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Influence of Sediment Types on the Sorption of Endothall

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Predicting the fate of chemicals using mathematical models requires accurate data derived from laboratory measurements of rate coefficients for the controlling processes (Neely 1979). The characteristics of the chemical and the aquatic environment determine which of the major fate processes, such as volatilization, hydrolysis, sorption, and biotransformation, are important in determining chemical fate and persistence. Sorption (partitioning) of compounds between water and solids occurs in all aquatic systems (Baughman and Lassiter 1978) and physical, chemical, and biological interactions are involved in the equilibrium of the chemical between the water and sediment (Dickson KL, Rodgers, Jr. JH, Saleh FY (1981) Measuring rate constants for chemicals in simple model aquatic laboratory systems. Report to the Chemical Manufacturers Assoc. CMA Project ENV-7-W). Also, due to the complexity and variability in sediment composition and chemical interactions, no simple systematic procedure for sorption prediction that is generally applicable is available (Karickhoff et al. 1979). Some relatively water soluble chemicals, such as the herbicide diquat, have large partition coefficients, and suspended solids and sediments play a major role in the persistence of these compounds (Simsiman et al. 1976).

Endothall (7-oxabicyclo (2,2,1) heptane-2, 3-dicarboxylic acid) is a relatively water soluble aquatic herbicide which is used for the control of numerous submerged aquatic weed species (Serns 1977). The recommended maximum allowable endothall concentration for domestic water supply and food additives is 0.2 mgL^{-1} (Fed. Regist. 1973). At recommended usage concentrations, endothall (Aquathol K) is not toxic to fish (24h LC_{50} bluegill=428 mgL^{-1}) (Pennwalt Chemical Corporation. Aquatic herbicide technical and sales literature. Pennwalt Chemical Corporation, Tacoma). The physical and chemical properties of endothall and the dipotassium salt of endothall which was utilized in this study are summarized in Table 1. This research on endothall sorption is part of a current study funded by the U.S. EPA to validate predictive fate models and decision support systems for control of nuisance aquatic vegetation.

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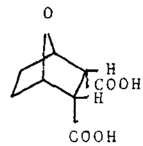
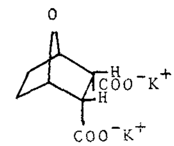
Table 1. Physical and chemical properties of endothall[1]

	Endothall	
Property	Acid	Dipotassium Salt
Structure		
Molecular Weight	186.06	262.26
Melting Point	$144^{o}C$	
Solubility in Water at $20^{o}C$	$100gL^{-1}$	$1228gL^{-1}$
Dissociation Constants	$pk_{a_1} = 3.4$ $pk_{a_2} = 6.7$	
Log Octanol/Water Partition Coefficient	1.91	0.132

[1] Pennwalt Chemical Corp.

MATERIALS AND METHODS

Two different water-sediment systems were employed in this study. Water was obtained from Pat Mayse Lake, a meso-oligotrophic reservoir in northeast Texas. Sediments were obtained from Pat Mayse Lake and Roselawn Cemetery Pond, a small eutrophic pond in north central Texas. Surface water was collected in a 21-liter Nalgene carboy, vacuum filtered through a glass - fiber filter (Schleicher & Schuell #30), and kept at $4^{o}C$ until use. Sediments were obtained using an Eckman dredge, wet-sieved to <2 mm particle size, dried at $103^{o}C$, and stored in a desiccator until use.

High purity (99.0%) endothall acid was obtained from the Quality Assurance Section of the U.S. EPA, Pesticides and Industrial Chemicals Repository, Research Triangle Park, North Carolina. The endothall-N- 2-chloroethylimide (99.0%) GLC standard and Aquathol K were obtained from the Pennwalt Chemical Corporation, Tacoma, Washington. Aquathol K was used in the experimental procedure. Pesticide-grade chloroform and A.C.S. grade carbon disulfide were used in sample cleanup and endothall extraction. Pesticide quality methanol was used in preparation of analytical standards. A.C.S. grade glacial acetic acid, 2-chloroethylamine hydrochloride (avail. from Aldrich Chemical Co.) and anhydrous sodium acetate were employed in the endothall extraction and derivitization procedure.

A Hewlett-Packard (HP) 5710 gas chromatograph equipped with a HP nitrogen-phosphorus detector was used for the detection of the endothall imide. The column, a glass 180 cm X 2 mm i.d., was packed with 10% SP 2100 on Supelcoport 100/120. The carrier gas was helium at a flow rate of 37.5 mL min^{-1}. Isothermal runs at 200°C oven temperature were employed with injection and detector temperatures of 250 and 300°C, respectively. A HP 3390A integrator was utilized for peak identification and quantitation. A Leco Carbon Analyzer model IR-12 was used for measuring the sediment organic carbon. A Servall RC2-B High Speed Centrifuge was employed for sediment centrifugation.

Water and sediment characteristics were determined according to standard procedures (Std. Methods 1975 and Black et al. 1965). Protocol for sorption measurement was that found essentially in the Federal Register (Fed. Regist. 1979). Sorption experiments were run at 1gL^{-1} sediment concentration. Desorption studies were not attempted due to destructive sediment analysis. The study was run in 500-mL glass-stoppered volumetric flasks which contained one-inch teflon magnetic stir bars, and the flasks were covered to exclude light. Initial endothall concentrations, using the herbicide formulation Aquathol K, ranged from 2.0 to 6.3 mgL^{-1}. Triplicates were run at each concentration level. Equilibration time (medium stir rate) was 4 days in order to ensure that complete chemical equilibration between phases had occurred. Test water with no chemical, test water and sediment with no chemical, and test water with chemical were run as procedure blanks and controls. After equilibration, each system containing sediment was separated using centrifugation for 30 minutes at 9,000 rpm. The supernatant was transferred to a teflon-lined screw-capped Erlenmeyer flask, acidified to pH 2, and held at 4°C until analysis. The sediment was transferred to an aluminum foil container and held at -4°C until analysis. Both water and sediment were analyzed according to the procedures outlined in Sikka and Rice (1973).

Quality control was achieved by (a) extraction efficiency analysis at representative test concentrations, (b) daily preparation of dilute endothall imide standards, and (c) frequent injection of standards. Extraction efficiencies for water and sediment ranged from 72 to 95%.

RESULTS AND DISCUSSION

The physical and chemical characteristics of the test water and sediments are shown in Tables 2 and 3, respectively. Wide variations in the sediment characteristics are illustrated; however, final system pH values ranged only from 6 to 7 in all tests. The Pat Mayse Lake sediment was predominantly sand with low percent organic carbon, while the Roselawn Cemetery Pond sediment was predominantly clay with more than one percent organic carbon. Six separate sorption experiments were run. The partition coefficient Kp was calculated for each test using the equation

$$Kp = \frac{[C]\text{sediment}}{[C]\text{water}},$$

Table 2. Physical and chemical characteristics of Pat Mayse Lake water[1].

Parameter	Value
pH at 25^{o}C	6.5-7.5
Alkalinity, mgL^{-1} as $CaCO_3$	60
Hardness, mgL^{-1} as $CaCO_3$	66
Orthophosphate, $mgPO_4$-P L^{-1}	0.02
Total Phosphate, $mgPO_4$-P L^{-1}	0.035
Ammonia, $mgNH_3$-N L^{-1}	0.03
Nitrate, $mgNO_3$-N L^{-1}	0.28
Total Dissolved Solids, mgL^{-1}	44
Total Suspended Solids, mgL^{-1}	5.9
Turbidity, NTU	22
Total Organic Carbon, mgL^{-1}	4-5

[1]All values for unfiltered samples except total dissolved solids.

Table 3. Physical and chemical characteristics of the test sediments.

Parameter	Sediment	
	Pat Mayse Lake	Roselawn Cemetary Pond
pH at 20^{o}C	6.2-6.4	8.3-8.5
Percent Total Organic Carbon	0.683 ± 0.069[1]	1.29 ± 0.03
Cation Exchange Capacity, meq/100g	16	34.2
Particle Size		
Percent Clay	26	60
Percent Silt	12	32
Percent Sand	62	7

[1]$\bar{x} \pm s$ (standard deviation).

where [C] represents the concentration of endothall in the sediment and in the water. All concentrations were measured at equilibrium (4 days), and both concentrations and calculated Kp values are shown in Table 4. Mean Kp values for each water-sediment type were 0.937 and 1.42 for Pat Mayse Lake and

Roselawn Cemetery Pond, respectively. A t-test was run on the data in Table 4, and the Kp values from each water-sediment type were not significantly different ($t_{0.05(2),9} = -2.02$; $p = 0.073$). A Freundlich sorption isotherm was constructed using the data presented in Table 4 according to the Freundlich equation:

$$\ln X/m = \ln K + 1/n\ C_e,$$

where X/m is equal to the amount of endothall adsorbed in mg kg^{-1} of dry sediment, C_e is the aqueous endothall equilibrium concentration in mgL^{-1}, and K and n are constants.

Table 4. Equilibrium endothall concentrations and calculated Kp values.

Sediment Type	Sediment Concentration, $mgkg^{-1}$	Aqueous Concentration, mgL^{-1}	Kp
Pat Mayse	0.823	1.93	0.426
Lake	2.13	1.58	1.348
	5.59	5.23	1.07
	3.72	3.35	1.11
	3.69	5.08	0.73
			$\bar{X} = 0.937$
Roselawn	5.92	2.79	2.12
Cemetery	4.79	4.67	1.03
Pond	6.92	4.34	1.59
	5.69	4.84	1.18
	6.65	4.16	1.6
	4.66	0.59	1.02
			$\bar{X} = 1.42$

Figure 1 shows the plot of ln X/m versus ln C_e for the combined test data plotted using linear regression. The actual values, predicted values, and upper and lower 95% confidence bands are plotted. A linear relationship between ln X/m and ln C_e exists for these data because the slope of the model was significantly different from zero ($p = 0.0026$); however, a low coefficient of determination, r^2, of 0.544 was observed. The use of more intermediate concentrations of endothall may have increased the r^2. The endothall equilibrium coefficient (K) calculated from the linear regression model for these systems was 0.958, which is relatively low.

These experimental results indicate that the sorption of endothall in two different water-sediment systems was not significantly different at the 0.05 confidence level. Due to the relatively low K exhibited for endothall sorption in this study, it can be concluded that sorption is not a significant process affecting the fate of endothall in the aquatic environments studied in this research. Other indirect evidence concerning the sorption of endothall indicated similar results. Analysis of the data reported in Simsiman and Chesters (1975) produced Kp values ranging from 0.41 to 0.90 for one water-sediment type. Also, a

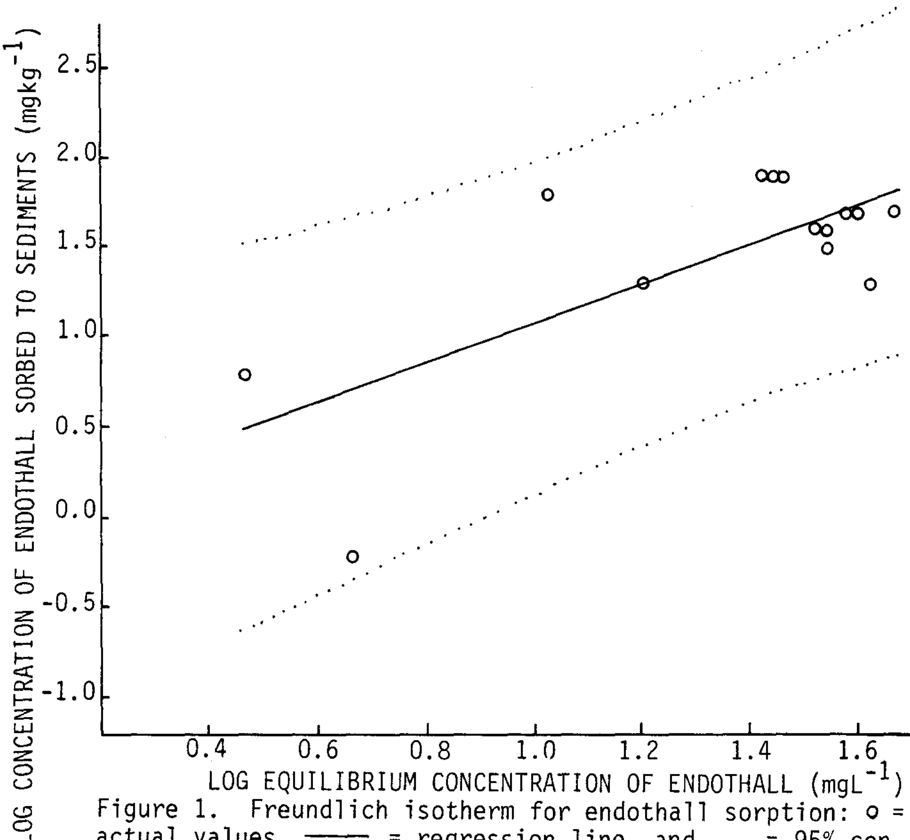


Figure 1. Freundlich isotherm for endothall sorption: o = actual values, ——— = regression line, and ... = 95% confidence bands (r^2 = 0.544; slope = 1.13; y intercept = -0.043).

calculated Kp value of 0.83 was obtained using the regression equation reported in Karickhoff et al. (calculated from K_{ow})(1979). Other fate processes that could affect the persistence of endothall in the aquatic environment are listed in Table 5. Except for biotransformation, the other fate processes probably play very minor roles in the fate of endothall in the aquatic environment (Simsiman and Chesters 1975).

A sorption protocol for the determination of sorption partition coefficients was applied to two different water-sediment systems containing endothall. Sorption of endothall in both system types was found to be relatively low and can be considered as a minor process in the fate assessment of endothall in aquatic systems. The relatively high concentration of endothall required for acute toxicity, a low sorption coefficient, and low environmental persistence ($t_{1/2}$) combine to make endothall a candidate for the control of nuisance aquatic vegetation.

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Table 5. Fate processes affecting endothall.

Process	Coefficient
Sorption	Kp = 0.958 (this paper) Kp = 0.56 (Neely and Mackay 1982)[1] Kp = 0.83 (Karickhoff et al. 1979)[1]
Volatilization	Not significant (Pennwalt Chem. Corp.)
Hydrolysis	Stable (Pennwalt Chem. Corp.)
Photolysis	Stable (Pennwalt Chem. Corp.)
Oxidation	Stable (Pennwalt Chem. Corp.)
Biotransformation	Major process (Pennwalt Chem. Corp.) 0.1 day^{-1} (water) and 0.45 day^{-1} (water and sediment)(IAS)[2]
Bioconcentration	BCF = 1.05 (Chiou et al. 1977)[1] BCF = 0.653 (Neely et al. 1974)[1]
K_T (overall)	0.27 day^{-1} (Hiltibran 1962)[3] 0.17 day^{-1} (Holmberg and Lee 1976)[3] 0.095 day^{-1} (Yeo 1970)[3] 0.45 day^{-1} (Frank and Comes 1967)[3]
$t_{1/2}$[4]	2.81 days (Frank and Comes 1967)[3]

[1]Value calculated using regression equation.

[2]Institute of Applied Sciences (1983) Sorption and biodegradation studies. Institute of Applied Sciences, North Texas State University, Denton, TX (unpubl).

[3]Value calculated from data presented in paper.

[4]The $t_{1/2}$ was calculated using the equation $t_{1/2} = \frac{0.693}{K_T}$, where K_T was the average K_T value reported in Table 4) (0.246 day^{-1}).

REFERENCES

Baughman GL, Lassiter RR (1978) Prediction of environmental pollutant concentration. In: Cairns, Jr. J, Dickson KL, Maki AW (eds) Estimating the hazard of chemical substances to aquatic life. ASTM, Philadelphia, p. 35.

Black CA, Evans DD, White JL, Ensminger LE, Clark FE, Dinavir RC (1965) Methods of soil analysis, vol. 1 and 2. American Society of Agronomy, Madison.
Chiou CT, Freed VH, Schmedding DW, Kohnert RL (1977) Partition coefficient and bioaccumulation of selected organic chemicals. J Agr Food Chem 11(5):475-478.
Fed Register (1973) Food additives: endothall. 38:10638.
Fed Register (1979) Toxic substances control: discussion of premanufacture testing policy and technical issues. 44:16250-16272.
Frank PA, Comes RD (1967) Herbicidal residues in pond water and hydrosoil. Weeds 16:210-213.
Hiltibran RC (1962) Duration of toxicity of endothall in water. Weeds 10:17-19.
Holmberg DJ, Lee GF (1976) Effects and persistence of endothall in the aquatic environment. J Wat Poll Contr Fed 48(12):2738-2746.
Karickhoff SW, Brown DS, Scott TA (1979) Sorption of hydrophobic pollutants on natural sediments. Water Res 13:241-248.
Neely WB (1979) An integrated approach to assessing the potential impact of organic chemicals in the environment. In: Dickson KL, Maki AW, Cairns, Jr. J (eds) Analyzing the hazard evaluation process. Amer Fish Soc and ASTM, Philadelphia, p. 74.
Neely WB, Mackay D (1982) An evaluative model for estimating environmental fate. In: Dickson KL, Maki AW, Cairns, Jr. J (eds) Modeling the fate of chemicals in the aquatic environment. Ann Arbor Science, Ann Arbor, p. 127.
Neely WB, Branson DR, Blau GE (1974) Partition coefficient to measure bioconcentration potential of organic chemicals in fish. Environ Sci Tech 8(13):1113-1115.
Serns SL (1977) Effects of dipotassium endothall on rooted aquatics and adult and first generation bluegills. Water Res Bull 13(1):71-80.
Sikka HC, Rice CP (1973) Persistence of endothall in the aquatic environment as determined by gas-liquid chromatography. J Agr Food Chem 21(5):842-846.
Simsiman GV, Chesters G (1975) Persistence of endothall in the aquatic environment. Water Air Soil Poll 4:399-413.
Simsiman GV, Daniel TC, Chesters G (1976) Diquat and endothall: their fates in the environment. Res Rev 62:131-174.
Standard methods for the examination of water and wastewater (1975) 14th ed. Amer Publ Health Assoc, Washington D.C.
Yeo RR (1970) Dissipation of endothall and effects on aquatic weeds and fish. Weed Sci 18:282-284.

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