporal variation of the DDE water column data, the settling rate \(w_s\) and average suspended solids concentration, \(m_1\), are fixed by the measured solids flux.

The Secchi disc readings after the initial period were generally 6 to 7 m, and aside from some initial variability which was attributed to algal effects \(2\) the readings were essentially constant in time. There were no other sources of solids to the quarry and since resuspension was probably negligible, \(w_s\) was likely to have been much lower than the 3.2 m/d estimated for the first 10 d. In view of these considerations, \(w_s = 0.1\ \text{m/d} \) was assigned for \(t > 10\ \text{d}\). This settling velocity essentially eliminates particulate transport as a mechanism of chemical transfer after Day 10. The use of a variable settling velocity is considered reasonable since it is likely that relatively coarse particles entered the quarry as a result of the intense storm on Day 1, and these would settle rapidly. The remaining particles are either settling much more slowly or not at all.

The sediment solids concentration is also required to perform the analysis. From reported water volumes in sediment samples the sediment porosity is estimated to be \(\phi = 0.45\), and from the reported bulk density of the sediment \(\rho_0 = 1.2\ \text{g/cm}^3\), \(m_2 = \rho_0 - \phi \rho_0 = 750\ \text{g/L}\). The sedimentation velocity, \(w_s\), was set to zero because the net chemical
transfer to the deep, inactive sediment was not considered as a loss of chemical from the system.

**CHEMICAL TRANSFERS AND KINETICS**

Limited data were available to characterize DDE and Lindane partition coefficients. Estimates of the DDE partition coefficient were based on the partition coefficient for DDT due to the similarity of the octanol/water partition coefficients [5]. At solids concentrations on the order of 10 mg/L, as in the quarry, available DDT data [6], shown in the upper panel of Figure 6, indicate a range of 50,000 L/kg on illite clay to 275,000 L/kg on montmorillonite clay. Figure 6 also illustrates the inverse relationship between partition coefficient, \( \pi \), and suspended solids concentration. It is expected that this trend would also apply to the quarry, although the slope may be different as a result of differences in the characteristics of the solids.

The lower panel of Figure 6 shows Lindane isotherm data obtained using water and solids from the quarry [7], and an average partition coefficient of \( \pi = 250 \) L/kg provides a good fit of these data. Suspended solids concentration dependent partitioning has also been observed with Lindane (upper panel). From the limited available data, however, it is difficult to estimate \( \tau_2 \) for either chemical at the estimated sediment solids concentration in the quarry of \( m_1 = 750 \) g/L. Thus, \( \tau_2 \) is not well defined and should be viewed as a calibration parameter.

**Diffusive exchange**

The diffusive exchange coefficient, \( K_{L} \), was estimated to be 50 cm/d from microcosm experiments performed with Lindane [8]. Since DDE and Lindane have comparable molecular weights (352 and 291, respectively), a value of \( K_{L} = 50 \) cm/d has been used for both compounds. This parameter should also be viewed as a calibrated value since no direct measurement is available for the quarry.

**Chemical decay**

DDE and Lindane decay rates used in the modeling analysis are summarized in Table 3. The most significant decay rate for Lindane, hydrolysis, was estimated from laboratory experiments [7] to range from .0018 to .0257/d. A rate at the lower end of this range (.0025/d) was needed to fit the field data. Information on photolysis and volatilization [7] suggested that losses of Lindane by these mechanisms occurred at an order of magnitude lower rate than hydrolysis.

The only significant loss rates for DDE were found to be photolysis and volatilization. An average annual photolysis rate of .013/d was estimated following the approach of Zepp [9]. A somewhat higher volatilization rate of .020/d was estimated from laboratory results [10]. The total water column decay rate for DDE of .033/d is thus an order of magnitude higher than the Lindane decay rate, suggesting that Lindane would be the more persistent chemical.

**MODEL CALIBRATION — LINDANE**

Physical and chemical parameters for Lindane and DDE were estimated in previous sections. It remains to compare the computed results and observed data and establish final values for calibration parameters. The difference in solids behavior during the first 10 d following the storm (the initial period) and subsequently (the second period) requires that the analysis be done in two steps. The procedure is to calculate the chemical concentrations in the water column and sediment for the first 10 d using the appropriate initial period parameter values. Then, using the calculated water column and sediment concentrations at Day 10 as initial conditions, continue the calculation using the parameters that are appropriate for the second period. These parameters are listed in Table 4.

The calculated and observed Lindane distributions are shown in Figure 7 using linear and logarithmic concentration scales for the water column. The predicted initial rapid decrease of Lindane is somewhat overestimated. This is due to the stratified conditions in the quarry during the initial 100 days (see Fig. 3) which prevented the Lindane from being vertically well-mixed, as is assumed in the model. This discrepancy is also apparent in the sediment calculation. After vertical mixing, however, the comparison is satisfactory.

A better understanding of the behavior of Lindane in the quarry can be obtained by considering the form of the simplified analytical solutions, Equations 11 and 12, and the relative magnitudes of the parameters affecting chemical fate. As can be seen in...
Table 3. Summary of DDE and Lindane decay coefficients (L/d)

<table>
<thead>
<tr>
<th></th>
<th>DDE</th>
<th>Lindane</th>
<th>Water</th>
<th>Sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis</td>
<td>.0018-.0257</td>
<td>.0018-.0257</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Oxidation</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Biodegradation</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Photolysis</td>
<td>.0026</td>
<td>—</td>
<td>.013</td>
<td>—</td>
</tr>
<tr>
<td>Volatilization</td>
<td>.0018</td>
<td>—</td>
<td>.020</td>
<td>—</td>
</tr>
</tbody>
</table>

*Used .0025/d for calibration and projections

Table 4, the differing water column solids concentrations (m = 24 mg/L → 5 mg/L) and settling velocities (w = 3.2 m/d → 0.1 m/d) have only a small effect on the relevant rates that control the chemical fate of Lindane. This is due to the relatively low partition coefficient of Lindane, which at these solids concentrations, results in most of the Lindane being the dissolved fraction in the water column (f_d = 0.9940 → 0.9988). Thus particle transport is small relative to diffusive exchange as the mechanism which transfers Lindane from the water column to the sediment.

The total water column transfer-decay rate, s_1, is dominated by the diffusive exchange rate: K_{f_d}/H_1 as is the total sediment transfer decay rate, s_2 = K_{f_d}/H_2. As can be seen from the form of the solution for the water column Lindane concentration, c_{1w}, these rates control the relative amount of Lindane which is initially transferred to the sediment via diffusive exchange (s_1/s_1 + s_2 = 27%) and that which remains in the water column (s_2/s_1 + s_2 = 73%). These determine the rate at which the initial transfer takes place: s_1 = s_1 + s_2 = 0.15/d, and together with the total apparent removal rate, K_{f_1}, the slow overall loss rate: s_2 = (s_1/s_1 + s_2)K_{f_1} = 0.0029/d. The contribution of sediment decay, K_2, is small relative to water column decay even though they are both nearly equal (K_1 = 0.0029/d; K_2 = 0.0025/d). The reason is that β_{f_1} is small due to the relatively low partition coefficient for Lindane.

Model Calibration - DDE

Differences in particulate transport between the initial ten days of rapid solids deposition and the subsequent period are important in determining the fate of DDE in

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*Parameter values for t < 10 days/t ≥ 10 days, when two values are shown.
the quarry. The physical and chemical parameters for both periods are shown in Table 4, and a comparison of calculated and observed DDE distributions is presented in Figure 8. The calculated water column DDE concentrations in the two upper graphs of Figure 8 are in very good agreement with the data. During the first 10 days of the experiment the calculated and observed water column concentration decreased from about 53 ng/L to less than 10 ng/L, while the total sediment concentration of DDE increased sharply to more than 25 µg/L. The rapid decrease in the water column DDE and the corresponding increase in the sediment DDE is due to adsorption of DDE onto the water column solids which settle to the sediment. After Day 10, there is a much more gradual decrease in the water column DDE concentration, since the net flux of solids to the sediment is essentially zero.

The calculated sediment DDE concentration reaches a maximum of 34.5 µg/L by approximately Day 40, at which time a local equilibrium condition between the water column and sediment concentrations is approached. After Day 100, the calculated water column concentration of 1.3 ng/L decreases slowly, while the sediment concentration of slightly more than 30 µg/L decreases at a rate which is in proportion to the water column concentration. All removal of DDE occurs in the water column as a result of photolysis and volatilization. As the water column concentration decreases, DDE diffuses from the sediment interstitial water into the overlying water (the resuspension rate is zero), and the sediment concentration decreases. As long as there is water column decay, equilibrium conditions between dissolved concentrations in the water column and sediment layer interstitial water cannot be established and the decrease of water and sediment concentrations will continue until the DDE is depleted from the system.

It is of interest to further consider the computed total and dissolved DDE concentrations, both shown in the linear scale water column comparisons of Figure 8. The reported total DDE concentrations were actually measured after a glass wool filtration, which probably removed a significant portion of the adsorbed particulate DDE. Mass budget calculations [2] indicated an apparent loss of total DDE mass during this time period. The model computations suggest that the missing DDE was associated with the water column particles removed by the filtration.

Additional insight into the fate of DDE can be obtained by considering the analytical solutions and the magnitudes of the parameters affecting chemical fate. For the initial period, the total water column transfer-decay rate, $s_1$, is dominated by the solids settling velocity term. In contrast to the Lindane situation, the water column partition coefficient of DDE is large enough ($\tau_1 = 50,000$ L/kg) to make the particulate fraction significant ($f_p = 0.545$) and removal by settling dominates over water column decay and diffusive exchange. By contrast, the total sediment transfer-decay rate, $s_2$, is controlled by the diffusive exchange rate, $K_d f_p/H_2 = 0.002$/d which is substantially less than that for Lindane (0.107/d) due to the higher sediment partition coefficient of DDE. As a consequence, the initial rapid depletion of water column DDE and the corresponding sediment increase is entirely controlled by the fast decay rate:

$$g_1 = s_1 + s_2 = w f_p/H_1$$

This fact is reflected in the choice of $t = 10$ days as the dividing point between the two periods. At the end of 10 d the sediment has increased in concentration to $c_T = 32.6$ µg/L which is a tenfold greater concentration than that achieved by Lindane in the same time period. The difference is due to the markedly different mechanisms which transferred each chemical to the sediment: whereas diffusive exchange dominated Lindane transport, particle settling dominated DDE transport.

During the second period, the total water column transfer-decay rate, $s_1$, is dominated by diffusive exchange and water column decay as a result of reduced particle settling. The total sediment transfer-decay rate, $s_2$, is the same as during the initial period. As a result, the ratio controlling the slow decay rate, $s_2 b_1 + s_2$, increases markedly, as does the slow decay rate, $g_2$. The half life of DDE decreases almost threefold as a result of the decrease in settling velocity, since decay occurs only in the water column and settling provides a mechanism whereby DDE is transferred to the sediment.

The behavior of the water column concentration after the initial period can be viewed as the sum of the DDE responses due to the DDE in the water column and...
that in the sediment at \( t = 10 \, \text{d} \) \((t' = 0)\). The formula that results is:

\[
\phi_t(t) = 8.93 \left( 0.968 \, e^{-t/6} + 0.032 \, e^{-t/20} \right) + 1.12 \left( e^{-t/24} - e^{-t/6} \right)
\]

where the first line is the water column concentration due to the initial condition in the water column, and the second line is the contribution due to the sediment initial condition. Note that a significant contribution to the early response \((t' \sim 3/\phi_1 = 47 \, \text{d})\) is due to the initial condition in the water column. Thereafter, however, its importance diminishes and its contribution to the response is negligible. By contrast, the DDE initially in the sediment then controls the response, and the water column concentration is determined by the \( g_1 \) decay term. Both water column and sediment concentration are decaying with a half-life of about 700 d.

The importance of the various parameters can be understood as follows. The long term fate of DDE is controlled by the initial quantity deposited in the sediment during the first 10 d, which in turn is controlled by the rapid decay rate, \( g_1 = w_{DDE}/\text{H}_A \). Hence, the settling velocity, water column partition coefficient and solids concentration is each important. The long term decay is determined by the slow rate:

\[
g_2 = \frac{g_2}{g_1 + g_2} \, K_T
\]

The ratio of the transfer-decay rates during the second period is dominated by the terms:

\[
\frac{g_2}{g_1 + g_2} = \frac{K_T \, f_{DDE}/\text{H}_A}{K_1 + K_T \, f_{DDE}/\text{H}_A} = 0.002
\]

The rate of diffusive exchange is of primary importance since it is this mechanism that is transferring DDE from the sediment to the water column, where it is subject to decay. Hence the diffusive exchange rate and the sediment parameters \( m_2 \) and \( n_2 \) which affect \( f_{DDE} \) are both important. Finally, the water column decay rates for photolysis and volatilization are, of course, critical since they sum to form \( K_T \) which is the second factor in the slow rate expression, Equation [16].

Figure 9 compares the calculated masses of Lindane and DDE in the water column and sediment during the calibration period. On Day 100, 2.07 grams (75%) of the initial 2.77 grams of Lindane can be accounted for in the water column and sediment layer of the quarry. Of this amount, more than 75% is present in the water column. Similarly, 1.93 grams (70%) of the initial input of DDE also remains on Day 100. This is somewhat surprising, in view of the order of magnitude higher water column decay rate of DDE relative to Lindane. The persistence of DDE is directly related to the relatively high percentage of that chemical stored in the sediment and hence not available for photolysis or volatilization. The model calculations show that more than 96% of the remaining 1.93 grams of DDE in the system at Day 100 is in the sediment layer.

**MODEL VERIFICATION AND PROJECTIONS**

Approximately five years after the initial dosing of the quarry, on June 21, 1977, several sediment samples were collected and analyzed for DDE (R. G. Zepp, personal communication). Although this follow-up sampling and analysis was of limited scope, it provides a basis for a preliminary verification of the model.

Two methods were used for sampling; in each case the depth of sample was only known to within a rough approximation. The reported DDE concentrations on a solids mass basis were converted to volumetric concentrations and adjusted to concentration ranges which reflect the uncertainty in sampling depth and which correspond to an assumed depth of DDE penetration of 1.5 cm. These DDE concentration ranges, 3.4 to 11.2 \( \mu \text{g/L} \) for Sample A and 2.9 to 4.2 \( \mu \text{g/L} \) for Sample B, represent almost an order of magnitude decrease in the sediment DDE concentration since the time of the quarry experiment. The DDE level in water column samples collected at the same time as the sediment samples was less than the detection limit (30 \( \mu \text{g/L} \)) of the analytical technique which was employed.

Model projections for DDE and Lindane are shown in Figure 10. These projections are simply a continuation of the previously presented model calibration with kinetic and transport parameters held constant in time after Day 10. The initial rapid decrease of DDE in the water column during the first year is followed by an exponential rate of decrease over the next 11 years. The sediment concentration time history parallels the water column profile, and at the time of the June 1977 sampling, the calculated sediment concentration is 5.6 \( \mu \text{g/L} \). Considering the simplifying assumptions in the modeling framework, the uncertainty associated with many of the parameter estimates, and the precision of the data, the calculated and observed concentrations at \( t = 5 \) years are considered to be in excellent agreement. The fact that the calculated and observed water column concentrations are less than the detection limit gives further credence to the modeling analysis. The model results also indicate the projected DDE levels in the quarry sediment 10 years after the original dosing, in June 1982, were approximately 1 \( \mu \text{g/L} \).

Lindane concentrations were not measured at the time of the 1977 sampling. The model projections indicate that the Lindane concentration in the water was eventually reduced to the same concentration as DDE.
after about five years, while the sediment Lindane concentration was two to three orders of magnitude lower than the sediment DDE concentration at that time. The estimated mass of Lindane remaining in the quarry of 0.014 grams is less than 5% of the mass of DDE in the system at that time (0.330 grams), even though the estimated water column decay rates for DDE were an order of magnitude higher than the decay rates for Lindane. This is especially surprising when one considers that the Lindane concentration in the water column was much higher than the concentration of DDE during the first year, thereby giving the appearance that Lindane was the more persistent chemical. These model results underscore the significance of chemical partitioning on chemical fate and highlight the importance and utility of a modeling framework which incorporates realistic mechanisms of water column and sediment interaction.

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