

# Dynamic simulation and modeling of PCP transport between sediment and water \*

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**Abstract**—A model to calculate the concentration of organic pollutant in the water column is presented. The inflow, outflow, adsorption of pollutant to the suspended particles and settling of particles, diffusion across the sediment-water interface, and volatilization to the atmosphere were considered in this model. Dynamic simulation experiment of pentachlorophenol(PCP) has been made in the laboratory. The model parameters were also estimated with experimental data(diffusion mass transfer coefficient,  $0.00112\text{m/d}$ ; net settling velocity of particles,  $0.323\text{ m. d}^{-1}$ ; volatilization rate constant,  $1.94 \times 10^{-4}\text{d}^{-1}$ ). There are little differences between calculated values and measured values. Adsorption of pollutant to the particles and settling of particles are very important mechanisms for removal of organic pollutant from the water. The principles and methods of this model are also applicable to the prediction of the concentration of other trace elements and organic constituents in aquatic systems.

**Keywords:** dynamic simulation; modeling; suspended particles; PCP transport; sediment/water interface.

## 1 Introduction

The conception of multimedia environmental model has been presented as people increasingly realized the issues about the multimedia environment in the early 1980's(Cohen, 1984). Many models have been rapidly developed and showed a potential prospect of application in the assessment and management of toxical and hazardous pollutants. There are four main types of multimedia environmental models(Ye, 1994): (1) box models of multimedia environment (Cohen, 1985); (2) plant roots model of pesticide(e. g. Carsel, 1985; Donigian, 1987); (3) accumulation models of aquatic food chains (Thomann, 1984); (4) fugacity models of multimedia environment (Mackay, 1982).

Multimedia environment has different environment interfaces, such as atmosphere-water interface, atmosphere-soil interface, atmosphere-organisms interface, water-sediment interface, and water-organisms interface. The distributions of pollutants in multimedia environment are results of the transport across these interfaces(Cohen, 1986). The transport in a water and sediment environment involves the adsorption of pollutants to particles, diffusion across water-sediment interface, settling and resuspension of particles(Snodgrass, 1984).

In this study a dynamic experiment was carried out to simulate pentachlorophenol(PCP) transport in a water column. Based on the experimental data a mass balance model was developed. The purpose is to provide the information needed in planning pollution abatement measures and the management of water quality.

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PCP is widely used as pesticide, herbicide, and wood preservation and exists in most areas of China, especially in area where schistosomiasis was once spread and paper mill wastewater is discharged (Luo, 1990). Because of its hard to solution property, PCP can remain in the environment and can be accumulated in the organisms through food chains. It can not only cause health hazard to human directly but can also from potential genetic hazard (Saber, 1985). So PCP is primarily concerned in this study.

Below, the structure and parameterization of the model is described, along with the dynamic simulation experiment. Finally model parameters are estimated and the results are analyzed.

## 2 Model structure

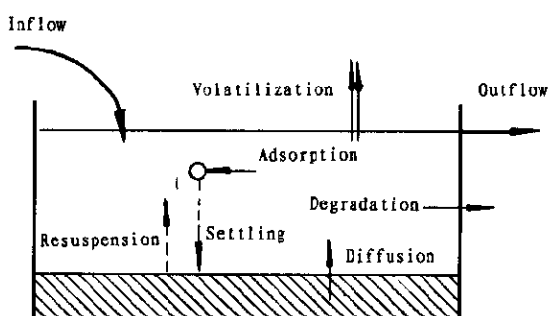


Fig.1 Sketch diagram of pollutant transport model

In an environmental system where water column, sediment, suspended particles, and atmosphere interplay with each other, pollutants get into water column with inflow, adsorb onto particles, diffuse across sediment-water interface, volatilize to atmosphere, and get out with outflow. Particles adsorbed with pollutants settle and resuspend in water column. The transport processes are described in Fig. 1.

According to Fig. 1, the differential mass balance equation for water column is

$$V \frac{dC}{dt} = W - QC - (V_s - V_r)fAC - k_s((1-f)C - C_{pw})A - K_vVC - K_dVC. \quad (1)$$

Where  $C$  is the total concentration of pollutant in water column ( $\text{g}/\text{m}^3$ );  $t$  is the time (day);  $V$  is the volume of water column ( $\text{m}^3$ );  $W$  is the pollutant loading rate ( $\text{g}/\text{d}$ );  $Q$  is the outflow rate ( $\text{m}^3/\text{d}$ );  $V_s$  is the settling rate of particles ( $\text{m}/\text{d}$ );  $V_r$  is the resuspension rate of sediment ( $\text{m}/\text{d}$ );  $A$  is the interface area ( $\text{m}^2$ );  $C_{pw}$  is the concentration of pollutant in porewater ( $\text{g}/\text{m}^3$ );  $k_s$  is the sediment-water transport coefficient ( $\text{m}/\text{d}$ );  $f$  is the fraction of pollutant that is particulate in water column;  $K_v$  is the volatilization rate constant ( $\text{d}^{-1}$ );  $K_d$  is the degradation rate constant ( $\text{d}^{-1}$ ).

While degradation of the pollutant can be neglected in the system, Equation (1) can be transformed to

$$\frac{dC}{dt} = - (Q/V + (V_s - V_r)fA/V + k_s(1-f)A/V + K_v)C + (W/V + k_sAC_{pw}/V), \quad (2)$$

$$\text{let } P(t) = (Q/V + (V_s - V_r)fA/V + k_s(1-f)A/V + K_v)$$

$$\text{and } R(t) = (W/V + k_sAC_{pw}/V),$$

then Equation (2) can be simplified to

$$dC/dt = -P(t)C + R(t). \quad (3)$$

The general solution of Equation(3) is

$$C(t) = e^{\int -P(t)dt} \left( \int R(t) e^{\int P(t)dt} dt + c_0 \right). \quad (4)$$

Where  $C_0$  is a constant dependent on boundary conditions.

### 3 Experiment section

#### 3.1 Adsorption experiment of PCP

50ml of known concentration of PCP solution and 2 g sediment sample were placed in each of a series of 100ml Erlenmeyer flask. The flask were sealed and shaken in an oscillator for 24 hours. The slurries were centrifuged at 4000r/min for 30min. The supernatant was filtered through 0.45 $\mu$ m micro filter membrane. The equilibrium concentration of PCP in liquid phase was determined by UV spectrophotometer (Huang, 1992). Freundlich isotherm was plotted in Fig. 2, and the adsorption constants  $K_f$  and  $1/n$  were calculated.

#### 3.2 Dynamic simulation experiment

The device of simulation experiment is illustrated in Fig. 3. The main part of the device is a retangulate glass tank(length 87.5cm, width 40.0cm, height 50.0cm), a baffle is placed near the water inlet to prevent the turbulence of sediment caused by inflow. 10L PCP solution of 13.3g/m<sup>3</sup> was added into a loading chamber every day and was pumped into the water tank. Because the main purpose of this work is to study the transport processes of pollutants through environmental interfaces, we added 2 g NaN<sub>3</sub> to the inflow daily to inhibit the biodegradation of PCP in experiment process. Concentrations of PCP in water column, sediment, and porewater were sampled and determined at regular intervals. Where porewater was sampled with centrifugation-filtration method (Steven, 1995) and determined by UV spectrophotometer(Huang, 1992), PCP concentrations in water column and sediment were also determined by UV spectroscopy after pretreatment as described by Huang(Huang, 1992). Suspended solid concentration(SS), pH value and temperature of water column were also determined in this experiment.

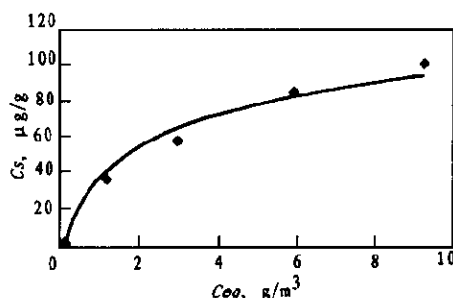


Fig.2 Isotherm of PCP

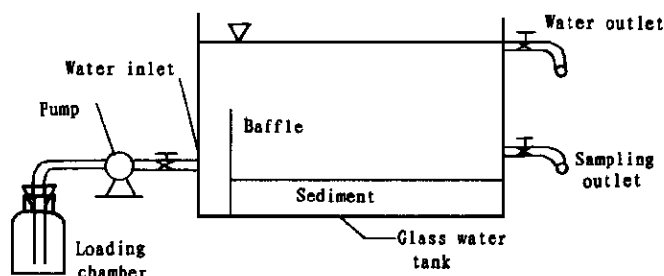


Fig.3 The sketch diagram of the device of simulation experiment

## 4 Results

Adsorption curve of PCP in the equilibrium experiment is shown in Fig. 3. With the least square method, the adsorption constants for the isotherm were calculated ( $K_f = 17.64$ ,  $1/n = 0.934$ ).

$C$ ,  $C_{pw}$ , the concentration of PCP in sediment  $C_s$ , SS and some environmental parameters such as pH and water temperature were all determined in the dynamic simulation experiment and the results are shown in Table 1.

Table 1 Measured results in the dynamic simulation experiment

Date	$t$ , day	$C$ , g/m <sup>3</sup>	$C_s$ , g/m <sup>3</sup>	$C_{pw}$ , g/m <sup>3</sup>	SS, g/m <sup>3</sup>	Water temperature, °C	pH
6.5	0	0.391	6.89	0	13.0	28.0	7.68
6.6	1	0.705	8.35	0.335	11.0	27.8	8.46
6.8	3	2.463	9.58	0.732	10.0	27.8	8.30
6.10	5	3.830	12.90	1.011	11.2	28.0	8.04
6.12	7	4.868	15.03	1.335	9.8	27.2	8.10
6.14	9	5.639	16.73	1.551	8.9	28.4	8.14
6.16	11	6.145	18.17	1.712	8.4	27.3	8.12
6.18	13	6.544	19.36	1.811	8.0	27.5	8.09
6.20	15	6.810	20.40	1.851	7.6	26.7	7.98
6.22	17	7.022	21.60	1.870	7.0	27.2	7.96
6.24	19	7.049	22.53	1.883	6.7	26.4	8.02
6.26	21	7.102	23.41	1.894	6.2	27.1	7.94

## 5 Discussions

### 5.1 Calculation of $f$

As  $f$  is the fraction of PCP that is particulate in water column, and can be expressed as

$$f = \frac{V \cdot SS \cdot C_s}{V \cdot C}, \quad (5)$$

where,  $C_s$  is sorbed concentration of PCP ( $\mu\text{g/g}$ ), which can be expressed as  $C_s = K_f C_{\text{dis}}^{1/n}$ .  $C_{\text{dis}}$  is the concentration of PCP that is dissolved in water column and is equal to  $(1 - f)C$ . So the expression of  $C_s$  is

$$C_s = K_f (1 - f)^{1/n} \cdot C^{1/n}. \quad (6)$$

Substitute Equation(6) into Equation (5) to yield

$$f = SS \cdot K_f \cdot (1 - f)^{1/n} \cdot C^{(1/n-1)}. \quad (7)$$

When  $SS$ ,  $C$ ,  $K_f$ , and  $1/n$  are all known,  $f$  can be calculated with Equation (7).  $SS$  in the water column was about  $10\text{g/m}^3$  in the dynamic simulation experiment process. Few data for adsorption coefficients have been reported for  $SS$  at concentration of  $10\text{g/m}^3$  (Snodgrass, 1984). Most of the experimental values are for relatively high  $SS$  value. The  $SS$  value in the adsorption

experiment of this study is about 40000g/m<sup>3</sup>. O’connor and Connelly(O’connor, 1980) have suggested that the adsorption coefficient should increase by 0.5 to 1 order of magnitude per order of magnitude decrease in suspended solids concentration. The SS value of adsorption experiment (40000g/m<sup>3</sup>) was about 4000 times of SS value of the simulation experiment(10g/m<sup>3</sup>).  $K_f$  can be approximately calculated as

$$K_f = 17.64 \times 4000^{0.75} = 8872.$$

Substituting the approximate value of  $K_f$  into the program, we calculated the  $f$  in experiment as shown in Table 2.

Table 2 Values of  $f$  during the experiment process

$t, \text{day}$	0	1	3	5	7	9	11	13	15	17	19	21
$f$	0.11	0.0913	0.0775	0.0838	0.073	0.0661	0.0623	0.0592	0.0563	0.052	0.0498	0.0462

5.2 Empirical expression of  $C_{pw}$

The concentration of PCP in porewater in experiment is shown in Table 1. To make easy the calculation of model,  $C_{pw}$  needs to be expressed as a function of time. According to the  $C_{pw}(t)$  curve in Fig. 4,  $C_{pw}$  can be approximately expressed as

$$C_{pw} = C_{pw0}(1 - e^{-kt}), \tag{8}$$

where  $C_{pw0}$ , and  $k$  are empirical constants, which can be estimated with the least square method ( $C_{pw0} = 2.018$ ,  $k = 0.1566$ ). The empirical expression of  $C_{pw}$  is

$$C_{pw} = 2.018 (1 - e^{-0.1566t}). \tag{9}$$

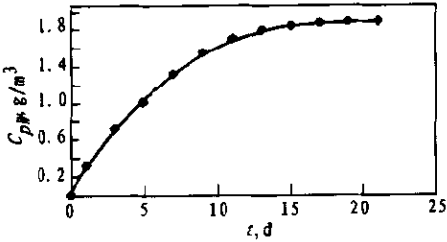


Fig.4 Concentration of PCP in porewater in experiment process

5.3 Volatilization rate constant  $K_v$

The determination of volatilization rate constant is based on the two - film theory(Jin, 1990). General expression of volatilization rate constant is

$$K_v = L^{-1}(1/K_1 + RT/(H_cK_g))^{-1}. \tag{10}$$

Where  $K_v$  is volatilization rate constant, h<sup>-1</sup>;  $L$  is depth of water, cm;  $K_1$  is mass transfer coefficient in liquid phase, cm/h;  $R$  is gas constant,  $82 \times 10^{-6} \text{ m}^3 \cdot \text{atm}/\text{K} \cdot \text{mol}$ ;  $T$  is absolute temperature, K;  $H_c$  is Hery’s law constant, atm.m<sup>3</sup>/mol;  $K_g$  is mass transfer coefficient in gas phase, cm/h; the property parameters of PCP are  $H_c = 3.4 \times 10^{-6} \text{ atm} \cdot \text{m}^3/\text{mol}$ ,  $K_1 = 12 \text{ cm/h}$ ,  $K_g = 1150 \text{ cm/h}$  (Lyman, 1991), water temperature in experiment process is taken as 300K, depth of water is 33.7 cm, with Equation(10),  $K_v$  was calculated as  $1.94 \times 10^{-4} \text{ d}^{-1}$ .

5.4 Estimation of model parameters

In Equation(4)  $P(t) = (Q/V + (V_s - V_r)fA + k_s(1 - f)A/V + K_v, Q(t) = (W/V + k_sAC_{pw}/V)$ . In the simulation experiment, some operational parameters are  $Q = 0.01 \text{ m}^3/\text{d}$ ,  $A = 0.336 \text{ m}^2$ ,  $V = 0.113 \text{ m}^3$ ,  $W = 0.113 \text{ g/d}$ . As shown in Table 2,  $f$  values in the experiment process did not vary very much. While in a natural water column,  $f$  value is often stable. To

simplify the calculation of model, we substituted the average value of  $f(0.069)$  to the expression of  $P(t)$ .  $K_v$  and  $k_s$  are constants. So  $P(t)$  can also be taken as a constant  $P$ .  $C_{pw}$  in the expression of  $Q(t)$  can be substituted as in Equation(9). The analytical solution of Equation(4) can be transformed to

$$C(t) = \frac{W}{VP} + \frac{2.018k_sA}{VP} - \frac{2.018k_sA}{V(P-0.1566)}e^{-0.1566t} + C_2e^{-Pt}. \quad (11)$$

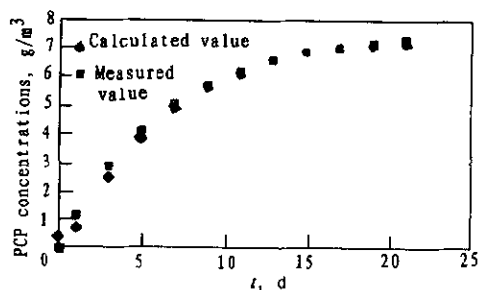


Fig.5 Comparison of measured and calculated value of PCP concentrations in water at the dynamic simulation experiment

Where  $C_2$  is a constant,  $C_2$ ,  $k_s$  and  $P$  are model parameters that need to be estimated. With net methods (Ye, 1989), model parameters were estimated and calculated as  $C_2 = -2.246$ ,  $k_s = 0.00112$ ,  $P = 0.1579$  in computer.  $f$ ,  $P$ ,  $k_s$ , and  $K_v$  were substituted to the expression of  $P(t)$  to calculate  $(V_s - V_r)$  as 0.323 m/d. Substituting the above parameters to Equation(11),  $C$  values

can be calculated at different time in the experiment. Twelve groups of calculated and measured values were compared in Fig. 5, and

small sum of squares of the differences as  $0.468(\text{g/m}^3)^2$  was obtained. It is thus clear that the model with estimated parameters can described the variations of concentration of PCP.

### 5.5 Determination of main transport process

In Equation(3), the term  $Q(t)$  represents the increase of concentration of pollutant in water phase, the term  $P(t)C$  represents the loss of concentration of pollutant in water phase.

As to  $Q(t) = (W/V + k_sAC_{pw}/V)$ , the first term  $W/V(1.177)$  presents the increase of PCP caused by inflow, the second term  $k_sAC_{pw}/V$  represents the increase of pollutant caused by the diffusion of PCP from sediment porewater to water column, with a maximum value of 0.0066. It is obvious that the increase of pollutant in water environment is mainly caused by the inflow loading.

As to  $P(t) = (Q/V + (V_s - V_r)fA + k_s(1-f)A/V + K_v)$ , the first term  $Q/V(0.0885)$  represents the loss of PCP in water phase with outflow, the second term  $(V_s - V_r)fA(0.0663)$  represents the loss of pollutant caused by settlings of particles adsorbed with PCP, the third term  $k_s(1-f)A/V(0.00305)$  represents the loss caused by the diffusion of PCP from water to sediment phase, and the last term  $K_v(1.94 \times 10^{-4})$  represents the loss by volatilization. The proportions of these terms in total loss are shown in Fig. 6. It is evident that loss of PCP caused by outflow and settling of particles adsorbed with PCP are main transport processes in the total loss of PCP in water phase. The two terms account for 56 percent, 42 percent of total

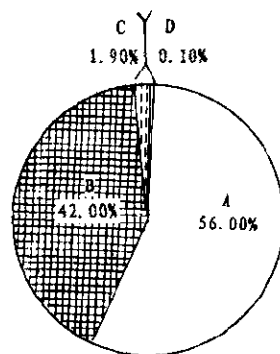


Fig.6 Sketch diagram of PCP loss in proportion

A. outflow loss; B. loss caused by the settling of particles adsorbed with PCP; C. loss by diffusion; D. loss by volatilization

loss respectively. Loss by diffusion accounts for 1.9 percent, and loss by volatilization accounts only for 0.1 percent of total loss and can almost be neglected.

## 6 Conclusion

PCP as a typical organic pollutant was considered and the transport processes such as adsorption, diffusion, settling and resuspension in water environment were involved. Dynamic experiment was made and model parameters were estimated. The results demonstrated that the model can accord with actual situation quite well and it is feasible to predict the concentration of pollutants with this model in a water environment without biodegradation.

The results of model calculation show that the main process that caused the increase of pollutant in water environment is inflow, the main process to cause the loss of pollutant besides the outflow is settling of particles with pollutant adsorbed. As we can see, suspended particles play an important role in the transport of pollutants in water environment.

For the simplification of the model, loss caused by the biodegradation was not considered in the model calculation. So the model can only describe the transport of hard to solution pollutants or the transport of pollutants in a water environment with little biodegradation. In future research work, more experimental results of pollutant transports are needed to calibrate the model to improve the universality of the model.

## References

- Carsel R F, Smith C N, Mulkey L A. *Ecol Modeling*, 1985, 30:49—69
- Cohen Y. Modeling of pollutant transport and accumulation in a multimedia environment. In the conference on "Geochemical and hydrologic processes and their protection". Council on Environmental Quality. Washington DC. September 25, 1984
- Cohen Y, Ryan P A. *Environ Sci Technol*, 1985, 19:412—417
- Cohen Y. Pollutants in a multimedia environment. Plenum: New York, 1985:7—48
- Donigan A S, Carsel R F. *Environmental Toxicology and Chemistry*. 1987, 6:241—253
- Huang J L. U V spectroscopy and the application. Beijing: Chinese Science and Technology Press, 1992.199—202
- Jin X C. Chemistry of organic pollutants. Beijing: Tsinghua University Press, 1990
- Luc Q X, Liu Y L, Song D L. Environmental behaviour and ecological toxicology symposium. Beijing: China Science and Technology Press, 1990.187—195
- Lyman W J, William F. Reehl and David Rosenblat. Handbook of chemical property estimation methods. New York: McGraw Hill, 1982.15—24
- Mackay D, Paterson S. *Environ Sci Technol*, 1982,16:654A—660A
- O'Connor D J, Connelly J P. *Water Res*, 1980, 14:1517—1523
- Saber D L, Crawford R L. *Appl Environ Microbiol*, 1985, 50:1512—1518
- Snodgrass W J, Lush D L, Walker R R, Bell W. Sediment/water interactions. Proceedings of the third international symposium on interactions between sediment and water. New York: Springer - Verlag, 1984. 229
- Steven E, Bufflap, Herbert E Allen. *Water Research*, 1995, 29:165—177
- Thomann R V, Connolly J P. *Environ Sci Technol*, 1984, 18:65—71
- Ye C M. *Journal of Advances in Environmental Science*, 1994, 2:9—25