


AN ABSTRACT OF THE THESIS OF

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A Langmuir sorption model incorporating a second step of irreversible absorption was applied to a model soil system. The column was packed with cellulose triacetate; pulse and step input tests with 3,4-dichlorophenol were performed; the effluent concentration was measured by electron capture detector gas chromatography and sorption rate constants were determined. Sorption equilibrium was not reached during the time scale of this study, therefore an equilibrium partition coefficient,  $K_{ad}$ , was not able to describe it. Therefore a kinetic approach is more appropriate in such situations and may be more accurate to describe the extent of groundwater contamination than the usual local equilibrium assumption.

A Kinetic Approach for the Determination  
of Sorption Rate Constants Using a Column-type Reactor

by

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# A Kinetic Approach for the Determination of Sorption Rate Constants Using a Column-type Reactor

## INTRODUCTION and OBJECTIVES

Some toxic organic chemicals are known to be transformed in groundwater aquifers (1,2,3,4). The removal processes involve several different mechanisms including sorption on the porous media, metabolism of primary substrates, cometabolism of hazardous compounds, and physical transport through the soil. To understand the interrelationship of these different processes and the enhancement of biodegradation, it is important to determine the rate limiting steps and the limitations on the overall process.

Of all the removal processes in groundwater aquifers, sorption and metabolism appear to be most important. However, the relationship between sorption and metabolism in groundwater aquifers has not been studied in detail. Important parameters such as the rate of desorption may play a critical role in degradation since competition exists between the rate of desorption from the solid phase and the rate of uptake by the microorganisms. The major focus of this research was the examination of sorption kinetics.

Often sorption in aquifers is described by an equilibrium partition coefficient ( $K_{ad}$ ) which relates the equilibrium concentration of the solute in the liquid and solid phases. Such a coefficient

provides limited information about the final state of a system, but fails to describe the rate at which this state is achieved. Recently, several studies have shown this constant to be a function of the sorbent (solid) concentration. This influence, called the "solids effect", is poorly understood, although semi-empirical models have been proposed to describe this phenomena.

Predictions of environmental impacts have often been made on the basis of two phase equilibrium partition coefficients. The conditions used to empirically determine these coefficients in the laboratory may be radically different from the field conditions. This may result in large errors for the predicted behavior of the chemical. Due to the dynamic nature of sorption and metabolism, estimates of the  $K_{ad}$  will be insufficient to describe such systems.

The experimental apparatus chosen for this study was a column packed with a porous media. The column was subject to transient loadings of a trace organic chemical. The objectives of this study were:

1. To develop an experimental method able to observe kinetic aspects of the sorption phenomena in a soil column.
2. To determine sorption and desorption rate constants by fitting the experimental data with a one dimensional model simulating the advection, dispersion, sorption and desorption steps, based on assumptions about the reaction mechanisms.
3. To compare the results of the sorption and desorption rates to equilibrium batch studies.



Results of this study may be applied to management of water supplies and to prediction of hazardous waste migration in soils. Specific applications may be to develop new treatment systems such as in situ processes to clean up leaking landfills, contaminated groundwater aquifers, nonpoint source pollution, etc.

To summarize, the following questions were posed:

Does the solids concentration affect soil column sorption?;

What is the reaction mechanism for sorption?;

How we can best estimate the sorption rate constants? and

How can we apply batch sorption data to a soil system?

#### THEORETICAL CONSIDERATIONS and LITERATURE REVIEW

Sorption refers to a combination of reactions including ion exchange, physical adsorption, chemisorption and absorption occurring at or through the solid surface. Because of the difficulties in identifying and evaluating the importance of each process, the term sorption is generally used.

The solid-liquid interaction is usually described by an equilibrium isotherm, which relates the sorbed concentration to the liquid concentration. Numerous fitting equations are used to model the data including the Freundlich and Langmuir isotherms. Both have been theoretically derived from kinetic or thermodynamic considerations. However, questions remain about the meaning of the fitting parameters in these models. Good discussions of this problem have been offered by Harter (5) and by Veith and Sposito (6).

At low liquid concentrations, the sorption isotherm is often observed to be linear. The slope is called the sorption partition coefficient,  $K_{ad}$ , which is defined as:

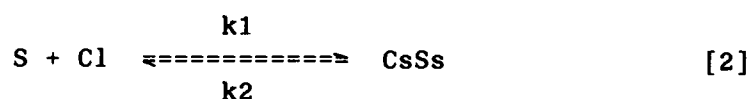
$$K_{ad} = \frac{C_s'}{C_l} \quad [1]$$

where  $C_s'$  : experimental measured mass of sorbed sorbate per mass unit of sorbent, (mg sorbate/g sorbent) and

$C_l$  : liquid concentration in mg sorbate/l.

The units of  $K_{ad}$  are consequently the inverse of sorbent concentration (l/g sorbent).

However,  $K_{ad}$  is not a true constant because of the experimental procedures used to measure  $C_l$  and  $C_s'$ . Measurement of the liquid concentration at equilibrium allows the determination of the amount sorbed by a mass balance. This mass balance can be checked by extraction of the solid phase and generally gives more than 90% recovery of the material.  $C_s'$  is the ratio of the sorbed sorbate concentration to the solids concentration. Since it is almost impossible to measure the degree of saturation of the sorbent, the  $K_{ad}$  value differs from the ratio of the kinetic constants by a factor  $S/S_0$  where  $S$  is the concentration of sorbate free solid at equilibrium and  $S_0$  is the initial or total solid concentration. A demonstration can be made as follows. Consider a batch system with a solid in a solution of sorbate; the sorption is assumed to follow a Langmuir isotherm (7), or in other words, there is only one thermodynamic equilibrium which characterizes this reaction:



where      S : sorbate free solid concentration in g/l;  
              Cl: sorbate concentration in mg/l;  
              CsSs: sorbed sorbate concentration in mg/l;  
              k1: second order rate constant in l/(g.s) and  
              k2: first order rate constant in s<sup>-1</sup>.

The velocity of the sorption reaction,  $v_s$ , can be expressed as:

$$v_s = k_1 * Cl * S \quad [3]$$

the velocity of the desorption reaction,  $v_d$ , is:

$$v_d = k_2 * (CsSs) \quad [4]$$

One should also consider the desorption velocity,  $v_d$ , to be proportional to the bound site solid concentration as:

$$v_d = k'_2 * (CsSs)/Cs \quad [5]$$

where      Cs: saturation capacity in mg/g;  
              k'2: first order rate constant in g/mg/s and  
               $k_2 = k'_2 / Cs$

At equilibrium, the velocity of sorption [3] and desorption [4] are equal, therefore the thermodynamic constant, K, is defined as:

$$K = \frac{k_1}{k_2} = \frac{\{ CsSs \}}{\{ S \} * \{ Cl \}} \quad [6]$$

where {} represents the activity at equilibrium.

The direct measurement of the sorbate free solid concentration,  $S$ , is impossible. Thus the partition coefficient ( $K_{ad}$ ) is expressed in terms of a measurable quantity,  $S_0$ , and is related to  $K$  as follows:

$$K_{ad} = \frac{(C_{l0} - C_l)}{S_0 * C_l} \quad [7]$$

$C_{l0}$  : initial sorbate concentration in mg/l and

$S_0$  : initial solid concentration in g/l;

when  $K_{ad}$  is determined by mass balance on the liquid solute concentration. When the partition coefficient is determined by extraction of the sorbed solute from the solid phase, the relation is expressed as follows:

$$K_{ad} = \frac{(C_s S_s)}{S_0 * C_l} \quad [8]$$

In either case, this result differs from the thermodynamic equilibrium constant,  $K$ . Consequently, the partition coefficient,  $K_{ad}$ , is dependent on the equilibrium constant and the fraction of the solid bound with sorbed solute:

$$K_{ad} = \frac{(C_s S_s)}{S_0 * C_l} = \frac{S}{S_0} * K \quad [9]$$

The first reports concerning the solids effect described sorption to soils and lake sediments (8, 9, 10). Certainly, many reports of solids effect may result because of experimental errors. However, improvement of experimental methods and apparatus have confirmed this unexpected dependence of sorption on solids concentration. The literature data (11) shows this apparent effect of the solid concentration.

Applications of the sorption partition coefficient have increased the importance of understanding the solids effect. This is especially true in the area of groundwater quality modeling where  $K_{ad}$  values are determined at low solids concentrations in batch reactors and are used to describe sorption in soil systems. This phenomena is usually modelled assuming local equilibrium in a system in which there is liquid transport inside the porous media and where high solid concentrations are present.

O'Connor and Conolly (11) have surveyed the literature data and compared them with an empirical model:

$$K_{ad} = K_{ad\#} + \frac{B}{C + S_0^a} \quad [10]$$

where  $K_{ad\#}$  : limiting partition coefficient

at high solid concentration in l/g;

$S_0$  : solid concentration in g/l and

a, B, C : empirical fitting constants

In most cases, due to the relatively low values of  $K_{ad\#}$  and C, this equation can be reduced to:

$$K_{ad} = \frac{B}{S_0^a} \quad [11]$$

O'Connor and Conolly's study revealed that empirically derived constants are a function of the sorbate-sorbent couple.

An alternate explanation of the solids effect came with the concept of a nonseparable third phase, where the solute is complexed or sorbed on colloids or microparticles which have a concentration proportional to the solids concentration. Solid separation techniques

such as centrifugation or filtration always leave microparticles in suspension. As is well known, the sorption activity increases as the radius of the particle decreases, and so the saturation capacity expressed per unit weight of these small particles increases.

Voice and Weber (12, 13) proposed that the partitioning of hydrophobic solutes associated with nonseparable colloids is empirically related to the organic solid concentration by the equation:

$$\text{TOC} = E * S_0^F \quad [12]$$

where TOC = total organic carbon in solution,

$S_0$  = solid concentration and

$E, F$  = empirical constants.

Including this relationship and developing the equations required to describe the three phases (liquid, solid and microparticles), Voice and Weber proposed a complex model which was able to fit literature experimental data but is difficult to use because of the number of parameters involved. After making simplifying assumptions, Gschwend and Wu (14) developed a simple model which strongly supports the third phase hypothesis.

The desorption of hydrophobic solute often exhibits a hysteresis effect in which desorption and sorption have different isotherms. Several authors have investigated the possibility of two different kinds of reaction sites: one assumed to be irreversible and another with forward and reverse velocities. This concept of an irreversible site explains the observed hysteresis, but this can also be achieved if the experimenter does not wait long enough to be sure to reach

desorption equilibrium with a completely reversible sorption mechanism.

DiToro et al. (15, 16) have described this hysteresis effect with a particle-particle interaction model occurring only at high solids concentrations. As the collisions occur between solids, the free particles are thought to destabilize the bound particles, thus lowering the  $K_{ad}$  value and suggesting the observed solids effect. The model developed fitted experimental data. In a later publication (16), DiToro, working with glass bead solid materials for which no microparticles and no colloids occurred, showed that although the third phase hypothesis does not apply in the completely reversible situation of heavy metals sorption, the solids effect was still observed.

This described solids effect becomes important when the  $K_{ad}$  value obtained under laboratory conditions (i.e. low solids concentration) is applied to models to assess the contamination risk of aquifers under the assumption of local equilibrium. Valocchi (17) offers a good discussion of this hypothesis. Even if the assumption of local equilibrium is checked; the  $K_{ad}$  value may vary from batch studies due to the different solid concentrations observed in the field.

Sorption has been modeled in different ways to assess groundwater contamination and to predict pollutant transport. Models can be divided into two categories: physical nonequilibrium models where the limiting step is the transport inside the solution and chemical nonequilibrium models where the overall sorption rate is limited by the reaction at the solid solution interface. This classification has been proposed by Valocchi (17). This study is best described by the second case.

Some chemical nonequilibrium models assume sorption to be a first order process with respect to the liquid concentration. Other investigators allow the sorbent to equilibrate with the liquid phase under the assumption of local equilibrium, even if transport is not the rate limiting step. Sometimes both first order sorption kinetics and equilibrium sites have been used in the same model (18).

Since the complete expression of each reaction is required to describe the mechanism of the equation [2], none of these models can be directly applied. Also because of the observed solids effect, the model should incorporate the free site solid concentration,  $S$ , as follows (for the sorption reaction only):

$$-(dC_l/dt)_{x,t} = (dC_s S_s/dt)_{x,t} = k_1 * C_l * S - k_2 * C_s S_s \quad [13]$$

$$(dS/dt)_{x,t} = (dC_l/dt)_{x,t} / C_s \quad [14]$$

at the location,  $x$  and for the time,  $t$

$C_s$  : surface saturation capacity per unit weight of sorbent, (mg sorbate/g sorbent ),

for one dimensional analysis, using the concept of a "mixing cell" (19,20). Analytical equations can be used to check the validity of a model in the case of advection and dispersion only.

The solid-liquid reaction in the model is assumed to be Langmuirian and the Langmuir derivation can be made from the kinetic equations. In a batch system of volume  $V$ , the fraction of used solids,  $a$ , can be defined as:



$$\frac{(CsSs)}{Cs} = a * S0 \quad [15]$$

where the Kad value as derived previously (equation [8]) is then expressed as:

$$Kad = \frac{S}{S0} * K = (1 - a) * \frac{k1}{k2} \quad [16]$$

the mass balance on the used solid can made as follows:

$$Cs*S0*V*da = + k1*Cl*(1-a)*S0*V*dt - k2*a*Cs*S0*V*dt \quad [17]$$

at any time, the rate of change of a is:

$$\frac{da}{dt} = \frac{(k1*Cl*(1-a)*S0 - k2*a*Cs*S0)*V}{Cs*S0*V} \quad [18]$$

at equilibrium, da/dt = 0 so:

$$\frac{k1*Cl*(1-a) - k2*a*Cs}{Cs} = 0 \quad [19]$$

then,

$$a = \frac{k1*(Cl/Cs)}{k2 + k1*(Cl/Cs)} \quad [20]$$

From equations [1] and [14], Kad can be expressed as:

$$Kad = \frac{Cs'}{Cl} = \frac{k1}{k2} * (1-a) = \frac{k1}{k2} * \frac{k2}{k2 + k1*(Cl/Cs)} \quad [21]$$

By comparison with the Langmuir relation, which is:

$$Cs' = \frac{Cs * b * Cl}{1 + b * Cl} \quad [22]$$

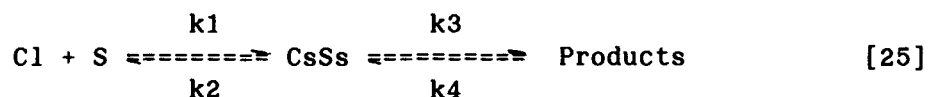
Equation [21] can be written:

$$Cs' = \frac{k1/(k2*Cs) * Cs * Cl}{1 + k1/(k2*Cs) * Cl} \quad [23]$$

and b, the Langmuir constant can be defined as:

$$b = \frac{k1}{k2 * Cs} \text{ with unit of l/mg sorbate.} \quad [24]$$

The sorption reaction proposed (equation [2]) is a simple case of more complex multistep reactions, such as:



for which the k3 and k4 constants are equal to zero. So if the simple Langmuirian model is not able to correlate the experimental data, the sorption reaction can be made more complex by adding a second irreversible or reversible step.

#### EXPERIMENTAL PROGRAM and ANALYTICAL TECHNIQUES

The objectives of this study are to determine rate constants for sorption and desorption and to develop a mechanistic approach for the study of solid-liquid interaction working with a simple system. A column was packed with cellulose triacetate and was used as a plug flow

reactor. Cellulose triacetate was chosen as the organic solid phase because it is insoluble in water and able to separate from the liquid readily. 3,4-Dichlorophenol (3,4-DCP) was selected as the sorbate. 3,4-Dichlorophenol's  $pK_a$  is 8.59 (21). The pH of the dichlorophenol solutions used in this study were between 4.7 and 5, thus the ionized form can be ignored.

The effluent of the column was collected as function of time. After dosage, the experimental data were fitted with a model developed from equations [13], [14] and [32] and assumptions about the mechanism of the sorption reaction. This model is presented in Appendix A. The model was able to describe advection and dispersion of a nonreactive tracer. Analytical equations have also been used to check the validity of the model. Because the model requires a description of dispersion, this coefficient must be evaluated before any experimentation with reactive compound. Since two unknowns  $k_1$ ,  $k_2$  (equation [13]) are required to describe the assumed system, the reactor was operated under pulse and step input conditions. The pulse input experiment provides information about both the forward and reverse rate constants because of the successive sorption and desorption through the column. The step input is more sensitive to  $k_1$  than to  $k_2$  due to the fact that the influent concentration pushes the sorption until equilibrium without major desorption effects. The TOC was measured to insure that the third phase of microparticles and colloids was not present in these experiments (Appendix B).

The experimental program was organized as follows:

1. The determination of the dispersion coefficient was accomplished using a non-reactive compound such as  $\text{Cl}^-$ ;
2. A pulse input of sorbate was completed; and
3. A step input was performed and the breakthrough curve was observed.

#### 1. Description of the reactor

A 50 ml glass burette (Figure 1) with a teflon stopcock was filled with 17.0 g of cellulose triacetate, previously ground at U.S.EPA facilities (Newport OR). The fraction of interest was collected on a 100 meshes per inch sieve. After double distilled water washing and drying under vacuum conditions, the solid was stored in a dessicator for future experiments.

An adjustable volumetric pump (Fluid metering Inc., Oyster Bay, N.Y.) and a flow control valve were used to set the flowrate to the reactor. Teflon tubing was used throughout the reactor to minimize sorption. Precautions were taken against photolysis by covering the pilot apparatus with aluminium foil.

The cellulose triacetate media was 30 cm long and occupied a volume of 27.3 ml; the average porosity was 0.48. Before each run, the bed was backwashed to eliminate fine particles and colloids, followed by flushing at high flow rates.

#### 2. Dispersion coefficient determination

The chloride tracer experiment was completed as follows. One ml of a 50 g/l solution of chloride was injected at the top of the column. The effluent was automatically sampled using a fraction collector at 6

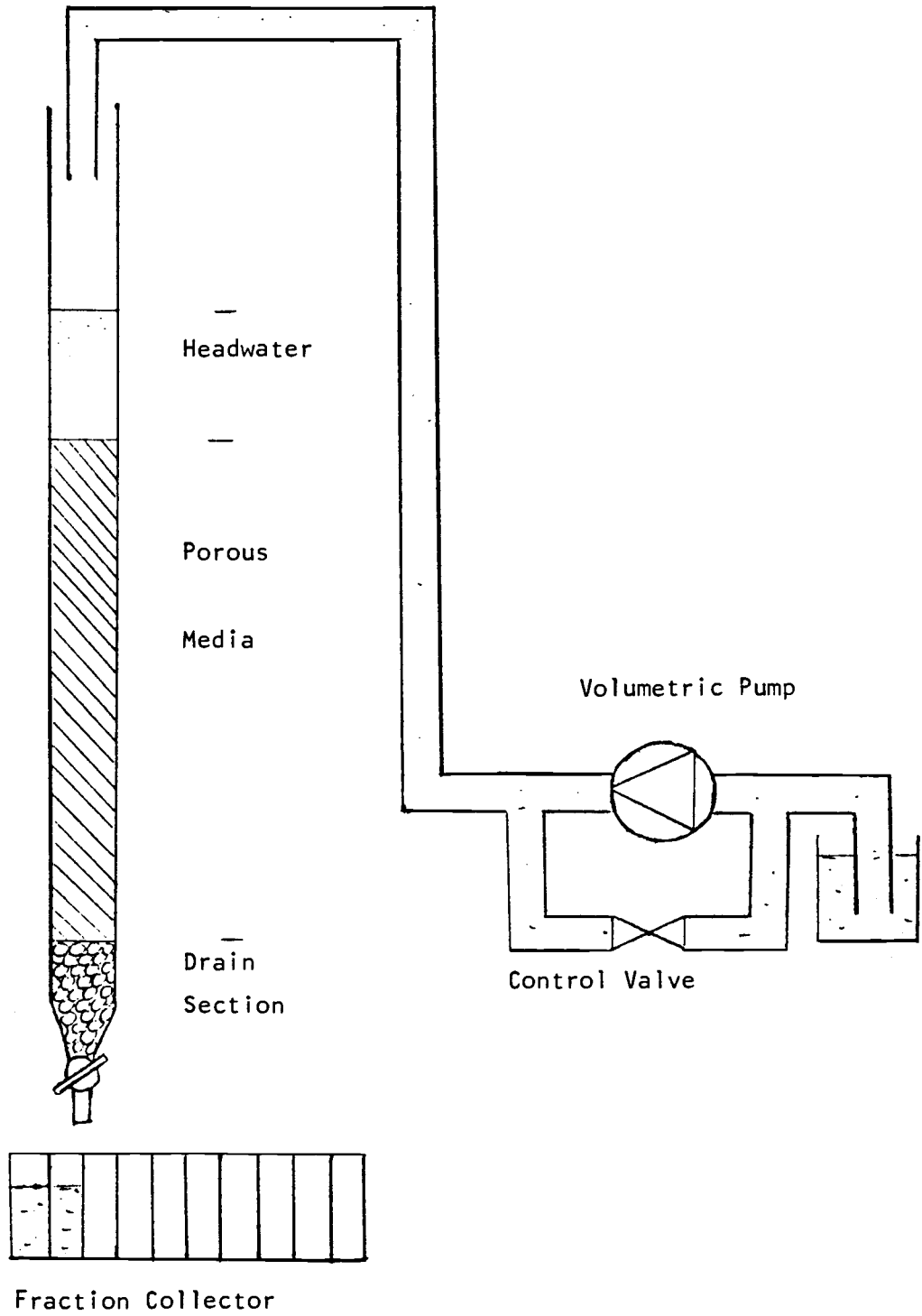


Figure 1: Pilot reactor description

second intervals from the injection time ( $t=0$ ). The concentration of chloride in the effluent was measured using the classical argentometric method (22) which is a precipitation of AgCl using  $\text{AgNO}_3$  as titrant in presence of  $\text{K}_2\text{CrO}_4$ .

The estimation of the dispersion coefficient ( $D$ ) for any reactor can be made as follows (23) using a nonreactive compound (chloride) by observation of the chemical distribution curve. The determination of the mean residence time,  $t$ , can be made by measuring the concentration of the tracer in the effluent with time.

$$t = \frac{\sum t_i \cdot C_i}{\sum C_i} \quad [26]$$

where  $C_i$  is the concentration at time  $t_i$ .

The standard deviation,  $s^2$ , is defined as:

$$s^2 = \frac{\sum t_i^2 \cdot C_i}{\sum C_i} - (t)^2 \quad [27]$$

and these statistical parameters are related to  $D$  by:

$$\frac{s^2}{(t)^2} = f(D/(U/p \cdot L)) \quad [28]$$

$$= 2 \cdot \frac{D}{L \cdot U/p} \cdot \left( 1 - \frac{D}{L \cdot U/p} \right) \cdot \left( 1 - e^{-U \cdot L / (p \cdot D)} \right) \quad [29]$$

where  $L$ : length of the reactor along the flow in cm;

$U$ : flow rate in cm/s and

$p$ : porosity, dimensionless.

An iterative computation can be used to solve this equation, substituting values for  $U \cdot L/p$ , the value of  $D$  can be used in the model to check the fit of the tracer curve. Numerical integration of the model also allows a check of the mass balance between the influent and the effluent, because the rate constants are set to zero in the case of a nonreactive chemical.

Samples of the reactor effluent were taken at 6 second intervals. Therefore the concentration measured was the average over this period of time. It was difficult to start the sampling at time  $t=0$  because the injection was not exactly synchronized with the first sample, but the mean residence time of the tracer was always lower than the hydraulic retention time. This experimental problem is more important at high flow rates where the detention time can be in the order of one or few sampling increments.

### 3. Pulse and step input experiments

The pulse input experiments were conducted similarly to the tracer experiment. The volume injected was 1 ml of a 3000 mg/l solution of 3,4-DCP in double distilled water. This mass was selected to allow accurate measurement of 3,4-DCP concentrations in the effluent. The step input experiment was completed by changing the feeding reservoir of double distilled water for a 3,4-DCP solution. Sampling was accomplished in the same way as the tracer experiment; however the time interval was changed.

The collected fractions were stored in glass vials with teflon screw caps and refrigerated at 5 degree Celsius. Chlorophenols were measured by gas chromatography after acetylation and extraction into

hexane. 2,6-Dibromophenol was used as the internal standard (Appendix C).

Samples were injected into a HP 5890A gas chromatograph with an electron capture detector and a capillary inlet system. The ratio of the 3,4-DCP area to the internal standard area was compared to the standard curve to give the concentration in the hexane phase.

## RESULTS

The experimental program has been executed as established previously. TOC measurements indicated that the organic carbon concentration in the liquid phase was below the detection limit and less than one ppm.

### 1. Tracer experiment

In the first experiment, the dispersion coefficient was determined using a nonreactive compound (chloride). The effluent chloride concentration was determined using the classical argentometric method (22). The observed distribution of the concentration versus time was computed to solve equation [29] and to estimate the dimensionless dispersion ratio  $D/(U'L)$  (23). Two experiments were conducted at different flowrates and the  $D/(U'L)$  ratio was approximately the same:



$$\frac{D}{U' * L} = 0.016 \quad \text{for } Q = 0.64 \text{ ml/s}$$

$$\frac{D}{U' * L} = 0.018 \quad \text{for } Q = 0.18 \text{ ml/s}$$

in which  $U' = U/p$

where  $U'$ : flowrate into the porous media

Therefore, an average dimensionless ratio of 0.017 was used to describe the dispersion, since the dispersion is mostly due to the packing characteristics. Thus, the model was able to fit both trials, with the sorption constants equal to zero. Therefore the mass balance requirement was checked for this conservative material. Figures 2 and 3 present the results of the computation.

## 2. Pulse input experiment

One ml of a 3000 mg/l solution of 3,4-DCP was injected into the top of the column at two different flowrates. During the first spike at a flowrate of 0.637 ml/s, almost no sorption occurred due to the high flow velocity which flushed the reactive chemical out of the reactor. Then the flowrate was reduced to 0.16 ml/s and the experiment was rerun. This second pulse showed a delayed peak which is characteristic of sorption-desorption reactions. It must be noted that the long tail was not expected in such a Langmuirian adsorption. The final results are presented in figures 4 and 5.

## 3. Step input experiment

The first experiment was conducted at a high influent concentration (3000 mg/l of DCP) and showed an unexpected shape, compared with the model computation using the same fitting parameters

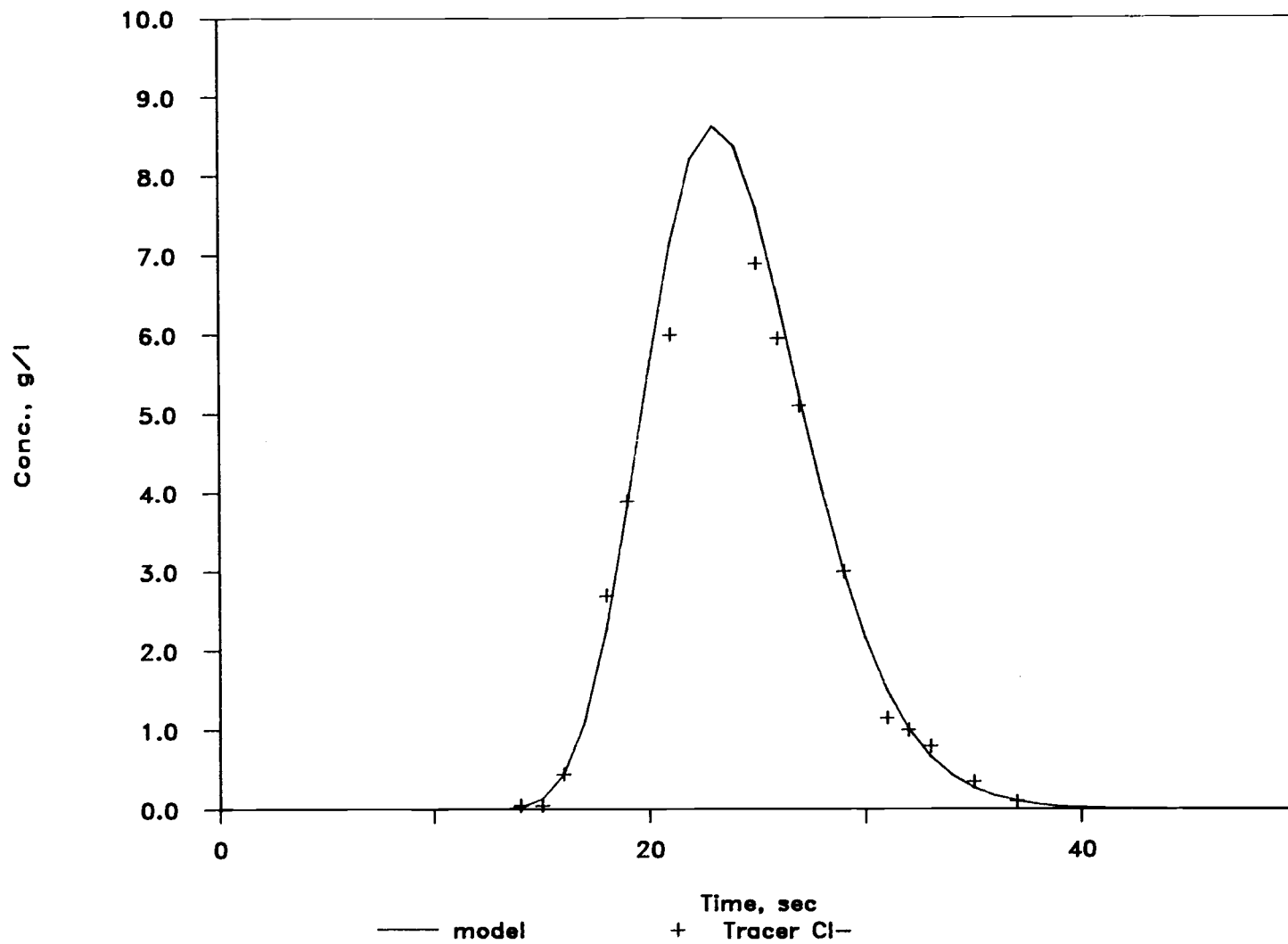


Figure 2: Tracer experiment at high flow, pulse input.

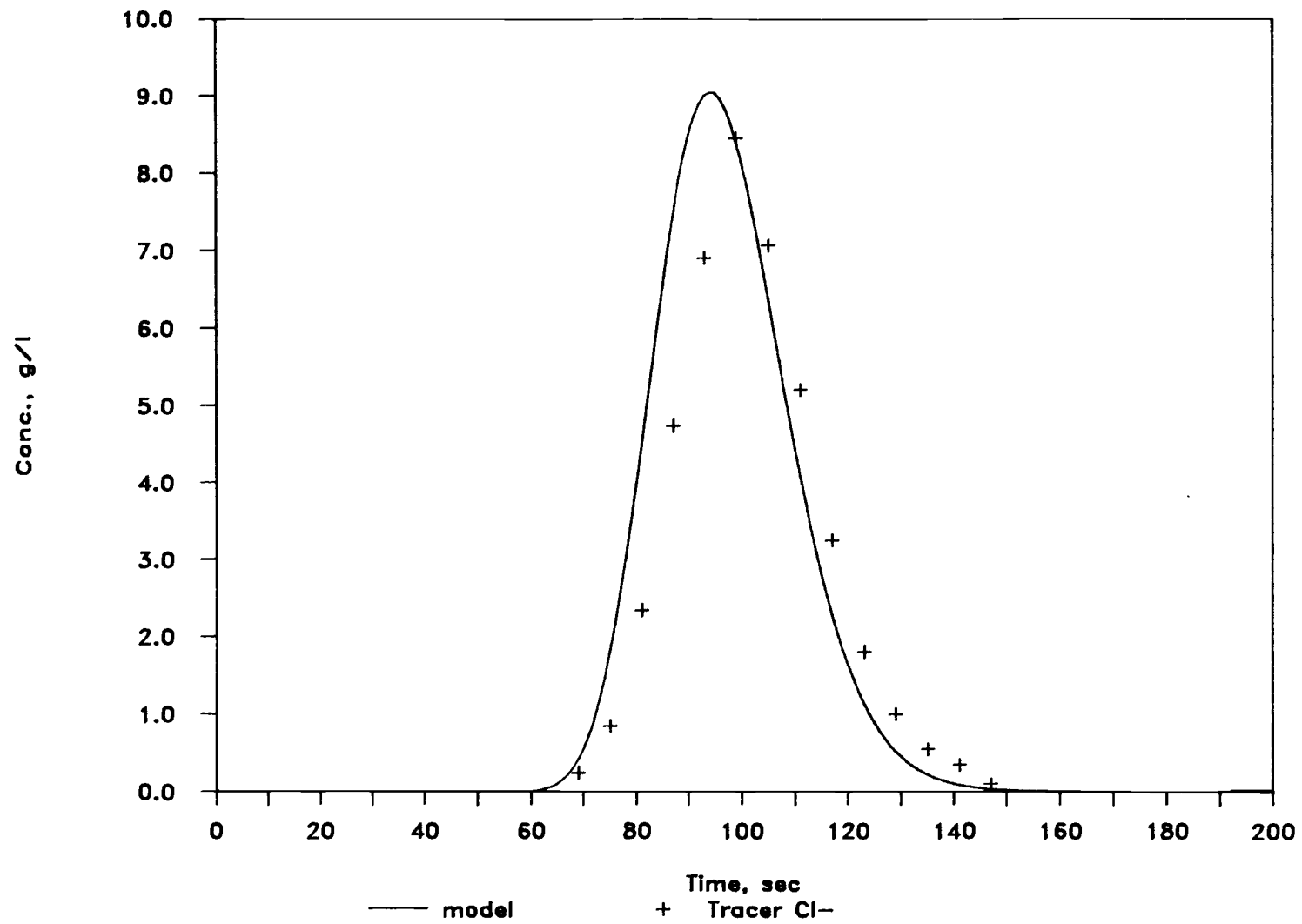


Figure 3: Tracer experiment at low flow, pulse input.

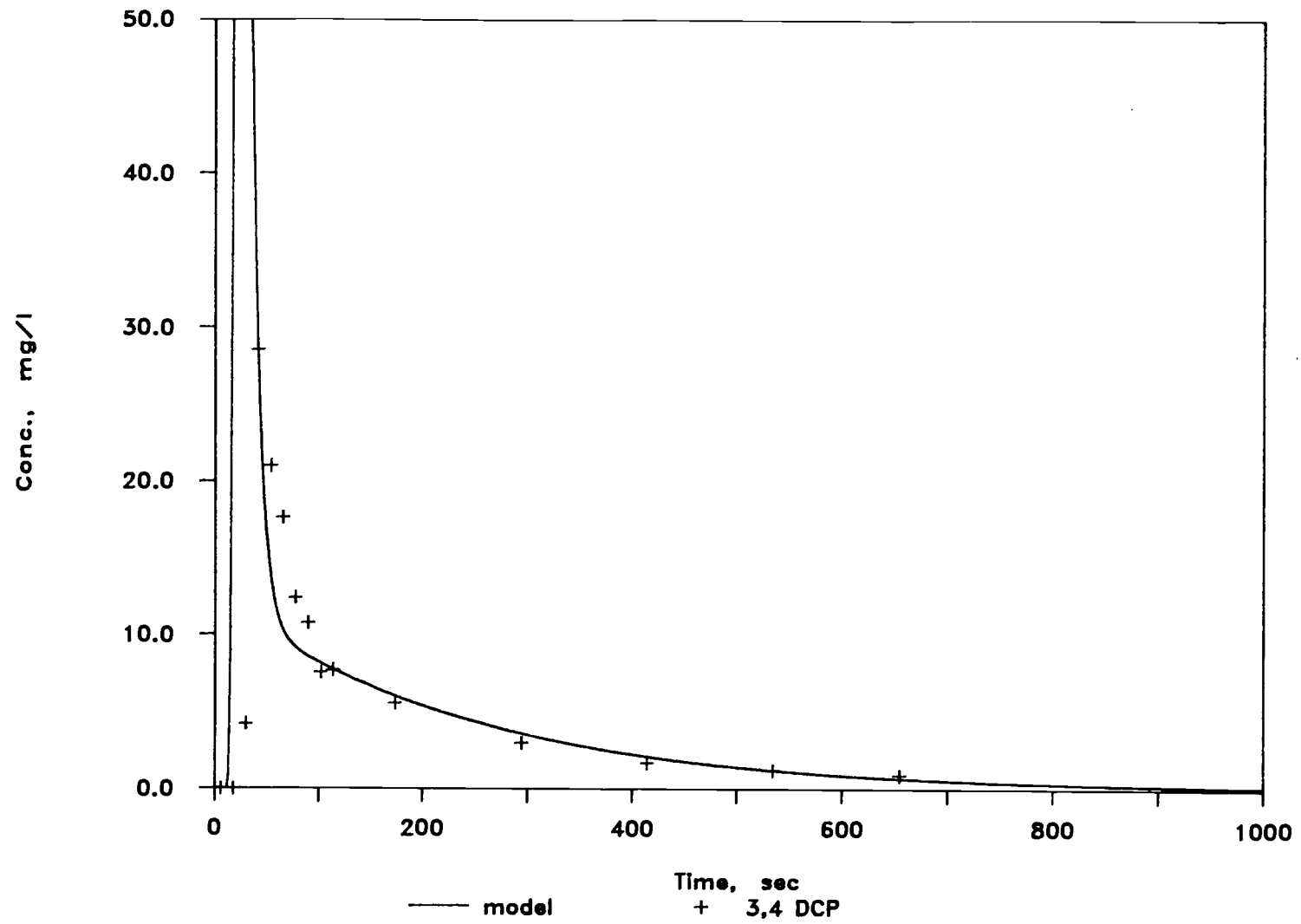


Figure 4: Reactive compound at high flow, pulse input.

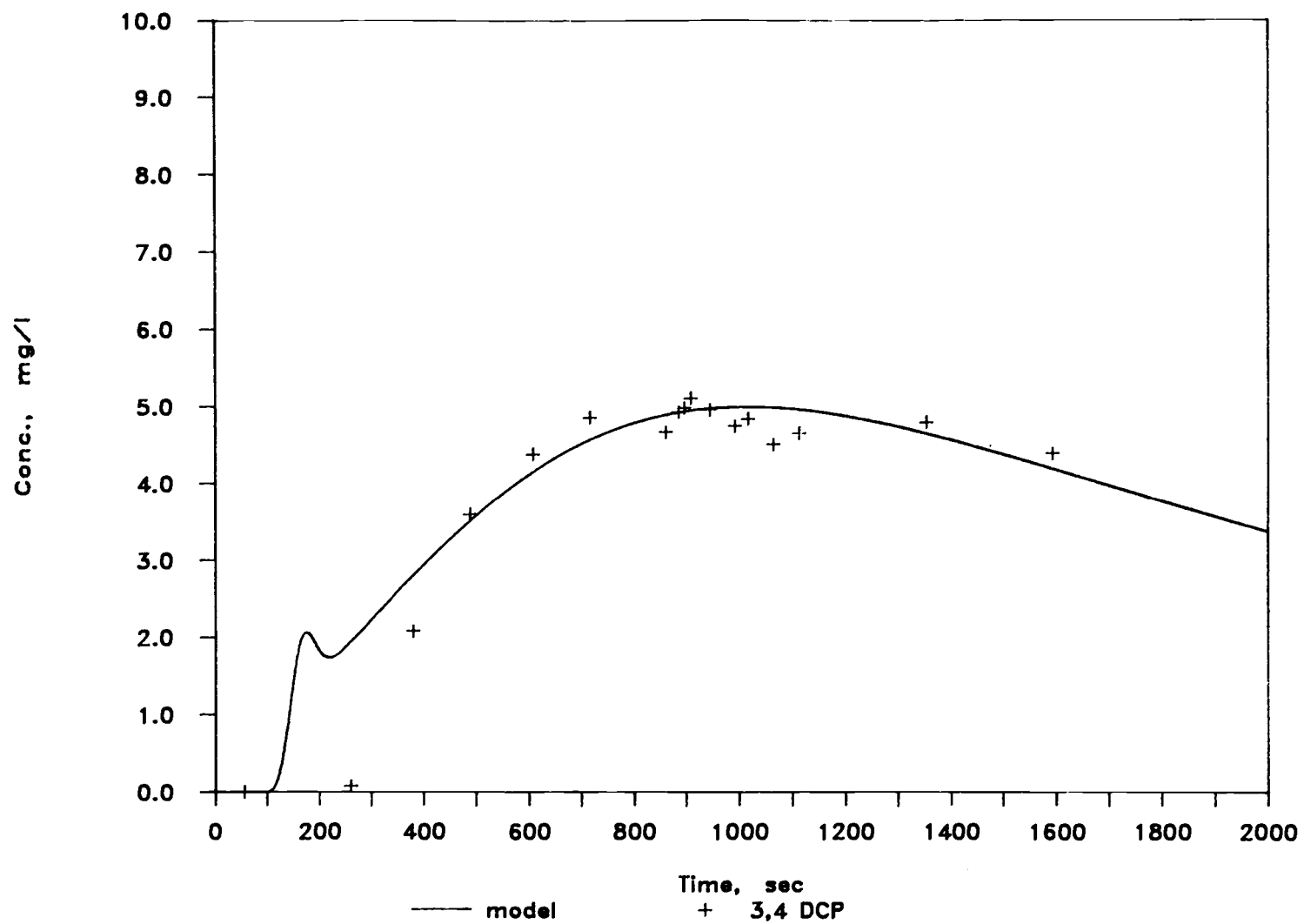


Figure 5: Reactive compound at low flow, pulse input.

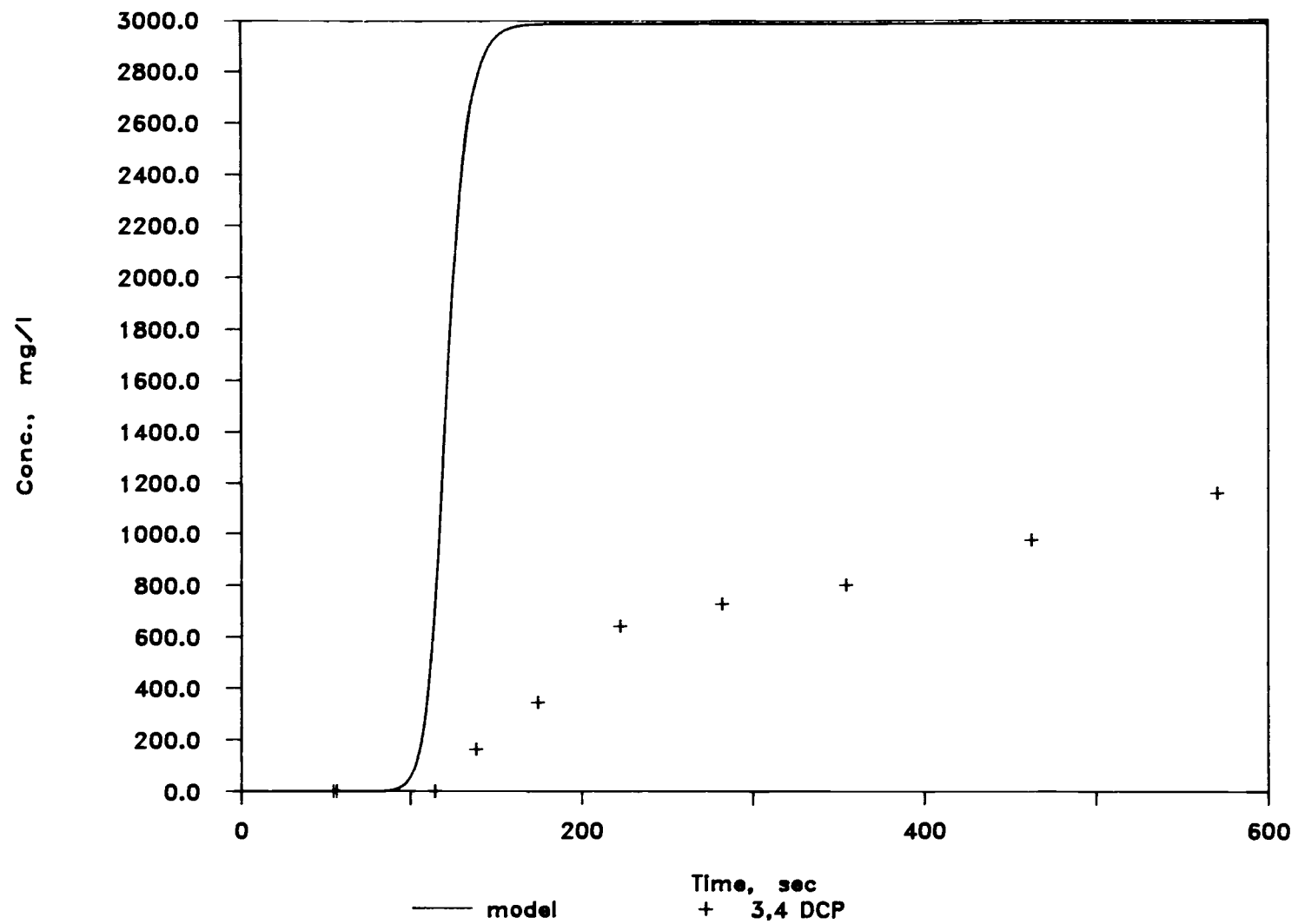


Figure 6: Reactive compound at high concentration, step input.

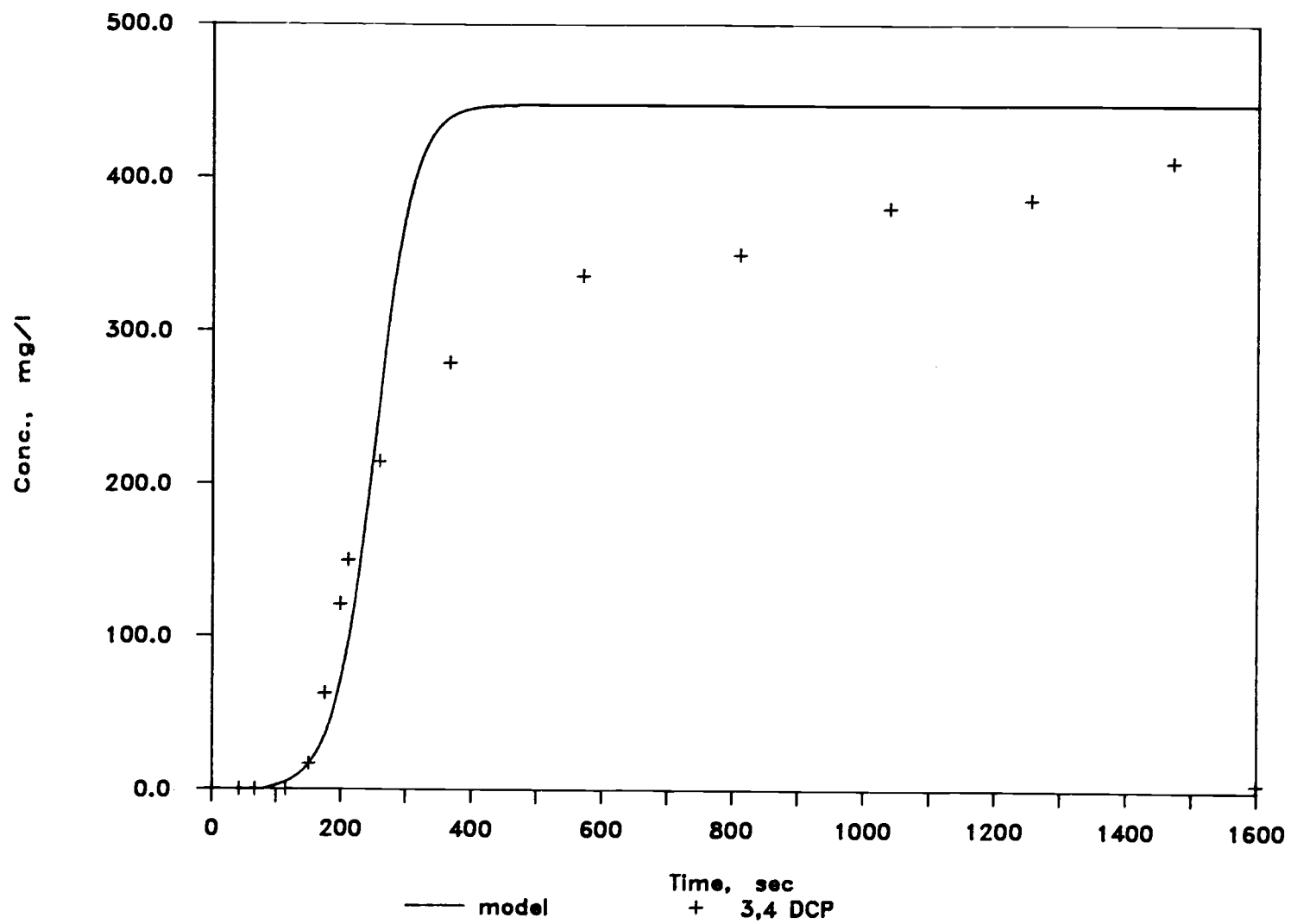


Figure 7: Reactive compound at low concentration, step input.

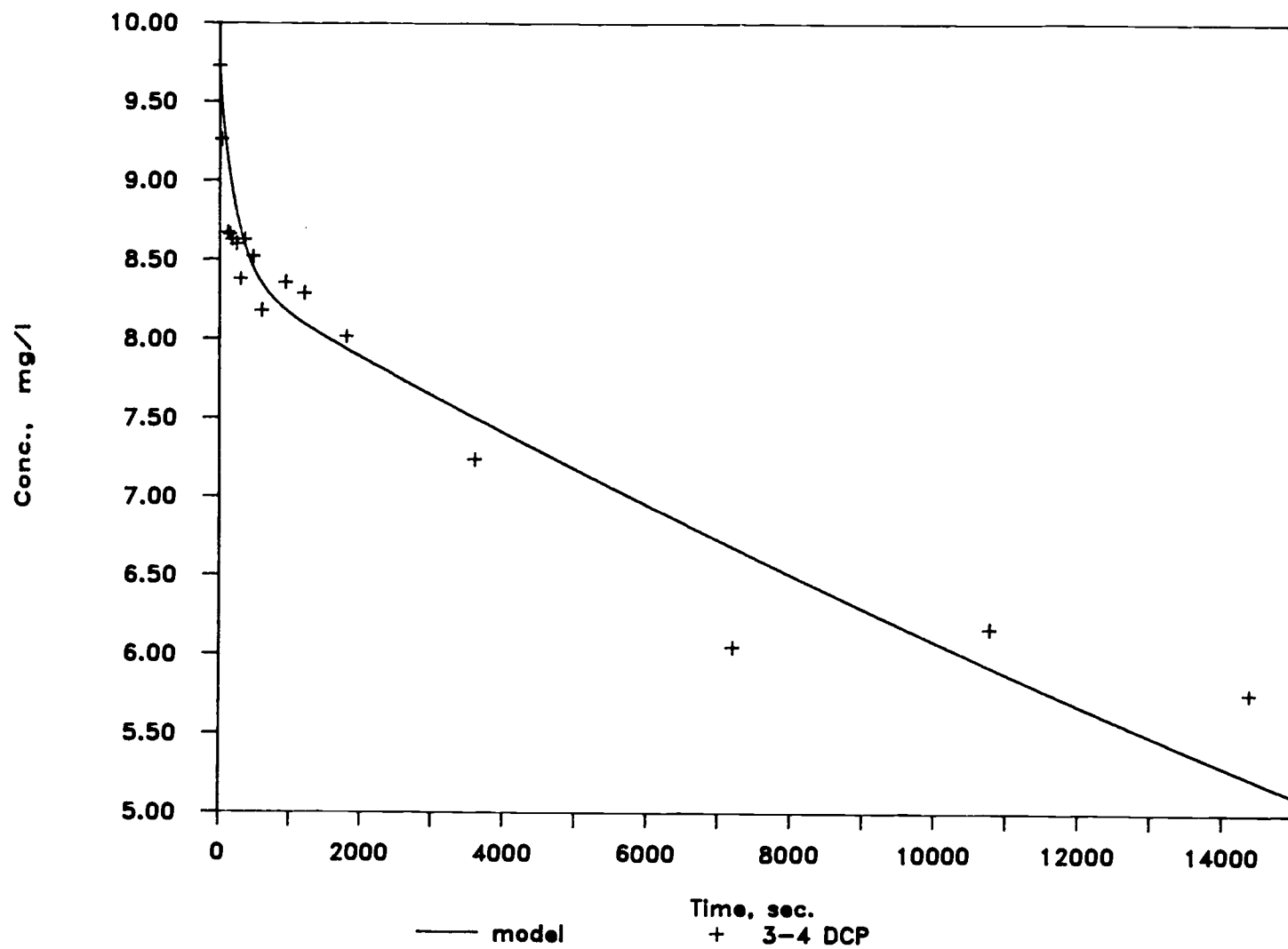


Figure 8: Kinetic batch at low solid concentration, 10 g/l.



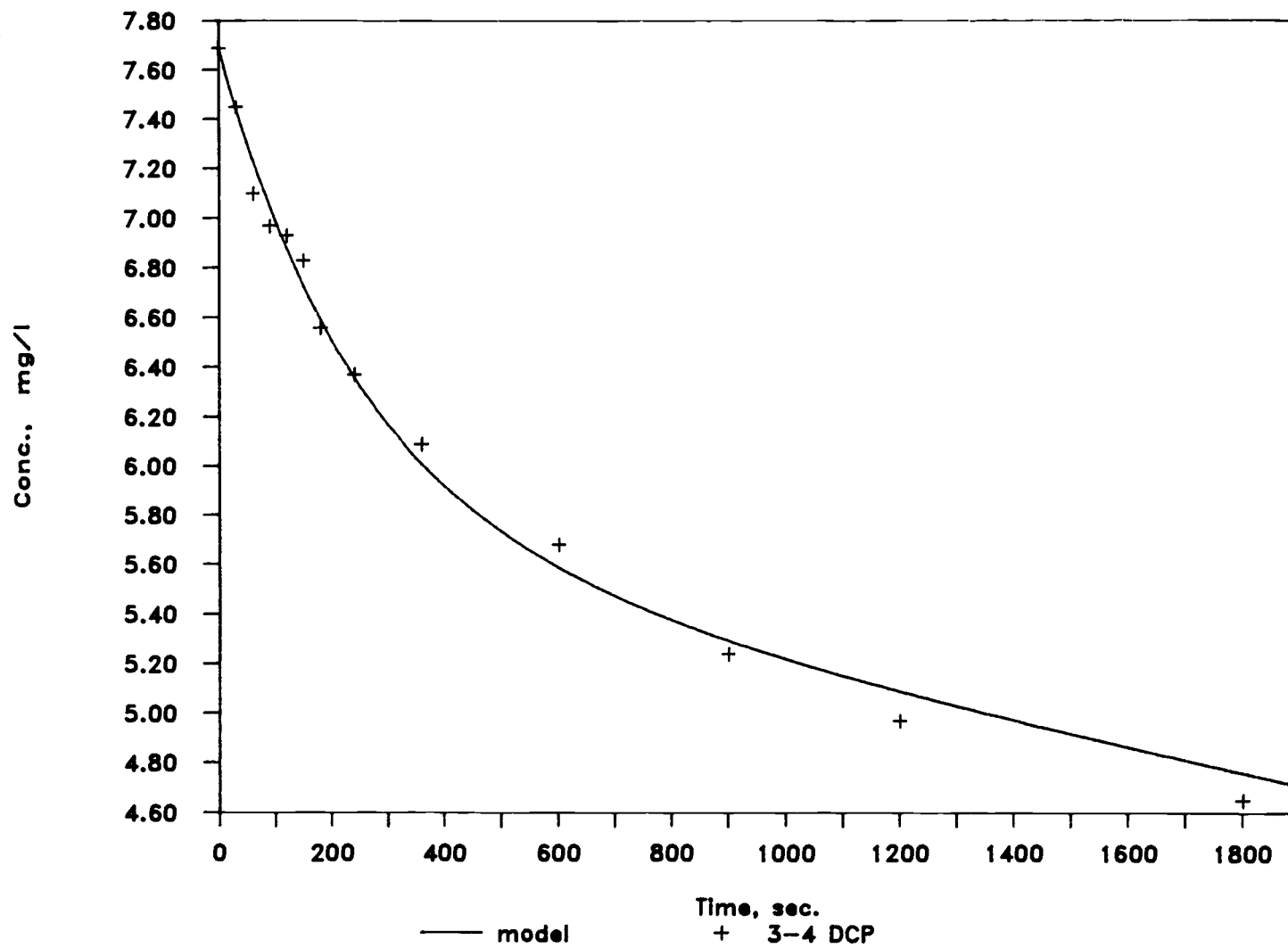
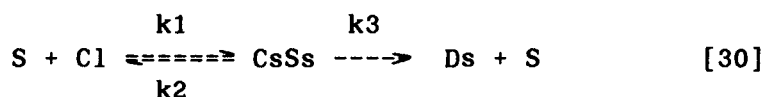


Figure 9: Kinetic batch at high solid concentration, 30 g/l.

as the previous pulse experiment. A second step input was done using 500 mg/l as the influent concentration. In this case, a typical breakthrough curve was observed. Figures 6 and 7 show these different observations.

#### 4. Computer Model Fitting

Because of the inability of the Langmuir model to fit the experimental data from the second pulse and due to the results of the kinetic batch experiments (24) which showed a continuous low trend of sorption (figures 8, 9), the model was modified to include an absorption step into the cellulose polymer from the surface with regeneration of the site. These data (24) have been used in a batch model simulating the same sorption mechanism in order to estimate the kinetic constants. The equations can be written as follows:



where  $Ds$ : amount of sorbate irreversibly absorbed in mg/l;

$k_3$ : first order kinetic constant with respect to  $CsSs$  in  $s^{-1}$ ;

and the other variables being defined as previously.

This assumed mechanism does not allow the experimenter to perform a mass-balance between the influent and the effluent of the column due to second step absorption into the solid. The corrected model was able to fit the second pulse experiment and almost the second step input. It was necessary to change the values of kinetic constants by a factor

of two in order to fit the experimental data. The following table summarizes the values of the fitting parameters used in the different situations.

Table of the Fitting Parameters

Experimental Conditions	k1 (1/g/s)	k2 (1/s)	k3 (1/s)	Cs (mg DCP/g solid)
Batch S0 = 10 g/l	5.73e-5	1.61e-3	1.95e-4	0.30
Batch S0 = 30 g/l	3.58e-5	2.01e-3	3.60e-4	0.35
Column pulse High flow	3.58e-5	2.01e-3	3.60e-4	0.35
Column pulse Low flow	6.04e-5	1.93e-3	3.35e-4	0.30
Column step High conc.	6.04e-5	1.93e-3	3.35e-4	0.30
Column step Low conc.	5.82e-5	1.94e-3	7.30e-4	0.75

#### DISCUSSION and INTERPRETATION of the RESULTS

Based on the results of the TOC test, the third phase effect has been assumed to be insignificant in this case. A value of 1 ppm TOC should not be completely rejected with respect to this concept which is certainly a valid explanation in different situations such as water

with high turbidity or wastewater sludge.

The description of a nonequilibrium transient flow system with a reactive chemical is possible. However a good knowledge of the reaction mechanisms involved is required in order to have a negligible residual between model and experimental data. The ability of a model to describe a system does not constitute proof of the mechanisms involved; and with more fitting parameters, a model is better able to accurately describe any experimental data. This has been a primary concern of the experimenter to keep the model as simple as possible in order to understand the meaning of the results. The scope was then focused on accessibility rather than resolution, also because the resolution of a fitting model does not need to be better than the precision of the experimental measurements.

An accurate simulation of the reactor hydraulics is also required for any fitting trial. The headwater of the column has been difficult to maintain at a fixed level and then was not simulated exactly by the computer model. Because of the reactor vessel design, the influent flow sometimes splashed and, therefore, created mixing conditions or traveled along the glass walls in a plug flow manner. The pulse experiments were much more sensitive than the step input to this problem because it affected the initial distribution of the chemical prior to any sorption; also the pulse injection itself created mixing turbulence. The model program accounted for that by computing an initial distribution based on a guess about the real mixed volume of the headwater. In fact, the overall reactor consisted of three different subunits: the headwater, the porous media, and the glass bead

drain section. The determination of the dispersion coefficient was made for the total system and can be related to each dispersion coefficient for each section of the reactor by the following equation:

$$[D/(L*U)]_t = \sum [D/(L*U)]_i \quad [31]$$

In the case of small amounts of dispersion (23), the equation [31] relates three unknowns with only one equation. So, there has been a simplifying assumption that all the dispersion occurred only inside the porous media. Before that, the initial distribution in the headwater was corrected for the injection mixing. The drain section was completely neglected based on the small length and the relatively large flow channel created by the glass beads. The step input experiments were less sensitive to this phenomena due to the continuous input of a constant concentration of the solute.

The second step of the chemical equation is significant because of the solubility of cellulose triacetate in chlorinated solvents (25). Therefore the DCP is thought to penetrate inside the polymer of the solid, due to the possible miscibility of the solute in the cellulose triacetate. The next question was whether the surface sites were irreversible or able to be regenerated. The modifications of the model and trials have shown that the second hypothesis is the more probable.

As observed before, this model has been unable to fit the data of the 3000 mg/l step input experiment, an explanation can be advanced. The hydrophobic molecules have the potential of forming more than one layer on the surface (multilayer sorption). Due to the very high local

concentration of the solute at the solid surface, formation of multilayers may occur which may explain this very high removal of chlorophenol. The  $C_s$  fitting parameter had been increased by a factor of two in order to fit the data for the last step input, and this may also be an indication of multilayer formation. That, indeed, could also occur in the pulse input experiment but only in a very narrow length at the top of the column where the concentration decreased from the input value of 3000 mg/l to perhaps several hundred mg/l. Multilayer sorption also could explain why we did not observe the flush-out peak on the second pulse input like the model suggested (see figure 5). The second step input still showed a higher removal than the program predicted, but in this case it was closer than for the first step.

These observations may be considered as indications that the assumed chemical mechanism described in equation [30] is true for low concentration ranges (less than 100 mg/l). Above this limit, the hydrophobic character of the DCP and its possible multilayer adsorption should be a valid explanation. Formation of froth at high liquid concentrations, caused by shaking has been observed for the 'pseudo-equilibrium' isotherm batch experiment. Moreover it seemed that the presence of the cellulose triacetate stabilized this formation longer than without solid.

This higher removal and this possible multilayer sorption can also be related to the discrepancy of the 'equilibrium' isotherm. In fact, the suggested reaction mechanism (Equation [30]) does not reach equilibrium. However, at low sorbate concentrations, this system

appeared and it was observed and was fit with a Langmuir isotherm. However, at high concentrations (from several hundred to several thousand mg/l), the pseudo-equilibrium isotherm behaved differently. Attempts to describe it with a B.E.T. isotherm (26) were unsuccessful. Adding one parameter, the model became more complex and less accessible.

#### SUMMARY and CONCLUSIONS

This study shows the ability of a continuous flow transient system to be an investigation tool for sorption. The accuracy of this method is directly related to the assumed sorption mechanism of the model. But a fitting model should not constitute a real proof. This must be achieved by other means such as kinetic batch experiments. The results do not present enough conclusive evidence to be directly applicable in the field of groundwater risk assessment; but the methodology used may be more appropriate to study the sorption chemistry because of the apparent  $K_{ad}$  solid concentration dependence and because of the question about the existence of the true equilibrium.

The example treated in this experiment shows that the partition equilibrium may not exist or is not able to be reached in the time scale of the study. The  $K_{ad}$  value could be inadequate even if the hydraulic flowrate is very low. Kinetic modeling of the sorption process appears to be most applicable.

The results show strong evidence that the chemical sorption reaction behaves differently as a function of the liquid concentration. The proposed two step model may be a valid mechanism at low concentrations. In this type of reaction (Equation [30]), there is not an equilibrium partitioning value ( $K_{ad}$ ) due to the slow kinetics of the second absorption step. Therefore, local equilibrium cannot be assumed in this situation. Even if a time is defined after which the solid-liquid system is supposed to reach an equilibrium, the plot of  $K_{ad}$  will show an apparent solid concentration dependence, because the sorption kinetic equation is a function of the free site solid concentration. The consequences of such observations are important, each experimenter should check the existence of equilibrium by a kinetic study. Due to the hydrophobic character of the organic matter in soil, the absorption of hydrophobic solutes into such materials should be expected and may result in a nonequilibrium situation, in the time scale of the study. Consequently, the  $K_{ad}$  value will not be adequate to describe partitioning in soil systems.

Even under actual equilibrium conditions, a column study will give access to more information than the simple equilibrium batch study, due to the dependence of sorption on the forward and reverse rate constants. In complex systems, different sorption reactions can be identified by performing runs of the column at variable flow rate. Because the solid concentration is of the same order of magnitude as in the soil, the results more accurately simulate actual field conditions.

Due to the heterogeneous nature of natural soil systems, it is often difficult to identify mechanisms related to each component.



However, a soil or a groundwater porous media are often characterized by the percentage of organic matter and by the location on the texture triangle (silt, sand, clay) (27). If the sorption reactions are known for each component, they can be balanced proportionally to describe the overall sorption. However, if there is a major mechanism responsible for most of sorption, minor components could be neglected.

As a conclusion, the present work shows that the sorption between 3,4-dichlorophenol and cellulose triacetate can be described by a two step mechanism: starting with a reversible surface sorption and following by an absorption into the polymer of the solid. Due to both the slow second step rate constant and the hydrophobic character of the chemicals used, multilayer sorption on the surface is suspected at high sorbate concentration. The column study under transient conditions presents some advantages compared to the equilibrium partition coefficient procedure: investigation of sorption mechanism, determination of the rate constants, situation close to field conditions.

#### RECOMMENDATIONS for FUTURE WORK

The weak aspects of this study have been the inappropriate reactor design and the analysis procedure.

The headwater of the column has been the source of numerous problems, so future researchers should design a reactor with a constant level feeding reservoir or something similar to avoid this problem.

The analysis procedure should be run continuously, if possible in order to minimize the delay between experiments and the time to access the results and to increase the number of trials by using a spectrophotometric method (U.V or visible) at the effluent point. This procedure is very close to a chromatographic analysis. Also a great amount of time can be saved by using a nonlinear regression computer program based on the calculation of the residual between the model and the experimental data.

The choice of the solid in the present study may also be a source of criticism, because of the hydrophobic character of the cellulose triacetate. The structural organization of such compounds in micelles is well known and may explain the high removals observed. However, as the continuation of this research will involve biodegradation, the primary concern was to use a solid able to provide the carbon substrate. Interesting inert materials, such as clay may be used if the carbon source is supplied in the liquid phase.

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## **APPENDICES**

# APPENDIX A. Column Sorption-elution Model

The developed model simulating the experimental pilot is based on the following equation ( 29 ):

$$\frac{d C_l}{d t} = D_c * \frac{d^2 C_l}{d x^2} - U_x * \frac{d C_l}{d x} + \frac{1}{p} * \frac{d \text{ Sorbed}}{d t} \quad [32]$$

where  $D_c$ : dispersion coefficient along the pathflow

$x$ : length of the pathflow

$U_x$ : pore flowrate

$p$ : porosity

which describes dispersion, advection and sorption;

$$\frac{d \text{ Sorbed}}{d t} = - k_1 * [C_l] * [S] + k_2 * [CsSs] \quad [33]$$

$$\frac{d S}{d t} = ( -k_1 * [C_l] * [S] + ( k_2 + k_3 ) * [CsSs] ) * \frac{1}{C_s} \quad [34]$$

$$\frac{d CsSs}{d t} = k_1 * [C_l] * [S] - ( k_2 + k_3 ) * [CsSs] \quad [35]$$

$$\frac{d Ds}{d t} = k_3 * [CsSs] \quad [36]$$

for the following reaction mechanism:



The transformation of these differential equations to a system of finite element equations, allows us to develop the model using a single



step method. The model, in the case of only advection and dispersion has been compared with the analytical solution, described in the literature (29).

The dispersion coefficient has been corrected for the numerical mixing  $U/2(dx-U*dt)$ . Because of the small  $dx$ ,  $dt$  and the large dispersion coefficient used in this work, the single step method is accurate. The stability requirement has been checked by a small electronic spreadsheet program simulating the different species through the beginning of the column, as a function of time and space. It was observed that the pulse input experiment was more sensitive to the stability criteria and therefore was used as reference for the determination of  $dx$  and  $dt$ . The respective values for  $dx$  and  $dt$  were 0.5 cm and 0.25 s. However for the tracer experiment, these values can be larger because the rate constants ( $k_1$ ,  $k_2$ ,  $k_3$ ) are set to zero.

The sensitivity of the model to the values of the kinetic rate constants has shown that the parameters were estimated with only 10% error. Graphs 10, 11 and 12 illustrate the effect of the value of the rate constants on the shape of the fitting curve. The fitting procedure was only a trial and error method, but techniques of nonlinear regression can be used advantageously to save some time.

The headwater is modeled as an ideal plugflow reactor with a mixed initial distribution, created by the pulse injection itself. The glass bead drain section is neglected by overestimating the dispersion coefficient for the reactive solid, because of the large diameter of the channels and due to the small length of this section.

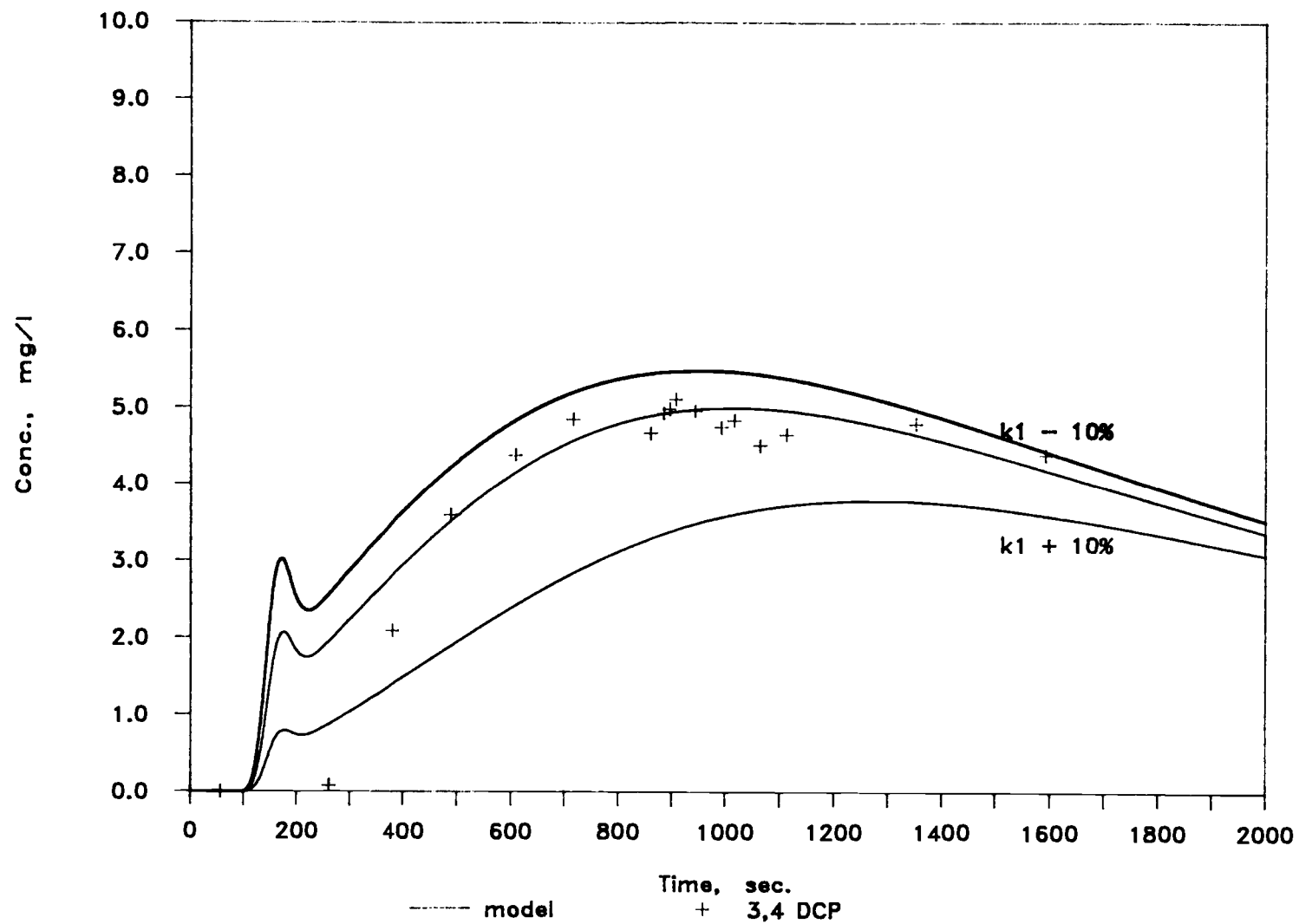


Figure 10: Model sensitivity to  $k_1$

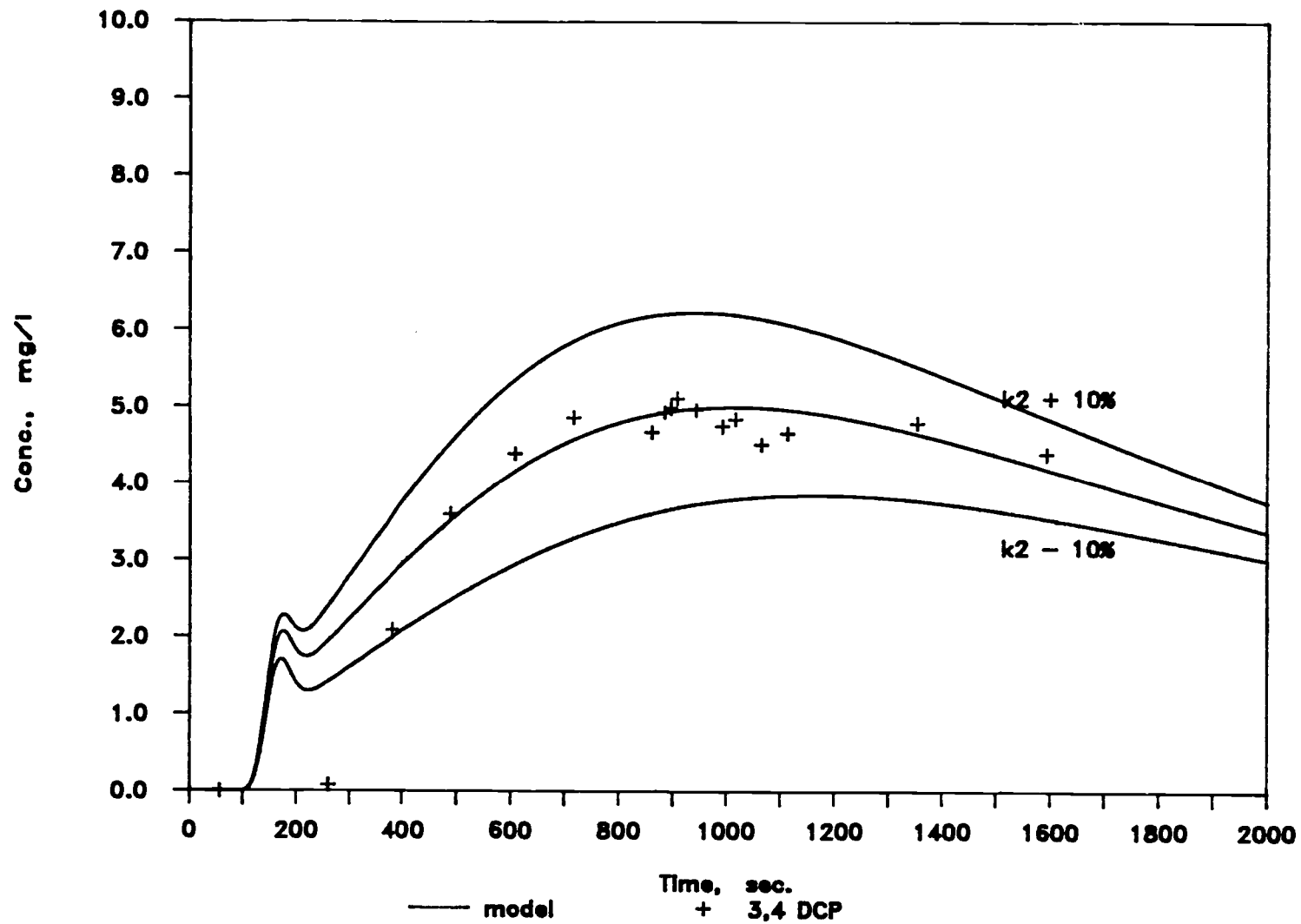


Figure 11: Model sensitivity to  $k_2$

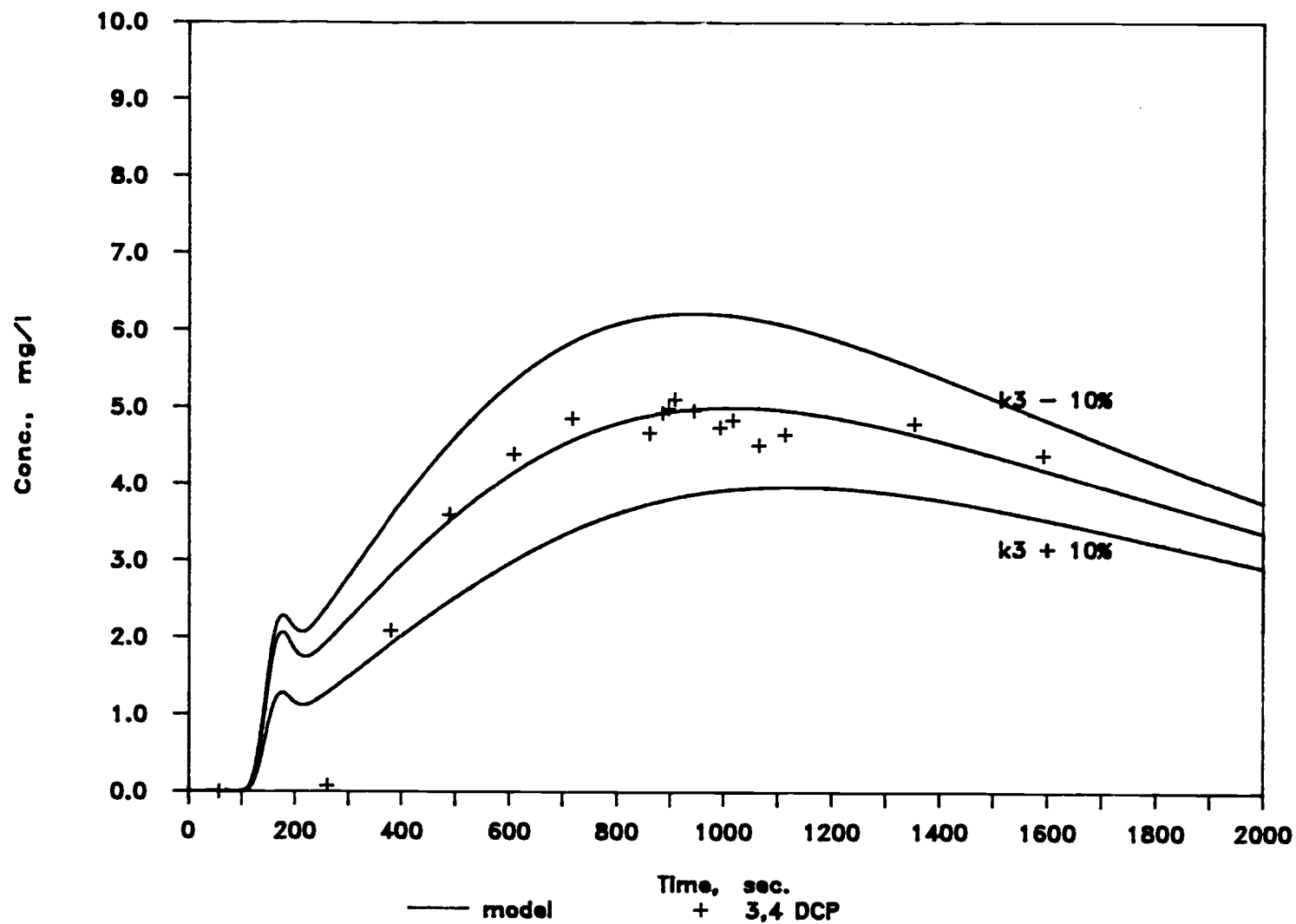


Figure 12: Model sensitivity to  $k_3$

\$Debug

```

C*****
C
C          Soil column sorption-elution model
C
C*****
      Dimension CsSs(500,2),S(500,2),Cl(500,2),Clw(500,2),Ds(500,2)
      Character*20 Result
      Integer Endt
      Real K1,K2,K3
      Write(*,'(/A)') Results filename   .dat  '?'
      Read(*,1) Result
1  Format(A)
      Open(5,File=Result,Status='New')
      Write(*,'(/A)') Enter parameters as listed'
      Write(*,'(/A)') Column flow  Q  ml/s  '?'
      Read(*,*) Q
      Write(*,'(/A)') Column cross-section  A  cm^2  '?'
      Read(*,*) A
      Write(*,'(/A)') Media porosity  p  '?'
      Read(*,*) p
      Write(*,'(/A)') Poreflow velocity  U/p  cm/s  '?'
      Read(*,*) U
      Write(*,'(/A)') Column dispersion coeff.  Dc  cm^2/s  '?'
      Read(*,*) D
      Write(*,'(/A)') Solid conc.  S0  g/l  '?'
      Read(*,*) S0
      Write(*,'(/A)') Capacity  Cs  mg/g  '?'
      Read(*,*) Cs
      Write(*,'(/A)') Porosity sorption rate cst  K1/p  1/g/s  '?'
      Read(*,*) K1
      Write(*,'(/A)') Porosity desorption rate cste  K2/p  1/s  '?'
      Read(*,*) K2
      Write(*,'(/A)') Porosity partitionning rate cste  K3/p  1/s  '?'
      Read(*,*) K3
      Write(*,'(/A)') Delta t  Dt  s  '?'
      Read(*,*) Dt
      Write(*,'(/A)') Delta x  Dx  cm  '?'
      Read(*,*) Dx
      Write(*,'(/A)') Completely mixed headwater  Vcm  ml  '?'
      Read(*,*) Vcm
      Write(*,'(/A)') Cell number  N =L/Dx  '?'
      Read(*,*) N
      Write(*,'(/A)') End time  Endt  s  '?'
      Read(*,*) Endt
      Write(*,'(/A)') Influent conc.  Cin  mg/l  '?'
      Read(*,*) Cin
      Write(*,'(/A)') Pulse input conc.  C10  mg/l  '?'
      Read(*,*) C10
      Write(*,'(/A)') Pulse input volume  V  ml  '?'
      Read(*,*) V

```

```

      Write(*,'(/A)')' Headwater above solid W ml ?'
      Read(*,*) W
      Write(*,'(/A)')' Print out time Ptime >= Dt s ?'
      Read(*,*) Ptime
c:
c: Wx cell length in the headwater (plugflow)
c:
      Wx=U*p*Dt
c:
c: Initialization reset
c:
      Do 5 I=1,N
      CsSs(I,1)=0
      S(I,1)=S0
      Ds(I,1)=0
5 Cl(I,1)=0
c:
c: Headwater initial distribution
c:
      Do 7 J=1,INT(Vcm/(A*Wx))
7 Clw(J,1)=Cl0*V/(INT(Vcm/(A*Wx))*A*Wx)
      Do 8 J=INT(Vcm/(A*Wx))+1,INT(W/(A*Wx))
8 Clw(J,1)=0
c:
c: Internal counters
c:
      Time=0
      Print=0
      Write(5,100) Time , CL(N,1)
c:
c: Loop over the time
c:
      Numb=NINT(Endt/Dt)
      Do 15 J=1,Numb
c:
c: Advection in the headwater
c:
      Clw(1,2)=Clw(1,1)+U*p*Dt/Wx*(Cin-Clw(1,1))
      Clw(INT(W/(A*Wx)),2)=Clw(INT(W/(A*Wx)),1)+U*p*Dt/Wx*(Clw(INT(W/(A*
$Wx))-1,1)-Clw(INT(W/(A*Wx)),1))
      Do 9 I=2,INT(W/(A*Wx))-1
9 Clw(I,2)=Clw(I,1)+U*p*Dt/Wx*(Clw(I-1,1)-Clw(I,1))
c:
c: Cli : liquid concentration entering the reactive media
c:
      Cli=Clw(INT(W/(A*Wx)),2)
c:
c: Values after dT for CsSs, S, Cl, Ds species at the last and the first
c:
      CsSs(1,2)=CsSs(1,1)+(K1*Cl(1,1)*S(1,1)-(K2+K3)*CsSs(1,1))*Dt
      CsSs(N,2)=CsSs(N,1)+(K1*Cl(N,1)*S(N,1)-(K2+K3)*CsSs(N,1))*Dt

```

```

S(1,2)=S(1,1)-(K1*Cl(1,1)*S(1,1)-(K2+K3)*CsSs(1,1))*Dt/Cs
S(N,2)=S(N,1)-(K1*Cl(N,1)*S(N,1)-(K2+K3)*CsSs(N,1))*Dt/Cs
Ds(1,2)=Ds(1,1)+K3*CsSs(1,1)*Dt
Ds(N,2)=Ds(N,1)+K3*CsSs(N,1)*Dt
Cl(1,2)=Cl(1,1)+(D-U/2*(Dx-U*Dt))*Dt/Dx**2*(Cl(2,1)-Cl(1,1))+U*Dt/
$Dx*(Cl(1,1)-Cl(1,1))-(K1*Cl(1,1)*S(1,1)-K2*CsSs(1,1))*Dt
Cl(N,2)=Cl(N,1)+(D-U/2*(Dx-U*Dt))*Dt/Dx**2*(Cl(N,1)-Cl(N,1))+U*D
$t/Dx*(Cl(N,1)-Cl(N,1))-(K1*Cl(N,1)*S(N,1)-K2*CsSs(N,1))*Dt
c:
c:   Increment for the species over dT between the first and the last
c:
      Do 20 I=2,N-1
        CsSs(I,2)=CsSs(I,1)+(K1*Cl(I,1)*S(I,1)-(k2+k3)*CsSs(I,1))*Dt
        S(I,2)=S(I,1)-(K1*Cl(I,1)*S(I,1)-(K2+K3)*CsSs(I,1))*Dt/Cs
        Cl(I,2)=Cl(I,1)+(D-U/2*(Dx-U*Dt))*Dt/Dx**2*(Cl(I+1,1)+Cl(I-1,1)-2*
        $Cl(I,1))+U*Dt/Dx*(Cl(I,1)-Cl(I,1))-(K1*Cl(I,1)*S(I,1)-K2*CsSs(I,
        $1))*Dt
        Ds(I,2)=Ds(I,1)+K3*CsSs(I,1)*Dt
20  Continue
      Print=Print+Dt
      Time=Time+Dt
c:
c:   Print out of the results
c:
      IF((Cl(N,2).GT.0).AND.(INT(Print).EQ.INT(Ptime))) Write(5,100) Tim
      $e,Cl(N,2)
      IF(INT(Print).EQ.INT(Ptime)) Print=0
c:
c:   Permutation   t+dt = t
c:
      Do 25 I=1,N
        CsSs(I,1)=CsSs(I,2)
        S(I,1)=S(I,2)
        Ds(I,1)=Ds(I,2)
25  Cl(I,1)=Cl(I,2)
      Do 10 I=1,INT(W/(A*Wx))
10  Clw(I,1)=Clw(I,2)
15  Continue
100 Format(11x,E12.7,12x,E12.7)
    Write(*,'(A)')'          *** FIN ***'
    End

```

### Appendix B. TOC analysis

The TOC measurement was done by the classical procedure of combustion at 950°C in a pure atmosphere of O<sub>2</sub> and measurement of the resulting CO<sub>2</sub> by infrared detection, the exact sequence of this analysis was as described below:

1. preparation of the standard curve from a stock solution (1 g/l acetic acid) 400 mg C /l to 4, 20, 40, 60, 80 ppm standards
2. acidification with 2 drops concentrate HCl, and aeration with nitrogen gas to remove the mineral carbon (bicarbonate, carbonate)
3. injection of a 10 ul sample and plot of peak height versus concentration for the standard curve
4. injection of the column effluent
5. determination of the concentration by interpolation of the standard curve

The instrument used in this experiment was a Beckman Carbonaceous analyzer, equipped with an IR-315 Infrared analyzer. The oxygen flow was 80 ml/s, the oven temperature was set to 950 C. The amplifier gain was 21 to avoid too much noise.

The linear regression of the standard curve gave a correlation coefficient of 0.99 and the limit of sensitivity was 1 ppm.



Appendix C. Acetylation-Extraction and GC analysis

The acetylation and extraction procedure was as follow:

1. Samples were stored at 5<sup>0</sup> C in glass vials with teflon lined caps until they could be extracted.
2. A suitable sample volume was brought to 50 ml with double glass distilled water in a 125 ml separatory funnel.
3. Eighty microliters of 15 ug/ml 2,6-dibromophenol in HPLC grade methanol was added as internal standard.
4. One ml of 0.72 g/ml K<sub>2</sub>CO<sub>3</sub> was added as buffer. The chemical was baked at 550<sup>0</sup> C prior to preparation of the solution.
5. One ml of acetic anhydride was added.
6. Separatory funnels were shaken for two minutes with frequent venting and were left quiescent two hours.
7. Acetylated samples were extracted with 5 ml HPLC grade n-hexane for two minutes.
8. Hexane extracts were transferred to brown glass vials with teflon lined caps and stored at 5<sup>0</sup> C until they were analyzed by ECD gas chromatography.

The splitless injection technique was used with a purge time of 0.5 minute. The temperature program was as follows:

initial temperature	45 C
initial time	2 min
first rate	15 C/min until 105 <sup>0</sup> C
second rate	5 C/min until 160 <sup>0</sup> C

The standard curve was constructed by plotting the mass of 3,4-DCP injected versus the ratio of the 3,4-DCP area to the 2,6-DBP used as internal standard, the eight points covered a range of 0 to 3 ng for a injection volume of 1 ul. The standards were shot for each series of analysis. The correlation coefficients of the linear regression have never been less than 0.99, the mass injected for the sample was estimated by interpolation. The aqueous concentration was then calculated using the following relationship:

$$Cl \text{ mg/l} = \frac{\text{mass injected ng}}{1 \text{ ul}} * 5000 \text{ ul} * \frac{1}{\text{sample vol. ml}}$$

Replicate injections have demonstrated the reproducibility of this method, however the overall accuracy of this procedure estimated by comparison between the estimated aqueous concentration of repeated extractions of the same sample has not been less than 5%

Data sheet

8/22/86

Tracer experiment: injection 1 ml 50 g/l  $\text{Cl}^-$ 

flow 0.637 ml/s

time increment for the sampling 6 s

triplicate

## Results:

Time, sec.	Conc., g/l $\text{Cl}^-$
-----	-----
0	0
14	0.05
15	0.05
16	0.45
18	2.7
19	3.9
21	6.0
25	6.9
26	5.95
27	5.1
29	3.0
31	1.15
32	1.0
33	0.8
35	0.35
37	0.1

Data sheet

9/02/86

Tracer experiment: injection 1 ml 50 g/l  $\text{Cl}^-$ 

flow 0.18 ml/s

time increment for the sampling 6 s

## Results:

Time, sec.	Conc., g/l $\text{Cl}^-$
-----	-----
0	0
69	0.25
75	0.85
81	2.35
87	4.75
93	6.91
99	8.46
105	7.06
111	5.21
117	3.25
123	1.80
129	1.00
135	0.55
141	0.35
147	0.10

Data sheet

8/22/86

Pulse input: injection 1 ml 3000 mg/l 3,4-DCP

flow 0.637 ml/s

time increment for the sampling 12 s

## Results:

Time, sec.	Conc., mg/l 3,4-DCP
-----	-----
6	0
18	0
30	4.25
42	28.60
54	21.0
66	17.65
78	12.41
90	10.75
102	7.56
114	7.72
174	5.55
294	3.0
414	1.70
534	1.23
654	0.94

Data sheet

9/07/86

Pulse input: injection 1 ml 3000 mg/l 3,4-DCP

flow 0.16 ml/s

time increment for the sampling 12 s

## Results:

Time, sec.	Conc., mg/l 3,4-DCP
0	0
56	0
260	0.08
380	2.09
488	3.60
608	4.39
716	4.86
860	4.67
884	4.93
896	4.99
908	5.11
944	4.96
992	4.75
1016	4.84
1064	4.51
1112	4.66
1352	4.80
1592	4.39

Data sheet

10/09/86

Step input: influent concentration 3000 mg/l 3,4-DCP

flow 0.147 ml/s

time increment for the sampling 12 s

## Results:

Time, sec.	Conc., mg/l 3,4-DCP
-----	-----
0	0
56	0
114	1.8
138	167
174	347
222	644
282	729
354	804
462	981
570	1161
C in	3081

Data sheet

10/18/86

Step input: influent concentration 500 mg/l 3,4-DCP

flow 0.18 ml/s

time increment for the sampling 12 s

## Results:

Time, sec.	Conc., mg/l 3,4-DCP
0	0
42	0
66	0
114	0.00
150	17.0
174	63.1
198	121
210	150
258	215
366	279
570	336
810	350
1038	380
1254	386
1470	410
C in	488