

ENVIRONMENTAL MODELING OF TOXIC VOLATILE  
ORGANIC COMPOUNDS IN RIVERS

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## ABSTRACT

Accidental or deliberate discharge of toxic volatile organic compounds (VOC) in rivers may jeopardize water supplies of urban centers located downstream from the discharge site. However, VOC may be removed from aqueous solution in rivers through the natural process of volatilization. An integrated theory of volatilization of VOC from aqueous solution was developed using results from disparate studies and was altered to model stream dynamics. Preliminary application to a single field study was used to demonstrate the validity of the model as a first approximation.

Keywords: volatile organic compounds, priority pollutants.

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## INTRODUCTION

### Background

The presence of toxic volatile organic compounds (VOC) in drinking water or in potential sources of potable water, including rivers, has been an acute source of concern since the early 1970s. For example, Rook [1] and Bertsch et al., [2] showed that toxic and perhaps carcinogenic organic compounds were present at concentration levels of 10 to 1000 ppb in river and drinking waters, respectively. Regular or accidental discharge of such VOC in rivers may lead to contamination of water supplies of urban centers downstream from the discharge site. Consequently, a particular concern to river systems such as the Mississippi, South Platte, and Rio Grande in North America is the chronic exposure of nearby inhabitants to anthropogenic VOC in river water used for domestic consumption [2]. Although some compounds actually may be generated during treatment and distribution of drinking water [1], many more compounds in raw water sources may come from domestic or industrial discharges into rivers [3]. Thirty-one of the 129 compounds established by the U.S. Environmental Protection Agency (EPA) as priority pollutants are purgeable VOC [4]. These compounds include trihalomethanes, benzene and tetrachloroethylene. Because these compounds commonly have been found in drinking water supplies and rivers in the United States and present a health hazard, such VOC were made the subject of this study. A major objective of this research was the development of a model to predict the movement and fate of toxic volatile organic compounds (VOC) following point discharge into a river upstream from an urban center where water is used for human consumption.

In the development and application of a mathematical model for removal or loss of toxic VOC in streams, at least four issues must be addressed. These include: (1) characterization of pattern and composition of discharge; (2) mechanism of interaction between VOC and water; (3) relationship between stream characteristics; and 4) verification of accuracy of the model using actual streams or rivers. Between 1976 and 1982, a large body of theory regarding VOC in aqueous solutions was developed. However, a generalized theory for application with streams was never developed. A considerable portion of our research included summarizing and assimilating disparate studies, several of which were released during the period of this project. While mechanisms of removal of VOC in streams include volatilization, biodegradation and adsorption on clays, only volatilization will be investigated here as the most important of the three possible mechanisms of removal.

#### Integrated Theory of Volatilization of VOC from Aqueous Solutions.

Movement of VOC between aqueous solutions and the atmosphere has been the center of many studies. However, models, terminology and results from these various studies do not necessarily agree. During the period of this project, several separate and important developments were reported. These developments further stimulated the need for a complete integration of various theories and experimental results. However, this work represents more than a literature survey, because new approaches to volatilization of VOC with respect to rivers have been developed at New Mexico State University. Furthermore, direct application of this integrated theory to river systems may be found in the Results and Discussion section (page 24).



Volatilization Theory. The classical double-film theory was first applied to natural aquatic systems by Liss and Slater (5) who used a steady-state model of mass transfer. In this model, the existence of two undisturbed thin layers near the gas-liquid interface was assumed. On either side of these films, the bulk of each fluid was considered uniform in concentration.

Under steady-state conditions, mass flow (F) of VOC from liquid to gas phase equalled individual flows of mass across the laminar gas film,  $F_g$ , and the liquid film,  $F_L$ . Mass transport of VOC across these laminar films was governed only by molecular diffusion and was described by Fick's first law of diffusion (when time is a constant)

$$F_g = D_g (dC_g/dZ) \quad (1)$$

and

$$F_L = D_L (dC_L/dZ) \quad (2)$$

where  $D_g$  is the diffusion coefficient of VOC in the gas phase,  $D_L$  is diffusion in the liquid phase,  $C_g$  and  $C_L$  are concentrations of VOC in gas and liquid phases, respectively, and  $Z$  is the distance from the interface as shown in Figure 1.

Assuming a linear gradient in concentration of components in the laminar films, the term  $(dC/dZ)$  is equal to  $\Delta C/\delta$ , where  $\delta$  is the thickness of the film. For boundary conditions as shown in Figure 1, the mass transfer equation across the gas and liquid films becomes:

$$F_g = D_g (C_g^s - C_g)/\delta_g \quad (3)$$

and

$$F_L = D_L (C_L - C_L^s)/\delta_L \quad (4)$$

where  $C^s$  and  $C$  are concentration of the VOC in bulk solution and at the interface, respectively. In a dilute solution, the relationship between

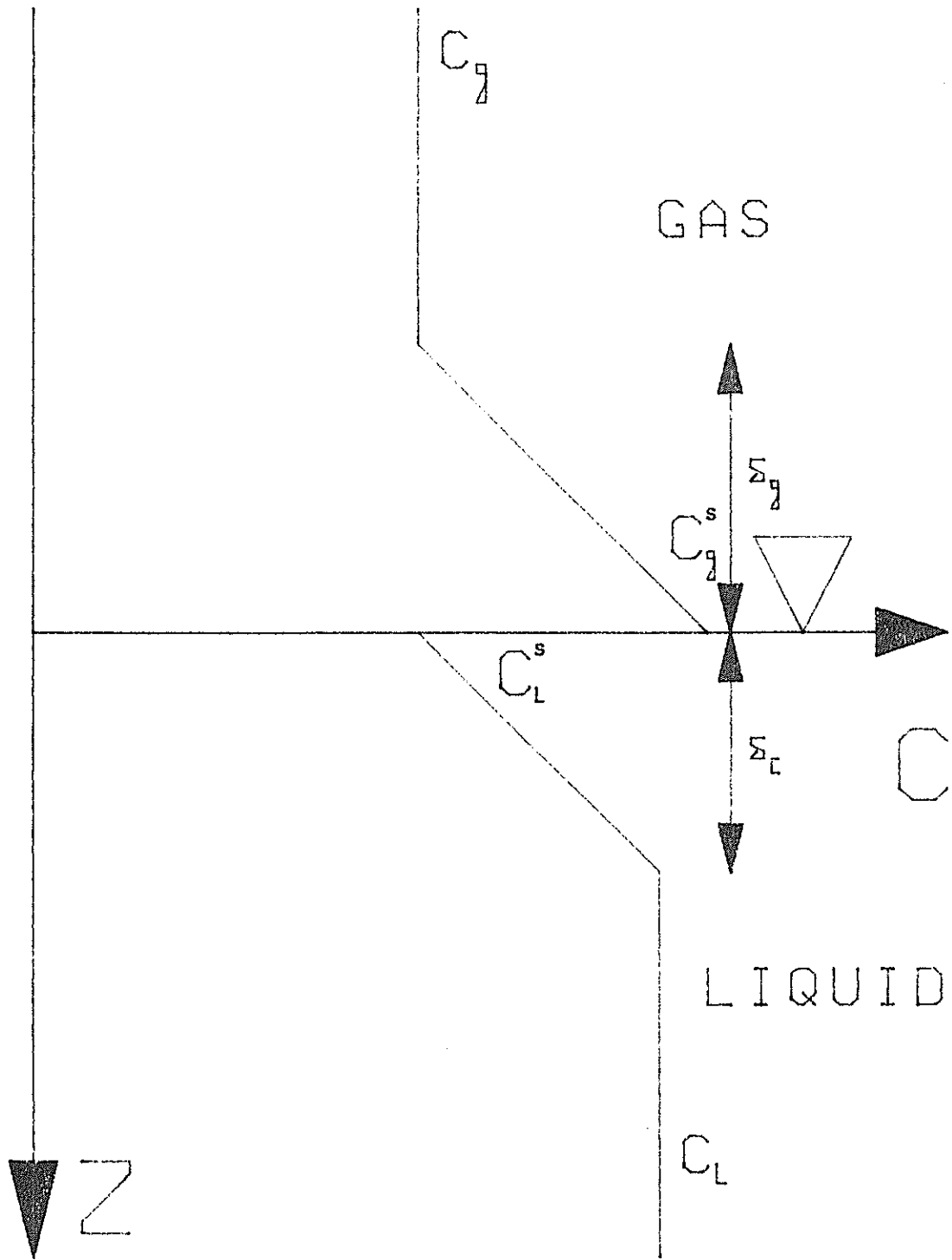


Figure 1. Concentration of VOC in Liquid and Gas Phases.

the concentration of the VOC at the interface may be described by Henry's law,

$$H = p^S/C_L^S = C_g^S RT/C_L^S \quad (5)$$

where H is the Henry's law constant for the dissolved gas,  $p^S$  is the partial pressure at the gas at the interface, R is the universal gas constant and T is the Kelvin temperature. Allowing k to represent the ratio between the diffusion coefficient and film thickness, the following relationship for the flux of the VOC is obtained by (equation 3 and 4) and using Henry's law to eliminate the interfacial concentrations

$$F = -K_L(C_L - C_g RT/H) \quad (6)$$

in which

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{RT}{Hk_g} \quad (7)$$

$$k_L = D_L/\delta_L \quad (8)$$

and

$$k_g = D_g/\delta_L \quad (9)$$

The overall rate transfer constant  $K_L$  is therefore dependent on the individual contributions of the diffusivity and film thickness in the liquid and gas phases. This simple model was used by Liss and Slater to calculate the flux of various gases across air-sea interface by estimating  $k_L$  and  $k_g$  [5]. Their results showed that mass transfer rates for most gases with low aqueous solubility were liquid phase controlled, while mass transfer rates for more soluble gases were vapor phase controlled. For compounds with intermediate solubility, both liquid and gas phase resistance contribute to the overall flux. There are serious limitations to the use of this model in actual environmental conditions. For example, the laminar film thickness and the Henry's law constant for VOC in dilute solutions are difficult to evaluate in streams and rivers.

The classical double-film theory is greatly simplified when the volatilization rate is controlled by either the liquid or gas transfer coefficient. According to Mackay and Leinonen [6], the phase resistances are approximately equal for Henry's law constants of less than  $1.6 \times 10^{-4}$  atm m<sup>3</sup>/mol. For higher values of H, the mass transfer process will be liquid phase controlled. Gas film transfer will control the transport process when the Henry's law constant is significantly lower than  $1.6 \times 10^{-4}$  atm m<sup>3</sup>/mol, based on the prior limitations. Rathbun and Tai [7] report that the transfer of the VOC priority pollutants is controlled by liquid film diffusion. For liquid film controlled compounds (i.e., high H values), the gas term in equations 6 and 7 may be neglected. Thus, for this case the computations of the overall transfer coefficient are simplified to:

$$K_L = k_L = D_L/\delta_L \quad (10)$$

Thus, according to the classical double-film theory for compounds with H considerably higher than  $1.6 \times 10^{-4}$  atm m<sup>3</sup>/mol, the mass flux and overall transfer coefficient are direct functions of the diffusion coefficient of the dissolved gas (VOC) in water to the first power.

Other Volatilization Models. A different model, the random surface renewal model as developed by Danckwertz [8], assumes that packets of bulk liquid travel to the interface where diffusion to the vapor phase occurs. In contrast with the classical theory, this model predicts that the liquid mass transfer coefficient,  $k_L$ , is a function of  $D_L^{0.5}$ . Dobbins [9] modified the previous model to allow for complete diffusion of the packets across the interface. This modification allows an agreement between the surface renewal model and the double-film theory. The improved model shows that  $K_L$  is a function of  $D_L^n$ , where n varies from

0.5 to 1.0 depending on the degree of turbulence of the liquid medium. The random renewal model predicts that in ideal stagnant conditions, the value of  $n$  is 1.0. As the degree turbulence increases,  $n$  approaches 0.5.

Smith et al. [10], experimentally evaluated the magnitude of  $n$  in agitated solutions and concluded that the value of the exponent  $n$  under agitated solution conditions should be 0.61. Matter-Müller et al. [11], also report that for all agitated solutions  $n$  may be considered to be constant and equal to 0.83. However, the effect of degree of turbulence on  $n$  has not been investigated further. The variability of  $n$  as a function of the degree of agitation in water bodies is presented in this report in the section entitled Dependence of Exponent  $n$  on the Degree of Agitation (page 19).

Overall Gas Transfer Coefficient. Overall transfer coefficients,  $K_L$ , of volatile organic compounds that are dissolved in the aqueous phase are required for calculations of mass transfer in the previous models. However, evaluation of  $K_L$  for specific compounds may be greatly simplified for highly volatile compounds which are relatively insoluble (i.e., high  $H$  values). For such compounds,  $K_L$  is approximately equal to the liquid transfer coefficient  $k_L$  (equation 10). Assuming that a value of  $K_L$  for a tracer,  $K_L^0$ , is known in a particular environmental system, the value of  $K_L$  for a contaminant of interest may be evaluated as a function of  $K_L^0$ . Since the laminar film thickness may be assumed identical for both tracer and volatile compounds, the ratio of  $K_L$  to  $K_L^0$  yields a relationship independent of  $\delta_L$ :

$$\frac{K_L}{K_L^0} = \frac{D_L}{D_L^0} \times \frac{\delta_L^0}{\delta_L} = \frac{D_L}{D_L^0} \quad (11)$$

Dobbins [9] suggested that to satisfy the film and surface renewal theories, equation 11 should be rewritten as follows:

$$(K_L/K_L^0) = (D_L/D_L^0)^n \quad \text{where } 0.5 \leq n \leq 1.0 \quad (12)$$

Thus, the overall mass transfer coefficient of a volatile compound may be estimated from experimentally- or mathematically-evaluated values of  $K_L^0$ .

Because oxygen is ubiquitous, nontoxic, and conveniently determined in aqueous solutions such as rivers, it is an excellent choice for tracer studies. Additionally, many mathematical models have been proposed to estimate reaeration (i.e., reoxygenation) coefficients in streams as well as in aeration towers and activated sludge reactors. The commonly used reaeration coefficient is related to  $K_L^0$  by the following relationship:

$$k_2 = K_L^0/L \quad (13)$$

where  $k_2$  is the reaeration coefficient base e, and L is the average liquid depth.

In theory, the nonideal effects of temperature variations, viscosity pressure, wind velocity, mass transfer reduction due to surfactants and oil films, and dissolved solids concentration should be reflected on both  $D_L$  and  $D_L^0$  in the same proportion. Thus, equation 12 may be used to calculate  $K_L$  in actual environmental conditions. For example, Smith et al. [10], demonstrated that the presence of surfactants in water tends to decrease values of  $K_L$ . However, the ratio of  $K_L$  to  $K_L^0$  remains approximately constant regardless of the concentration of surfactant. Measurements by Dilling et al. [12], showed that volatilization rates of various chlorinated hydrocarbons in water

decreased in the same proportion when kerosene was added to the system, independently of the structure of the chlorinated hydrocarbon. The same effect was observed at temperatures near the freezing point of water in comparison to the rates at 25°C.

A method for calculating the diffusion coefficients of dissolved VOC in water at standard conditions has been provided in the Wilke-Chang relationship (13)

$$D_L = \frac{1.51 \times 10^{-4}}{\mu V_b^{0.6}} \quad (\text{cm}^2/\text{sec.}) \quad (14)$$

where  $\mu$  represents the dynamic viscosity of water (cp) and  $V_b$  is the molal volume of solute at its normal boiling point ( $\text{cm}^3/\text{g} - \text{mol}$ ).

Based on experimental results, Smith et al. [10], predicted that a relationship of the form of equation 14 should give values of  $D_L$  within 15 percent of empirical results. If values of  $D_L$  and  $D_L^0$  as calculated above are replaced in equation 12, the effect of temperature variations may be eliminated (i.e.,  $\mu$  is temperature dependent).

$$K_L = K_L^0 (V_b^0/V_b)^{0.6n} \quad 0.5 \leq n \leq 1 \quad (15)$$

Since the diffusion coefficients and molal volumes at the boiling point are thermodynamic constants, equations 12 and 15 provide simple parallel techniques to evaluate the overall transfer coefficient of VOC as functions of  $K_L^0$  only. Values of molal volumes listed by Reid [13] and equation 14 may be used to compute the  $K_L$  and  $D_L$  ratios of several hundred compounds. The  $K_L$  ratios estimated from molal volumes for 20 volatile priority pollutants are listed in Table 1 (these ratios are not temperature or pressure dependent.) An exponent  $n = 0.83$  was used to compute these ratios. Matter-Müller et al. [11], found that this

value for the n exponent adequately described the volatilization of VOC in agitated conditions.

Rathbun and Tai [7], and Smith et al. [10], have experimentally determined overall transfer coefficients for a variety of volatile organic compounds and for oxygen in agitated solutions.  $K_L$  ratios from several studies [7, 10, 15] are shown for comparison in Table 2. The measured ratios favorably agree with the ratios calculated from thermodynamic data assuming an exponent  $n = 0.83$ . Thus, a value for the exponent  $n$  of 0.83 seems to adequately describe the mass transfer kinetics of volatile organic compounds from agitated aqueous solutions.

Volatilization of VOC from aqueous solutions also has been characterized by the use of half-lives ( $t_{1/2}$ ) instead of  $K_L$  the overall transfer rate constant [12, 15]. Comparison with other sets of data is difficult. However, results may be compared through normalization to a reference compound (R) as in equation 16

$$K_L/K_L^R = t_{1/2}^R/t_{1/2} \quad (16)$$

where  $t_{1/2}^R$  is the half-life of the reference compound. The basic relationship  $K_L/K_L^O$  may be obtained by multiplying equation 16 by  $K_L^R/K_L^O$

so:

$$K_L/K_L^O = (K_L^R/K_L^O)(t_{1/2}^R/t_{1/2}) \quad (17)$$

A comparison between data from half-life studies and results from  $K_L$  studies is shown in Table 3. Experimental  $K_L$  ratios were calculated using the above equation and the literature data of half-lives of the compounds [12, 15]. For most compounds, the experimental half-lives



Table 1

Ratios of Diffusion Coefficients and  
Overall Transfer Coefficients of  
Various Priority Pollutants.

---

Pollutant	$D_L/D_L^0$	$K_L/K_L^0$
1,4 Dichlorobenzene	0.38	0.45
1,2 Dichlorobenzene	0.39	0.46
1,3 Dichlorobenzene	0.39	0.46
Chlorobenzene	0.42	0.49
1,1,2 Trichloroethane	0.43	0.49
Tetrachloroethylene	0.44	0.50
Carbon Tetrachloride	0.45	0.51
Benzene	0.47	0.53
Trichlorofluoromethane	0.48	0.54
Chloroform	0.49	0.55
1,1 Dichloroethane	0.49	0.55
Phenol	0.51	0.57
1,2 Dichloropropane	0.51	0.57
1,2 Dichloroethane	0.52	0.58
Dichlorodifluoromethane	0.52	0.58
Acrylonitrile	0.53	0.59
Chloroethane	0.55	0.61
Dichloromethane	0.56	0.62
Vinylchloride	0.61	0.66
Methyl Chloride	0.68	0.73

---

Table 2

Comparison Between Experimental and Predicted Ratios  
 $(K_L/K_L^0)$  Based on  $K_L$  Measurements\*.

<u>Compound</u>	<u>Reference</u>	<u>Experimental</u>	<u>Theoretical</u>
Chlorobenzene	10	0.48	0.49
Toluene	10	0.64	0.49
Tetrachlorethylene	10	0.52	0.50
Carbon Tetrachloride	10	0.63	0.51
Benzene	7, 10, 15	0.54, 0.56, 0.67	0.53
Chloroform	7, 10, 15	0.54, 0.57, 0.67	0.55
1,1-Dichlorethane	10	0.71	0.55
Propane	10	0.72	0.60
Dichloromethane	7, 15	0.70, 0.90	0.62
Ethylene	10	0.87	0.76
Carbon Dioxide	10	0.89	0.88

\*Experiments performed under agitated conditions.  $n=0.83$

Table 3

Comparison Between Experimental and Predicted  $K_L$   
Ratios Based on Half Lifetimes.

Compound	Experimental			$(K_L/K_L^o)$			
	$(t_{1/2}^R/t_{1/2})$			Experimental			Theoretical
	Max	Ave	Min	Max	Ave	Min	
Tetrachloroethylene	1.09	0.86	0.73	0.67	0.53	0.45	0.50
Chloroform	1.19	1.00	0.80	0.74	0.62	0.50	0.55
Dichloromethane	1.30	<u>1.00</u>	0.78	0.80	0.62	0.48	<u>0.62</u>
Chloromethane	0.78	0.77	0.74	0.48	0.47	0.46	0.73
1,2,3-Trichloropropane	0.60	0.55	0.49	0.30	0.28	0.25	0.46
Carbon tetrachloride	1.17	<u>1.00</u>	0.90	0.59	0.51	0.46	<u>0.51</u>
1,1-Dichloroethane	1.31	0.97	0.74	0.67	0.49	0.38	0.55
Allylchloride	1.16	1.08	1.01	0.59	0.57	0.52	0.57
1,2,-Dichloroethane	1.05	1.02	0.99	0.53	0.52	0.51	0.57
Ethylchloride	1.37	1.27	1.10	0.70	0.65	0.56	0.61
Vinylchloride	1.14	1.06	0.97	0.58	0.54	0.49	0.66

were in close agreement with the theoretical values. The considerable low experimental value for 1,2,3-trichloropropane (1,2,3-TCP) may be explained because this relatively large molecule has a low H value in comparison with other compounds used here. Thus, volatilization kinetics of 1,2,3-TCP may be controlled not only by the liquid phase, but by a combination of liquid and gas phase resistance.

All the experimental half-lives reported in Table 3 were obtained under similar agitated conditions by Dilling [15] and Dilling et al. [12]. The reference compound used to calculate experimental ratios was dichloromethane for the first four compounds and carbon tetrachloride for the remaining compounds.

The values of  $K_L^R/K_L$  for dichloromethane and chloroform used to calculate the experimental  $K_L$  ratios are 0.62 and 0.51, respectively. Seventeen data points were available for the first four compounds. Four or five data points were available for the remaining compounds.

## EXPERIMENTAL PROCEDURES

### Introduction

Although a major portion of the project was assimilation of disparate models and data in theoretical development of a model of vaporization, three separate experimental projects were completed toward refining the preliminary testing of this model. These projects included two major laboratory studies and one field study.

Distilled water has been used as the liquid medium in most experimental volatilization studies. However, river water, especially downstream from wastewater treatment plants, may contain surfactants or fats either in suspension or in the dissolved state. While theoretical arguments may show that vaporization rate constants from aqueous solutions are affected by detergents and hydrophobic solutes, the objective of this experimental phase was to determine the magnitude of such changes. This concept has been neglected in all references regarding VOC in aqueous solutions except for studies by Smith et al. [10] and by Dilling [12]. In Part A of the laboratory studies presented later in this section, rate constants for transfer of four VOC were determined at New Mexico State University using distilled water, actual wastewater (purged free of naturally abundant VOC) and water containing two concentration levels of ordinary animal fat.

In the mass transfer model developed above,  $K_L/K_L^0$  was directly proportional to  $D_L/D_L^0$  raised to the first power for quiescent conditions and to 0.5 for agitated conditions. An exponent of 0.83 has been proposed as a constant value to describe transfer of VOC in all moving waters, regardless of the degree of agitation [11]. Nevertheless, dependence of this exponent on the degree of agitation is unknown. The

objective of Part B of our experimental studies is to determine the magnitude of the exponent as a function of degree of agitation. Nearly all prior studies on volatilization of VOC from streams are extrapolations of small scale (i.e., less than one liter) batch reactors to actual streams. An exception is the work by Rathbun and Tai (16) where volatilization of ethylene and propane was predicted using in-situ measurements of several small streams.

The volatilization rates of benzene and chlorobenzene and the reaeration coefficient were measured in Part C of this study using a 1000 liter closed circuit circular channel. The advantages of using such a bench model over small natural streams are obvious since parameters such as stream regularity, flow rate, velocity and surface roughness coefficient are subject to considerable changes in small streams but can be easily controlled in the model.

Although numerous field studies were completed near Las Cruces to assess the feasibility of testing the model on the Rio Grande near Las Cruces and El Paso, only one study for the Rio Grande downstream from Albuquerque will be reported. The absence of sufficient VOC in the Rio Grande near Las Cruces was responsible for failed field studies. However, VOC were detected in river water below Albuquerque and results from that study are described later in Part D. Field studies also were carried out in the South Platte River below Denver, and in the Pecos River below Artesia. VOCs were detected in these rivers at extremely low concentrations. Application of the proposed model therefore was not implemented in these two rivers.

## Part A: Matrix Effects on Volatization

Samples and Reagents. Samples of treated wastewater were drawn just prior to the point of chlorination at the Las Cruces Municipal Wastewater Treatment Plant using a metal bucket and rope. The samples were transferred to freshly cleaned four liter amber glass bottles with teflon lined screw caps. The samples had average values of roughly 75 mg/l and 1200 mg/l for biological oxygen demand and total suspended solids, respectively. Deionized water was available in-house in the Department of Chemistry. The organic compounds chosen to represent a relatively wide range of volatility for compounds encountered in wastewater were methylene chloride, chloroform, benzene and chlorobenzene. All compounds were reagent grade and were used as received. Fat was obtained from a domestic source and purified through filtration using glass wool and a filtering funnel.

Instrumentation. A Hewlett-Packard 5721A gas chromatograph was equipped with heated inlets, flame ionization detector, heated switching valve (Valco Co., Houston, TX), model 3380A reporting integrator, and 2m long x 2mm ID-6mm borosilicate tube containing 3 percent OV-101 on 100/120 mesh Supelcoport (Supelco Co., Bellefonte, PA). A purge and trap device with Tenax-GC sorbent traps was used to analyze aqueous solutions for VOC. Flow of He gas was optimized at 200 ml total for compounds used here with flow of 40ml/min for purge time of 5 min and sample volume of 15 to 25 ml.

Preparation of Calibration Curve. Two sets of standard solutions in n hydrocarbon solvents were prepared;  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  (in octane) and  $\phi$  and  $\phi\text{-Cl}$  (in pentane) were diluted to 0.1, 1.0, 10.0 and 100 mg/ml. The standards were analyzed using direct injection. The  $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$  standard solutions were analyzed isothermally at  $10^\circ\text{C}$ , and the  $\phi/\phi\text{-Cl}$

solutions were analyzed at 50°C. An additional calibration curve for  $\text{CH}_2\text{Cl}_2$  and  $\phi\text{-Cl}$  (in  $\phi$ ) was prepared for the 0.1 - 1.0 mg/ml range.

Preparation of Saturated Solutions. Individual saturated solutions of VOCs were prepared by adding 20.0 ml each of  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  (Baker analyzed) and 10.0 ml of  $\phi$  and  $\phi\text{-Cl}$  (Baker) to 500 ml of distilled water in a teflon-capped glass bottle. All four solutions were vigorously shaken for five minutes and allowed to set undisturbed for eight hours. Undissolved VOCs were observed on the bottom, or top (in the case of  $\phi$ ), of the bottles. Solutions were shaken briefly about eight hours before each analysis.

Preparation of Diluted Solutions for Analysis. Dilute solutions of VOCs were based on the solubilities of each VOC (17);  $\text{CHCl}_3$ -0.82g/100ml  $\text{H}_2\text{O}$ ,  $\text{CH}_2\text{Cl}_2$ -1.32g/100ml  $\text{H}_2\text{O}$ ,  $\phi$ -0.070g/100ml  $\text{H}_2\text{O}$ , and  $\phi\text{-Cl}$ -0.049 g/100ml  $\text{H}_2\text{O}$ . Dilutions were made by delivering the appropriate amount of saturated solution with a Hamilton Microliter syringe into a one-liter volumetric flask and diluting to the mark with distilled or purged wastewater. Concentrations of the final solutions were  $\text{CHCl}_3$ : 328 ppb,  $\text{CHCl}_2$ : 588 ppb,  $\phi$ :101 ppb, and  $\phi\text{-Cl}$ : 99.1 ppb. (Care was taken to avoid piping in pure VOC from the saturated solution.)

Kinetic Studies. Dilute solutions were prepared as above and placed in a two-liter beaker and stirred by a jar test stirring device at 80 rpm. At periodic intervals, 15 ml aliquots were drawn with a 50 ml syringe at a depth of 2 cm below the surface of solution and analyzed using the purge and trap device. Traps were then analyzed using the GC as follows:

1. Traps were attached to the gas switching valve and pretreated using a heat gun (about 100°C) for 15 seconds.



2. The valve was switched while heating was continued for two minutes.
3. The valve was then returned to its original position.

During this thermal desorption procedure, the column oven of the GC was isothermal at 10°C. After six minutes from the time the valve was first switched, a temperature program of 12°C/min was started. Final temperature was 110°C. Inlet and detector temperatures were 250°C. The valve and trap lines were thermostatted at 150°C.

Treatment of Data. Results from kinetic studies were used to derive values for k. Peak values were converted to mass (or concentration) using the calibration curve. The natural logarithms of mass were plotted versus time to fit the first order, integrated general equation,

$$\ln C = \ln C_0 - akt \quad (18)$$

where  $a = 1$  and  $k$  was the slope. All values reported were averaged from three to five replicate analyses. Results from this study are reported in the Results and Discussion section.

#### Part B: Dependence of Exponent n on the Degree of Agitation

A detailed description of experimental procedures used in this section has been published [14] and will be presented only in summary here.

The experimental work involved the simultaneous measurements of the volatilization kinetics of four VOCs and of oxygen. The apparatus consisted of two identical 2000 ml beakers subjected to the same degree of agitation. Concentrations of organic substances were measured in the first beaker as a function of time, and analyses were performed using a purge and trap apparatus and a gas chromatograph equipped with a flame ionization detector. Oxygenation rates were measured with a

approximately 10 to 0.1  $\mu\text{g}/\text{l}$ , which is the range normally found in most rivers.

Camp and Conklin (18) determined the values of the velocity gradient  $G$ , in 2000 ml beakers, with and without stators, as a function of angular velocity for a standard jar test apparatus. Figure 2 shows the geometric properties of these vessels. The volatilization and oxygenation tests were performed at four constant velocities: 0, 20, 60 and 100 rpm in the vessels as described by these researchers. Values of  $G$  were obtained from their published results.

Quasi-quiescent state condition experiments were performed by eliminating mechanical agitation in the test vessel. These vessels were continuously ventilated to eliminate the possibility of gas phase rate control. Results of this study are summarized in the Results and Discussion section.

#### Part C: Pilot Studies

Experiment. Saturated aqueous solutions of two VOC chosen for modeling were prepared in amber glass bottles with Teflon-lined caps. Benzene and chlorobenzene which were both reagent grade without purification were used as VOC contaminants in water (both benzene and chlorobenzene are volatile toxic priority pollutants). The large-scale laboratory-based device for simulating river channels shown in Figure 3 was filled at various levels with DO free water. Portions of saturated aqueous solutions of benzene (1.5 l) and chlorobenzene (2 l) were added to water in the channel so final concentrations were approximately 1 ppm. Samples of water were drawn from the batch reactor at periodic intervals. Samples were analyzed immediately after sampling using gas chromatography with purge and traps methods.

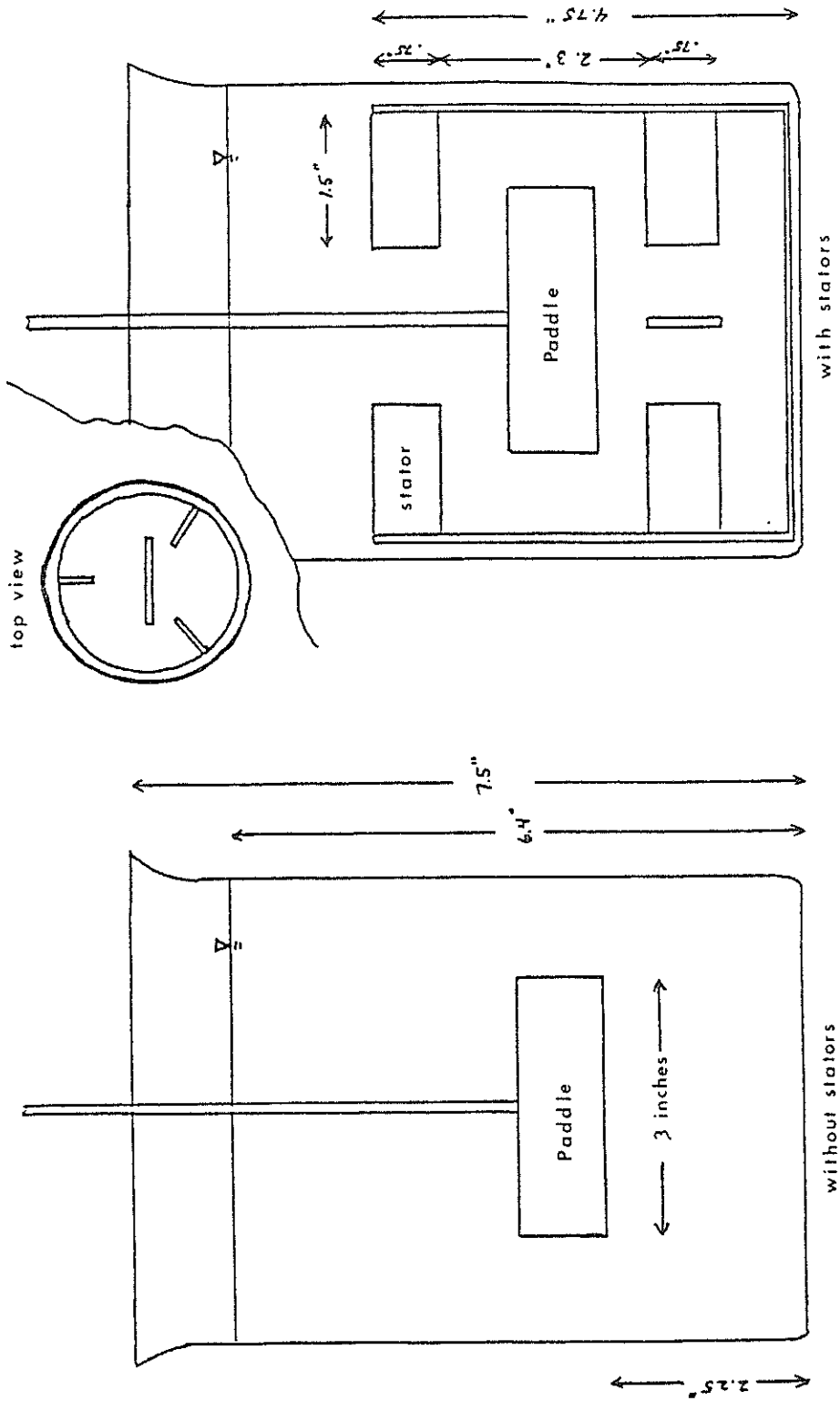
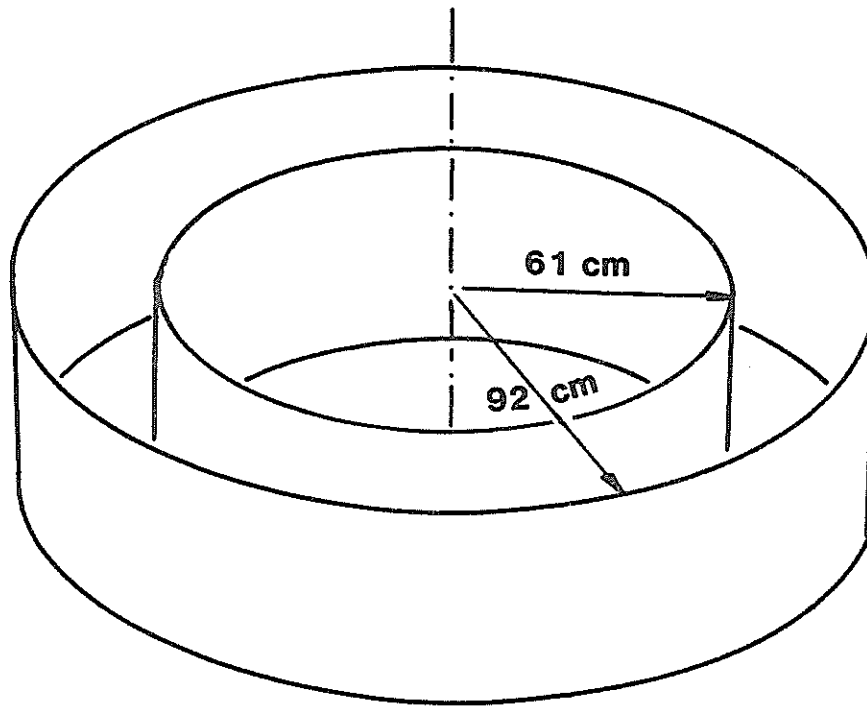


Figure 2. Two liter beaker, with and without stators.

(a)



(b)

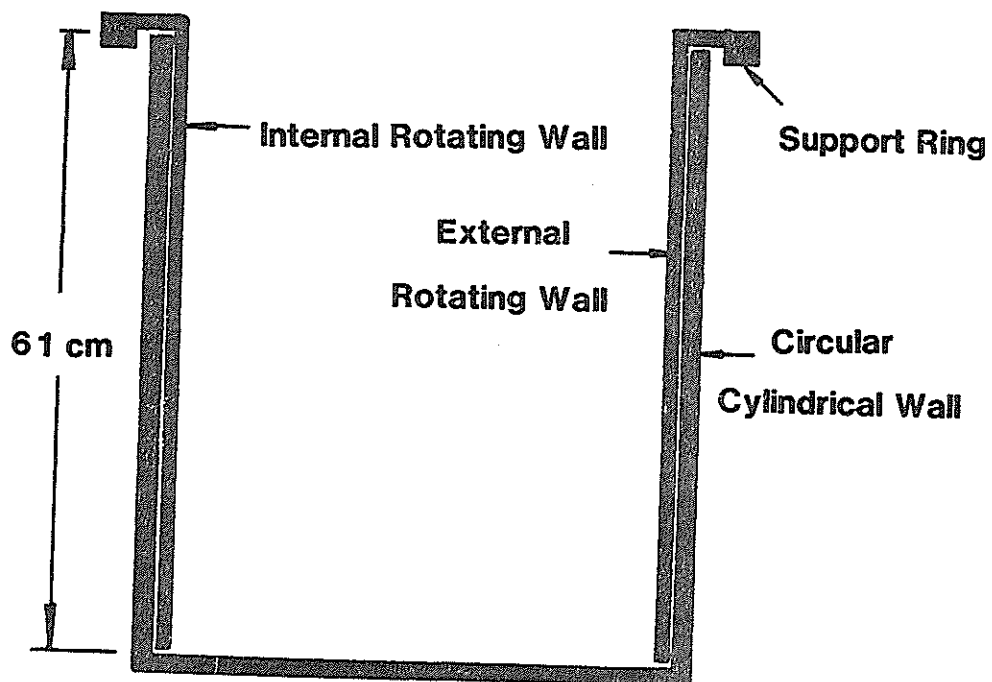


Figure 3. Pilot scale model of a continuous flow stream.

Instrumentation. A Hewlett-Packard 5721A gas chromatograph was equipped with heated inlets, flame ionization detector, a heated switching valve, recording integrator, and a 2 m long x 2 mm ID-6 mm borosilicate glass column containing 3 percent OV-101 on 101/120 mesh Supelcoport. A purge and trap device with Tenax-GC sorbent traps was used to extract the VOC from the liquid phase. Dissolved oxygen concentrations were continuously measured with a Beckman 777 Oxygen Analyzer equipped with an Omniscribe Recorder. The reaeration rate of the stream was controlled by changing the angular velocity of the rotating walls and by varying the water depth and bottom configuration.

#### Part D: Field Studies

Preliminary testing of the mathematical model developed in the previous chapter in an actual environmental setting was made using the Rio Grande below Albuquerque. Grab samples were drawn using a rope and bucket from points in the river made accessible through a bridge or dam. The sites, distances and times of sampling are summarized in the Results and Discussion section. Samples were stored in amber glass bottles, returned to the laboratory the same day and analyzed immediately using GC with purge and trap techniques. Results of this field study are also presented in the Results and Discussion section.

## RESULTS AND DISCUSSION

The bulk of the research completed in this project involved development of a model to predict movement of VOC in rivers. First, a comprehensive theory of volatilization was developed and then several aspects of the theory were studied in the laboratory. Results from the theoretical development will be addressed with particular attention to environmental significance. Secondly, results from laboratory studies will be described.

### Kinetics of Volatilization in Streams

Concepts of volatilization developed earlier may be used to compute the mass flux of VOC across the liquid-gas interface in rivers. Assuming no other losses or gains in mass, the change in mass across an interface surface, A, in a batch reactor during any time period equals the total mass flux rate:

$$AF = - dC_L/dt \quad (18)$$

and

$$F = k_L(C_L - C_L^S) = K_L(C_L - C_L^S) \quad (19)$$

where V is the reactor volume and  $C_L^S$  is the saturation concentration under a known partial pressure of the compound in the gas phase. Under adequate ventilation conditions, it may be assumed that  $C_L^S$  is zero for compounds not normally found in the atmosphere. Also, for reactors with minimal air entrainment, the mass flux will largely occur horizontally across the liquid surface. For regular shaped reactors, the ratio of the reactor volume to the total surface area is equal to the average depth, L. Thus, volatilization kinetics will be described as:

$$-dC_L/dt = K_L C_L / L \quad (20)$$

Multiplying and dividing the right side term by  $K_L^0$  and recalling that this constant equals  $k_2 L$  the following relationship is obtained

$$-dC_L/dt = k_2 C_L (K_L/K_L^0) \quad (21)$$

The ratio  $(K_L/K_L^0)$  may be obtained from Tables 1 or 2.

Integration of the above equation from  $t = 0$  to  $t$ , and  $C_L = C_L^i$  to  $C_L$  yields:

$$C_L/C_L^i = \exp[-k_2 t (K_L/K_L^0)] \quad (22)$$

Equation 22 may be used in describing loss of VOC in rivers due to volatilization if the effects of longitudinal diffusion and dispersion are unimportant.

Application to Stream Modeling (Theoretical). The volatilization kinetics of VOC in streams may be approximated by the equations developed for batch processes if other secondary phenomena such as longitudinal dispersion, photolysis, biodegradation, dilution and sorption are negligible by comparison. However, use of equation 22 requires prior measurement or evaluation of the reaeration coefficient  $k_2$  in each specific stream. Fortunately, these values are often available. For example, Nemerow [19] has presented an excellent review of various techniques available to compute  $k_2$ . All the information needed to estimate VOC residence in a particular stream after a given distance or stream travel time are the values of  $(K_L/K_L^0)$ , as presented in Tables 1, 2 and 3, and the reaeration coefficient of the stream. To illustrate the use of equation 22 in streams, the loss of several VOCs will be predicted in two very different rivers. The first river, the Rio Grande, is a relatively fast river with a correspondingly high value for  $k_2$ . The second river, the Tennessee River, flows slowly from one reservoir to the next with a relatively low value for  $k_2$ . Reaction coefficients and travel times are taken from information by Barkley [20], and Higgins and Kim [21]. The more critical, minimum flow conditions for the Rio Grande were selected

for the first example. The effect of dilution in the Tennessee River is ignored in the second example.

Results from theoretical modeling of these two rivers are shown for two priority pollutants with extreme values for  $k_2$  in Figures 4 and 5. The effect of stream characteristics as described by  $k_2$  may be seen through comparison of expected decay curves. Not surprisingly, in the faster more turbulent river, VOC should be lost in much shorter time while the slower river showed slower volatilization rates per unit distance. These results may explain in part why water pollution by VOC in rivers such as the Mississippi River is apparently more severe than in rivers of the Rocky Mountain region when other factors such as extent of industrial activity are considered.

Experimental Part A: Effect of Matrix on Volatilization Kinetics.

Results from determination of mass transfer coefficients for four VOCs in solutions with differing matrices are shown in Table 4. Chromatographic performance measured using peak height and resolution was good. The effect of fats and actual wastewater was negligible on the rate of volatilization as seen in Table 4. These results show that use of ordinary water without surfactants or matrix near that of river water will be satisfactory for modeling studies.

This result is significant, inasmuch as nearly all volatilization studies were completed using distilled water and results from these studies may be considered reliable for in-stream applications.

Experimental Part B: Effect of Agitation on  $n$  in  $(K_L/K_L^0)^n$ . The measured concentrations of the four organic compounds and oxygen as functions of agitation velocity and time with and without stators are



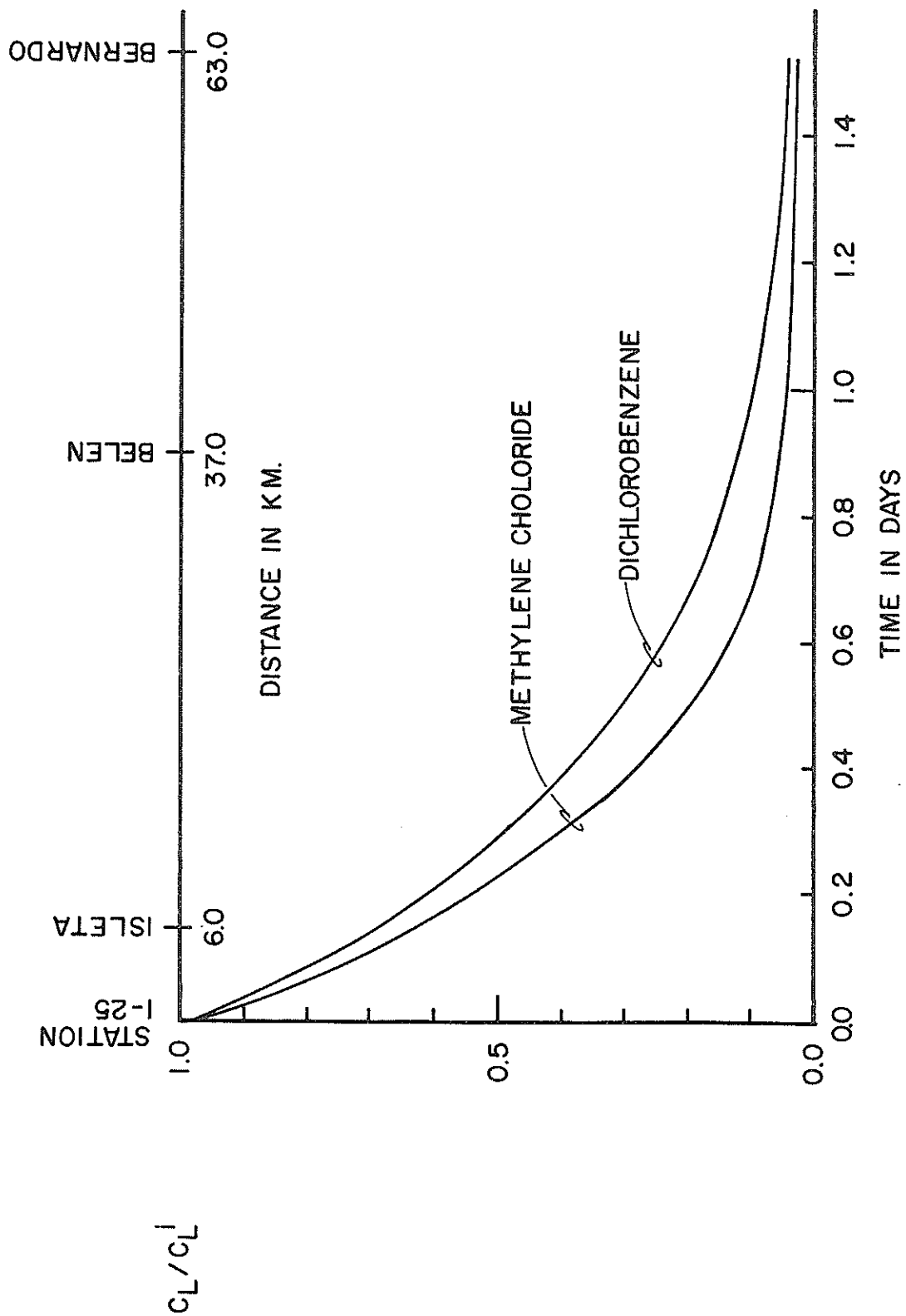


Figure 4. Volatilization of VOC in the Rio Grande.

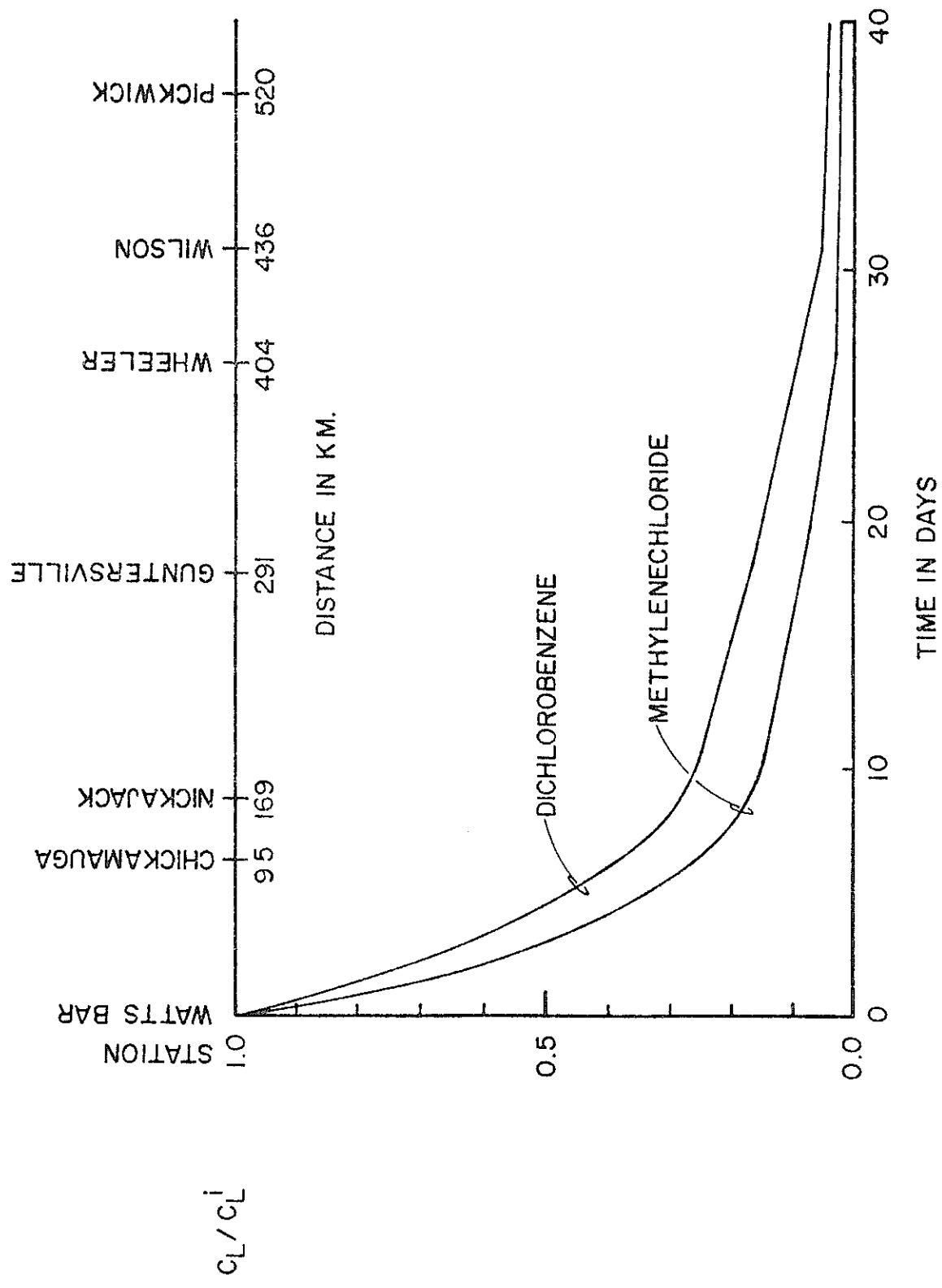


Figure 5. Volatilization of VOC in the Tennessee River.

Table 4

Matrix Effect on Volatilization Rates  
(Average values of  $K_L/L$  in  $\text{min}^{-1}$ ).

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<u>Compound</u>	<u>Distilled Water</u>	<u>Wastewater</u>	<u>Fat #1</u>	<u>Fat #2</u>
$\text{CH}_2\text{Cl}_2$	0.014±0.0060	0.0095	0.0105	0.0123
$\text{CHCl}_3$	0.0106±0.0061	0.0060	0.0156	0.0103
$\phi$	0.0128±0.0047	0.0103	0.0106	0.0111
$\phi\text{-Cl}$	0.0120±0.0051	0.0095	0.0125	0.0106

---

shown graphically in Figures 6 through 12. The first order kinetic constants calculated from the previous experimental data for the organic compounds were divided by the oxygenation rate. A summary of volatilization constant ratios for the four compounds at various degrees of agitation is presented in Figure 13.

The following conclusions may be drawn from a comparison of the data from Figure 13 with the theoretical  $K_L$  ratios in Table 1:

1. The volatilization constant ratios appear to be independent of the degree of agitation over the range of velocity gradient studied. Thus, it is likely that for most streams from slow flowing to highly turbulent, the volatilization kinetics of organic compounds may be described as a function of their respective diffusion coefficients to a constant power  $n$ , regardless of the degree of agitation.
2. True quiescent flow conditions are practically impossible to find in natural surface water conditions. Even the small degree of agitation created by wind activity would eliminate the possibility of describing the volatilization kinetics according to the mathematical model developed for static flow conditions. Thus, the volatilization kinetics of volatile dissolved compounds in lakes may be predicted by the model developed for agitated conditions in rivers and streams.
3. The average  $K_L/K_L^0$  ratios presented in Figure 13, with the exception of those of dichloromethane, tend to be slightly lower than the expected values for agitated conditions as listed in Table 1. The exponent  $n$  that best fits these data is 0.84, which is almost identical to the value recommended by

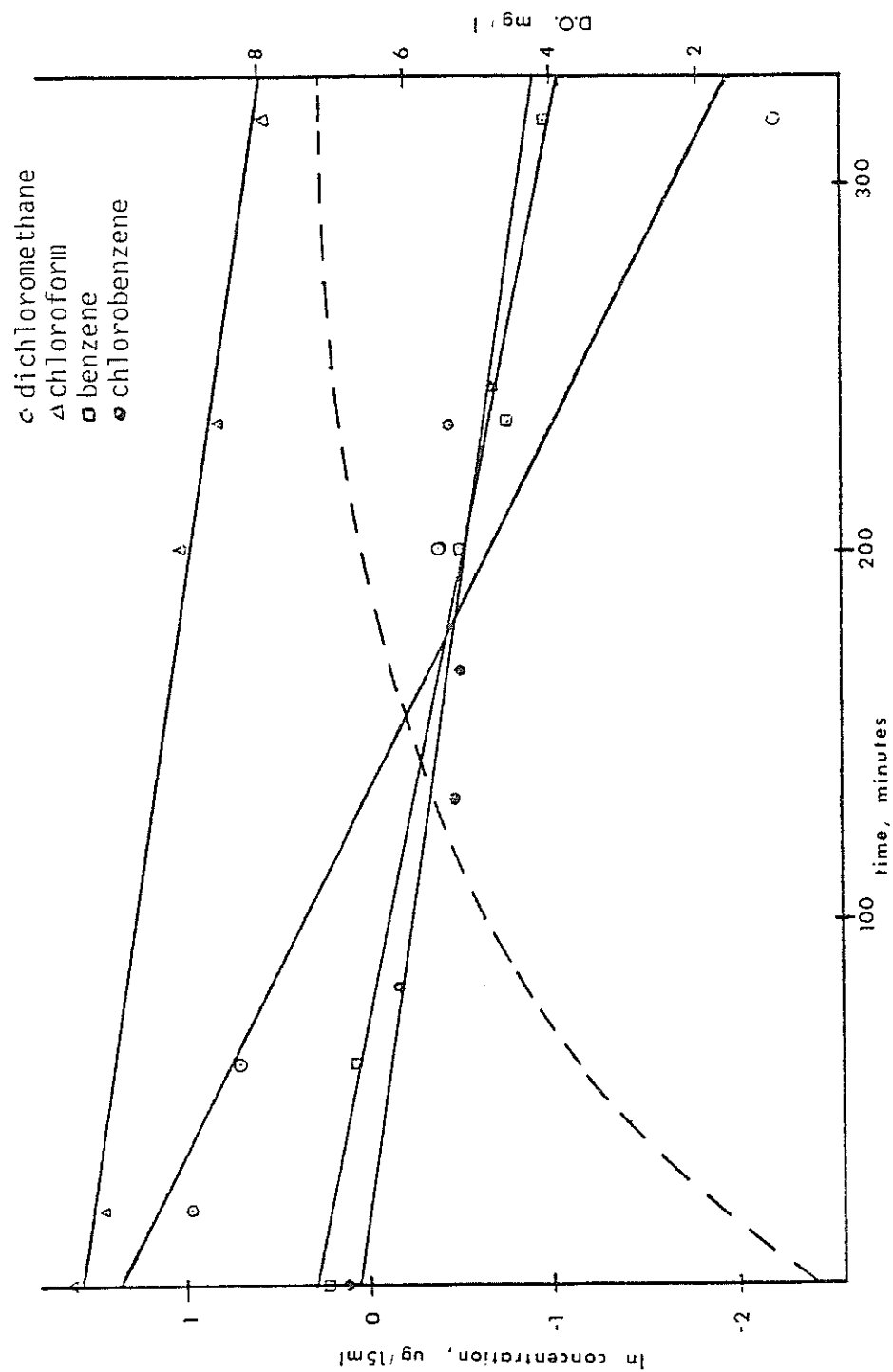


Figure 6. Kinetics run at 100 rpm

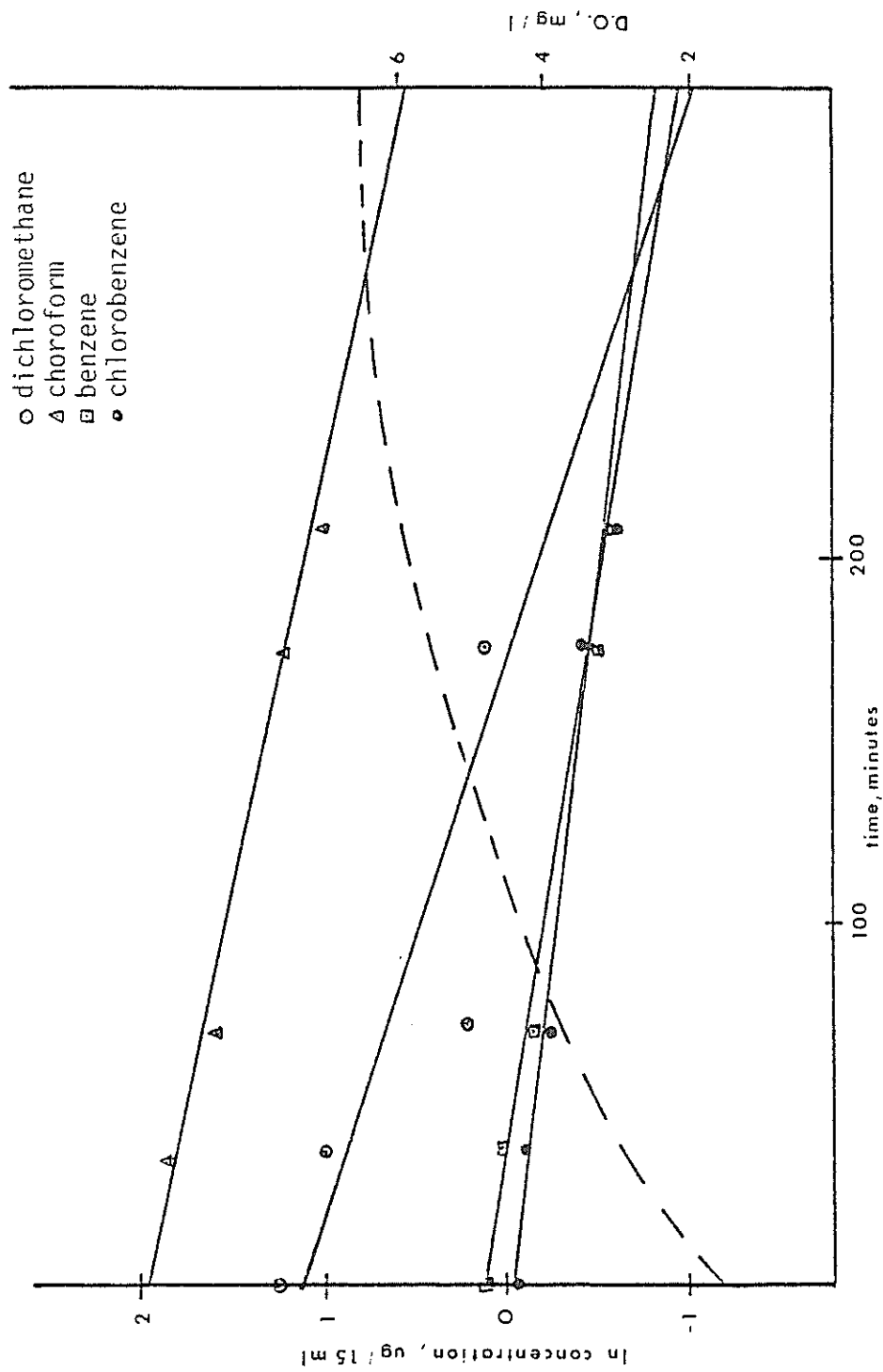


Figure 7. Kinetics run at 60 rpm.

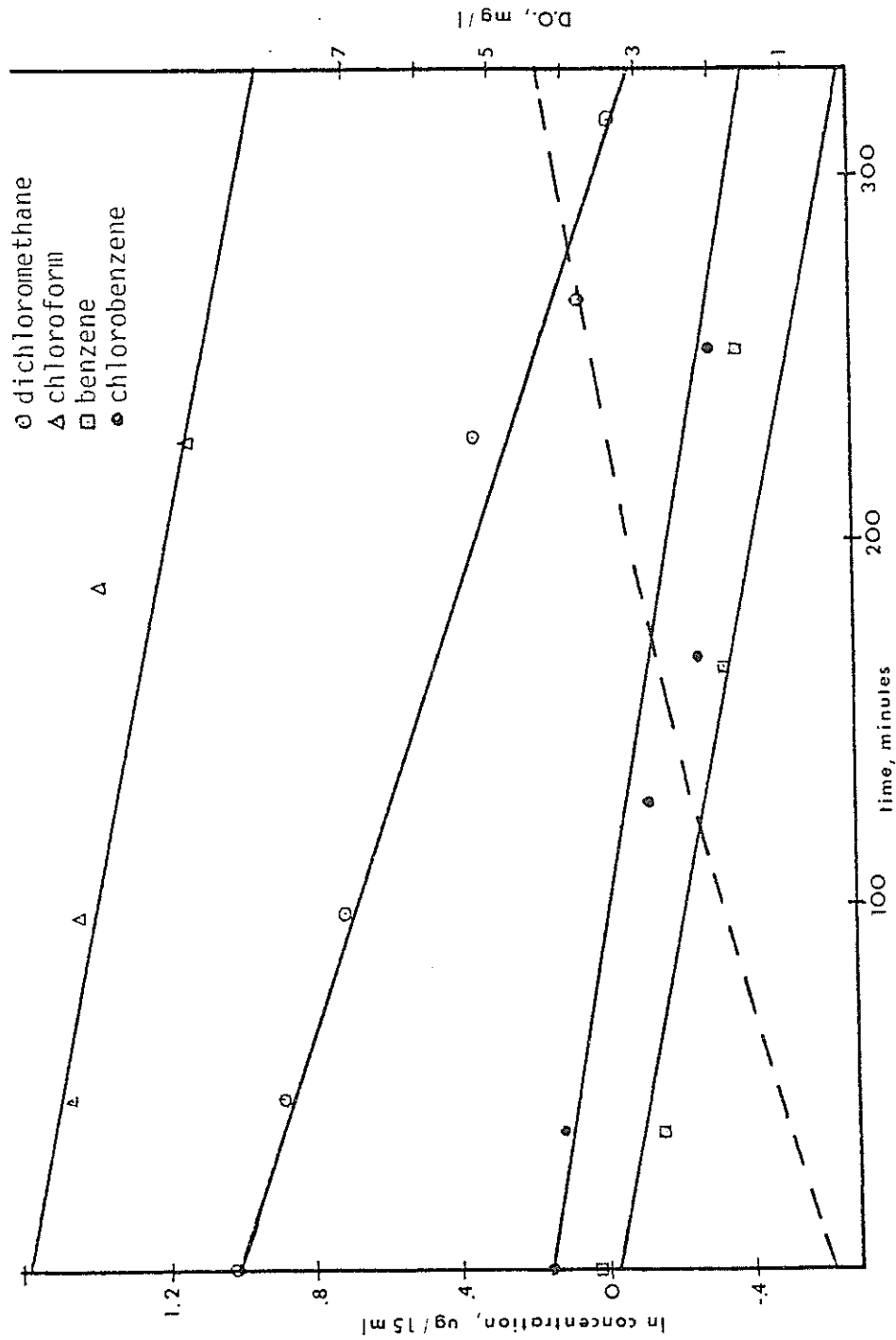


Figure 8. Kinetics run at 20 rpm.

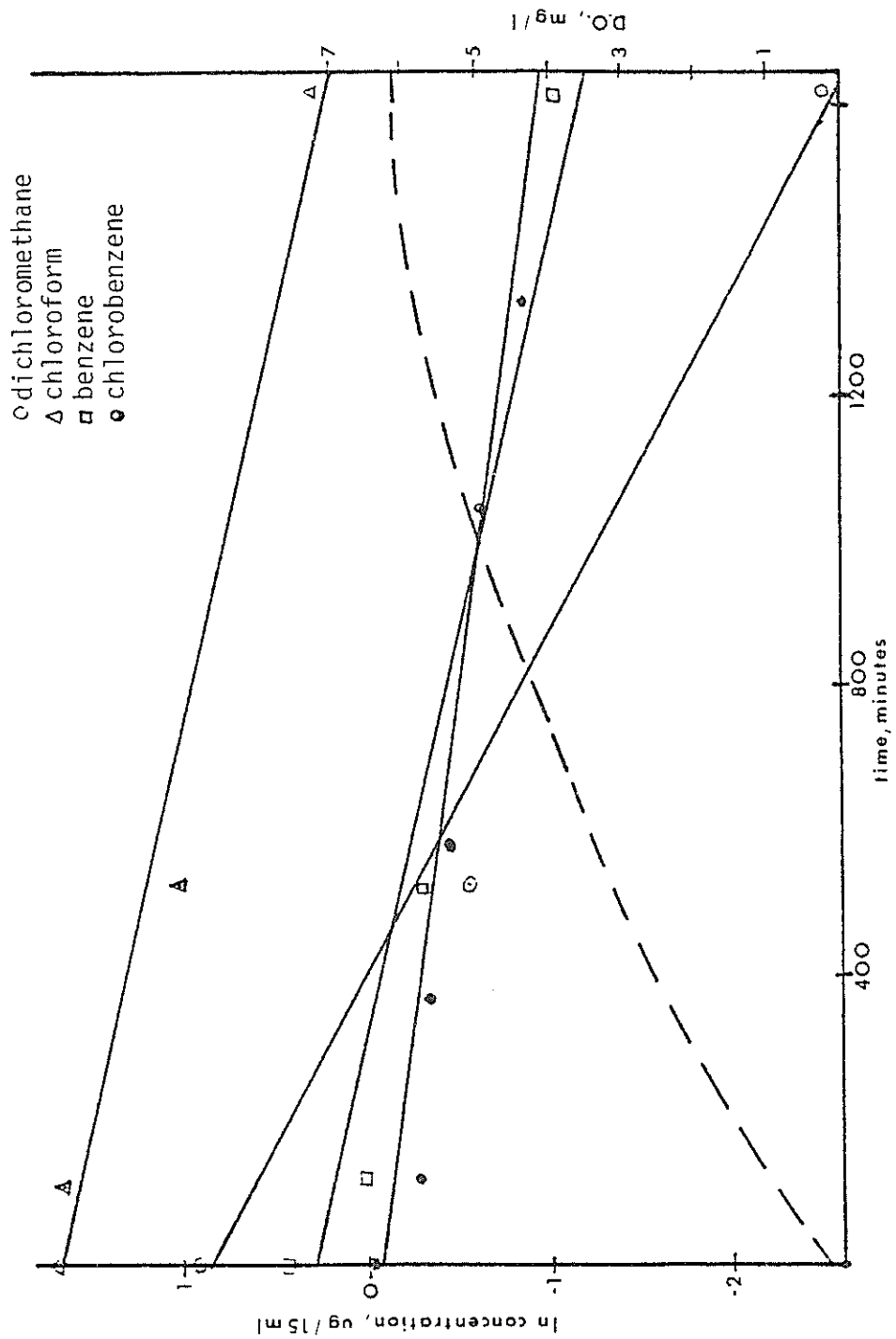


Figure 9. Kinetics run at 0 rpm.



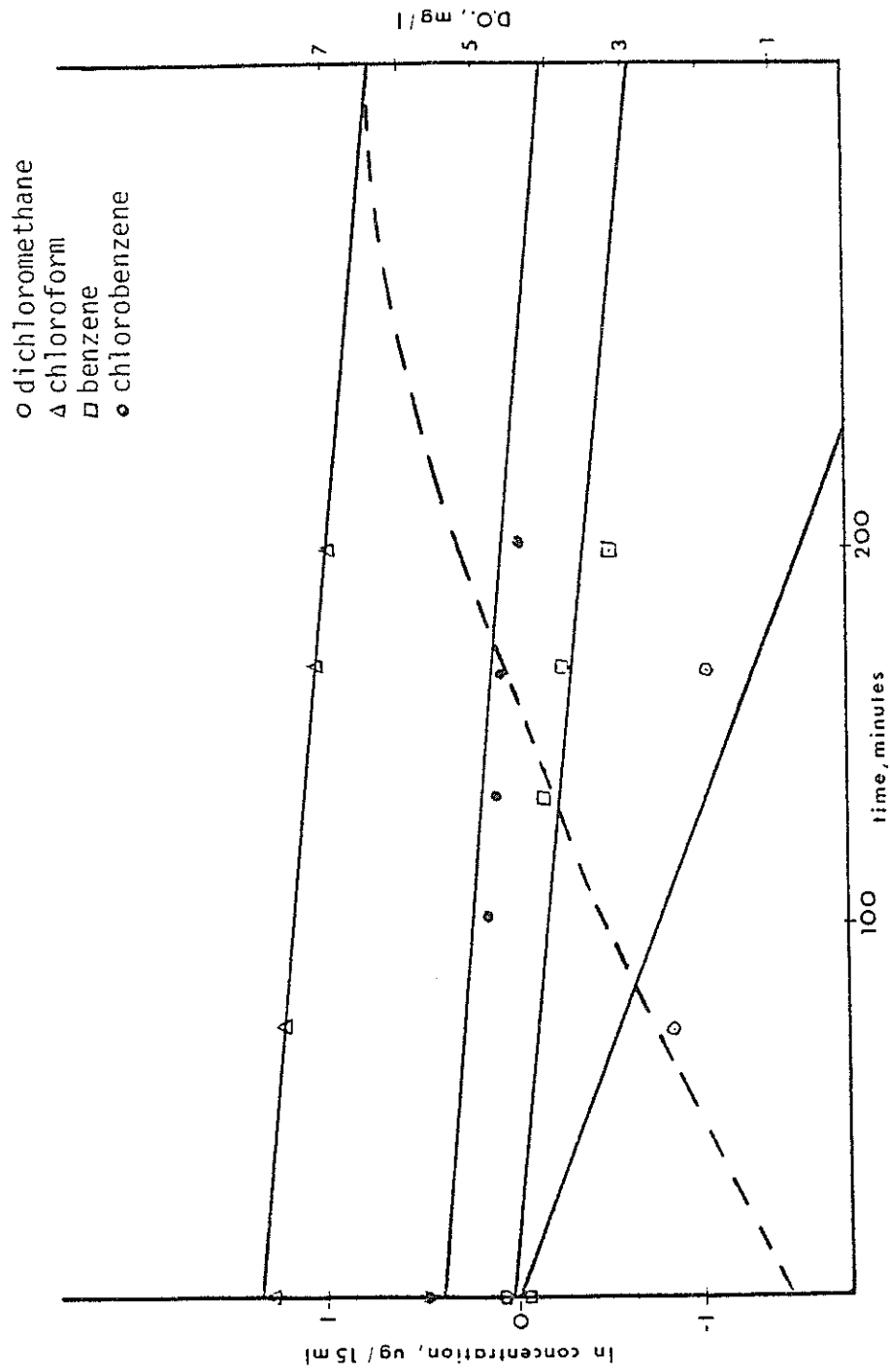


Figure 10. Kinetics run at 100 rpm, with statocors.

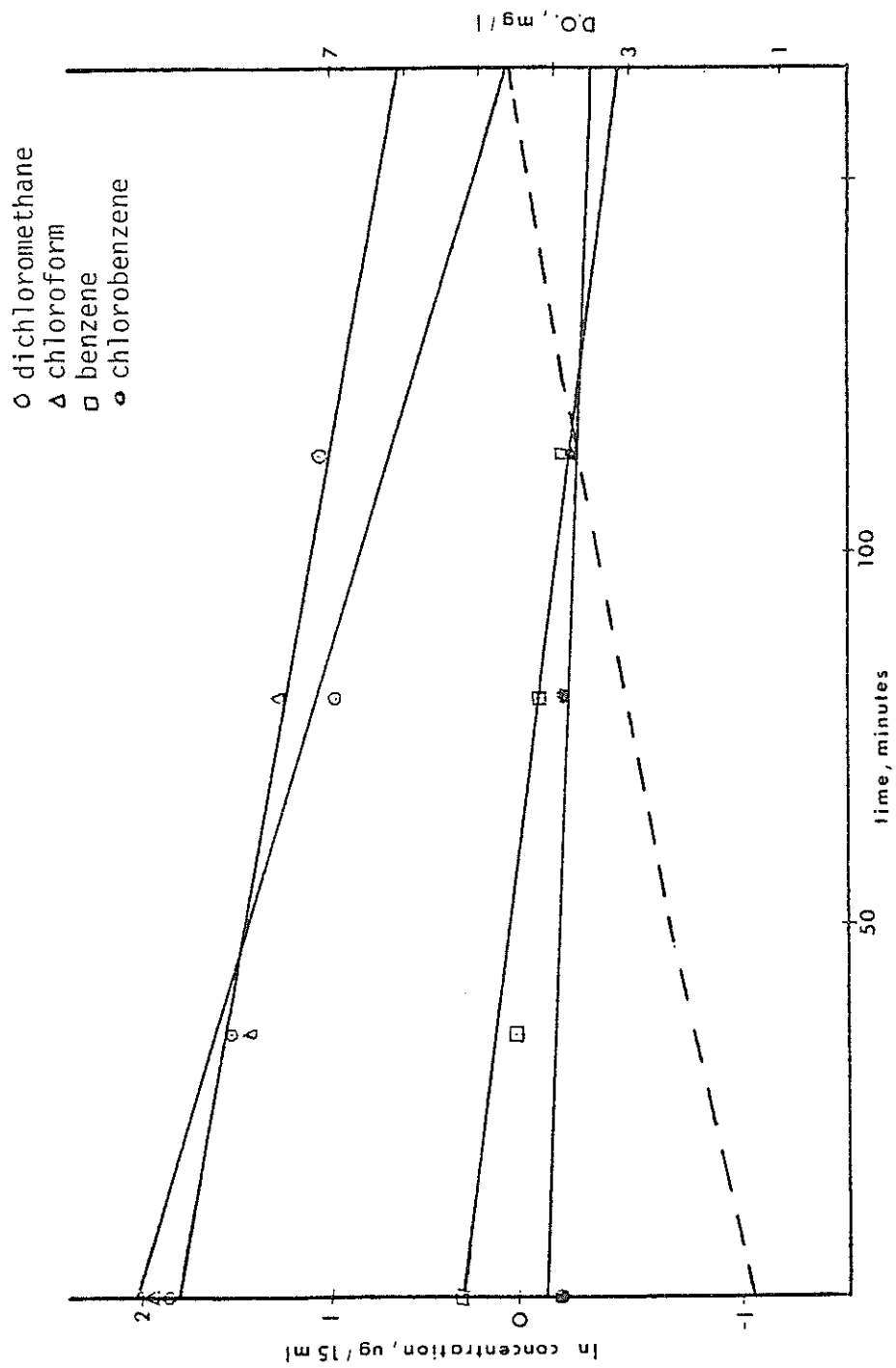


Figure 11. Kinetics run at 60 rpm, with stators

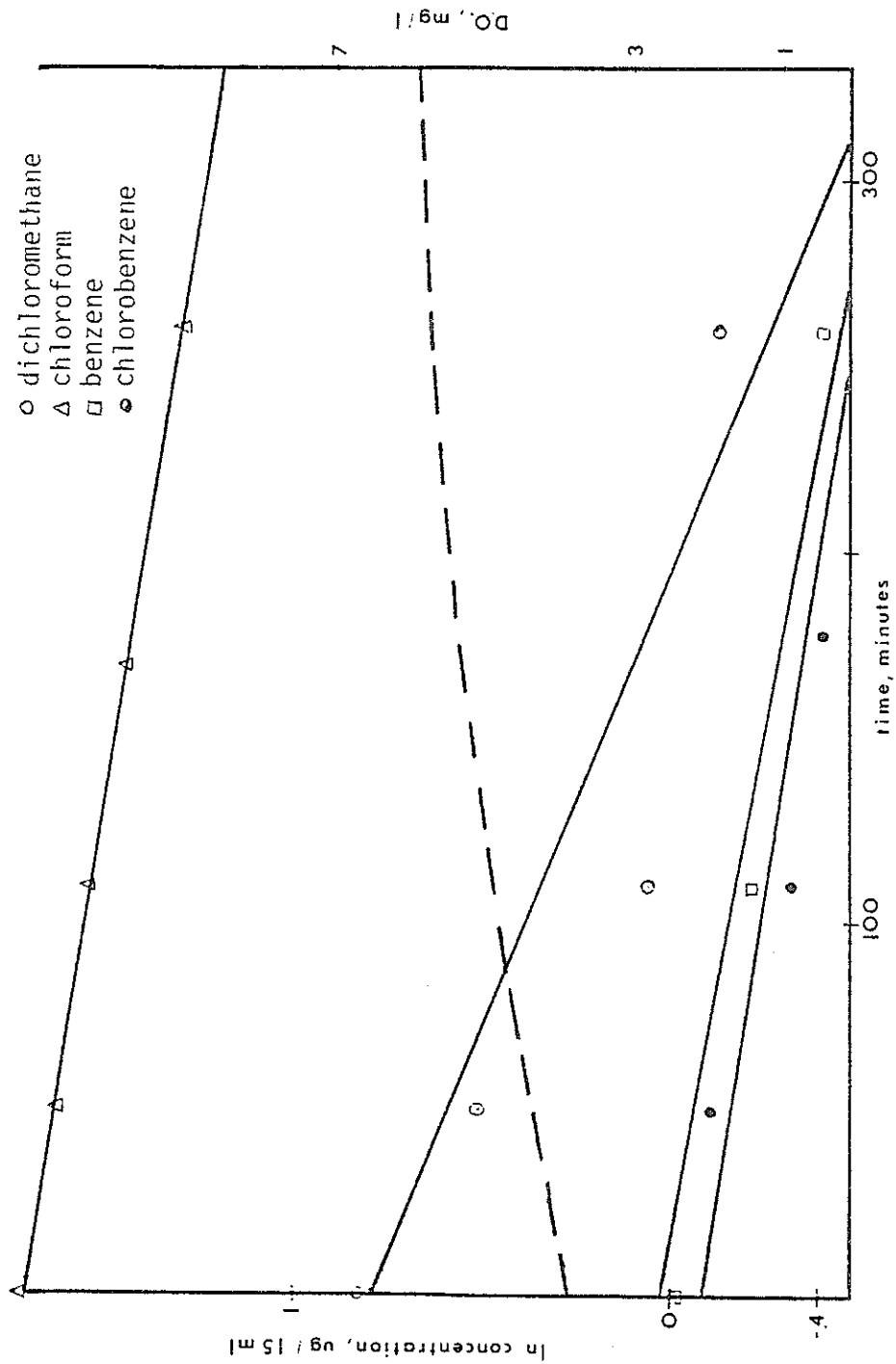


Figure 12. Kinetics run at 20 rpm, with stators.

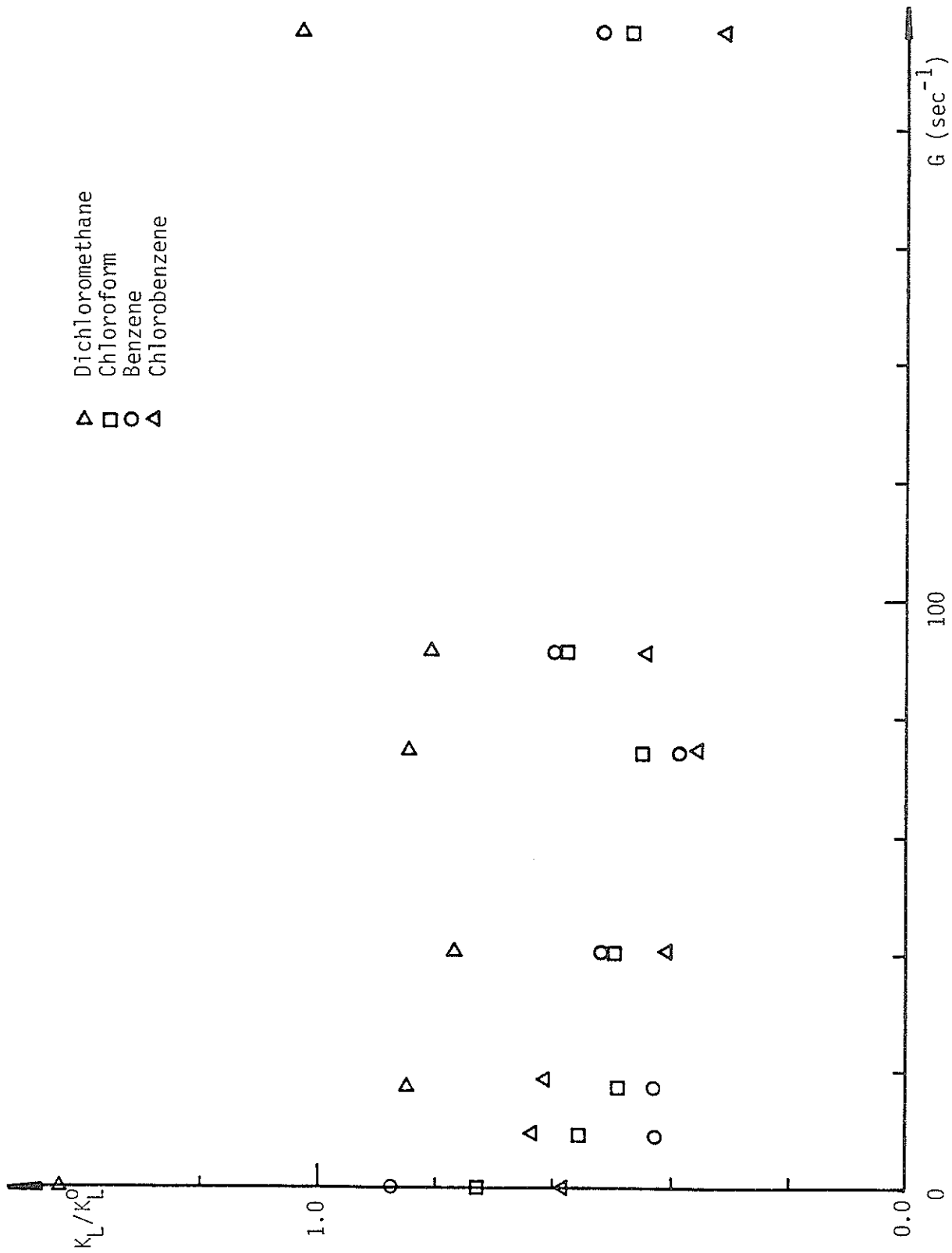


Figure 13. Dependence of the overall gas transfer coefficient ratio on agitation

Matter Müller et al. [11]. Considering the excellent agreement between the recommended and the value of  $n$  experimentally determined in this study, the second phase of this research project included the testing of the model in a pilot model river and actual field conditions. The execution of "closer to reality" pilot studies in Part C of this project resulted in the clarification of the value of  $n$  to be used in field conditions. Finally, testing of the refined model in actual stream conditions in the last stage of this project elucidated the potential and accuracy of the model.

Experimental Part C: Pilot Stream Studies. The measured fraction of benzene and chlorobenzene  $C/C_i$  remaining in the solution has been plotted as a function of elapsed time in Figures 14 and 15, respectively. A minimum of three points is reported for each run (For the sake of simplicity, only points in the range  $0.8 < C/C_i < 0.01$  are plotted in these figures.) The value of the reaeration coefficient,  $K_2$ , was determined for each run by mathematical interpretation of the continuous DO measurements. (The reoxygenation of an abiotic batch process follows a first order kinetics with respect to the DO deficit.)

The solid lines in Figures 14 and 15 represent the VOC concentration fraction remaining as predicted by equation (22) when using the corresponding values of  $K_L/K_L^0$  listed in Table 1, and the experimentally determined  $K_2$  values. It may be observed from these figures that the decay rate of VOC follows a first order kinetics with respect to the VOC concentration, as predicted by equation (22). Additionally, the theoretical  $C/C_i$  lines closely predict the experimentally determined points throughout the duration of the experiment. This agreement

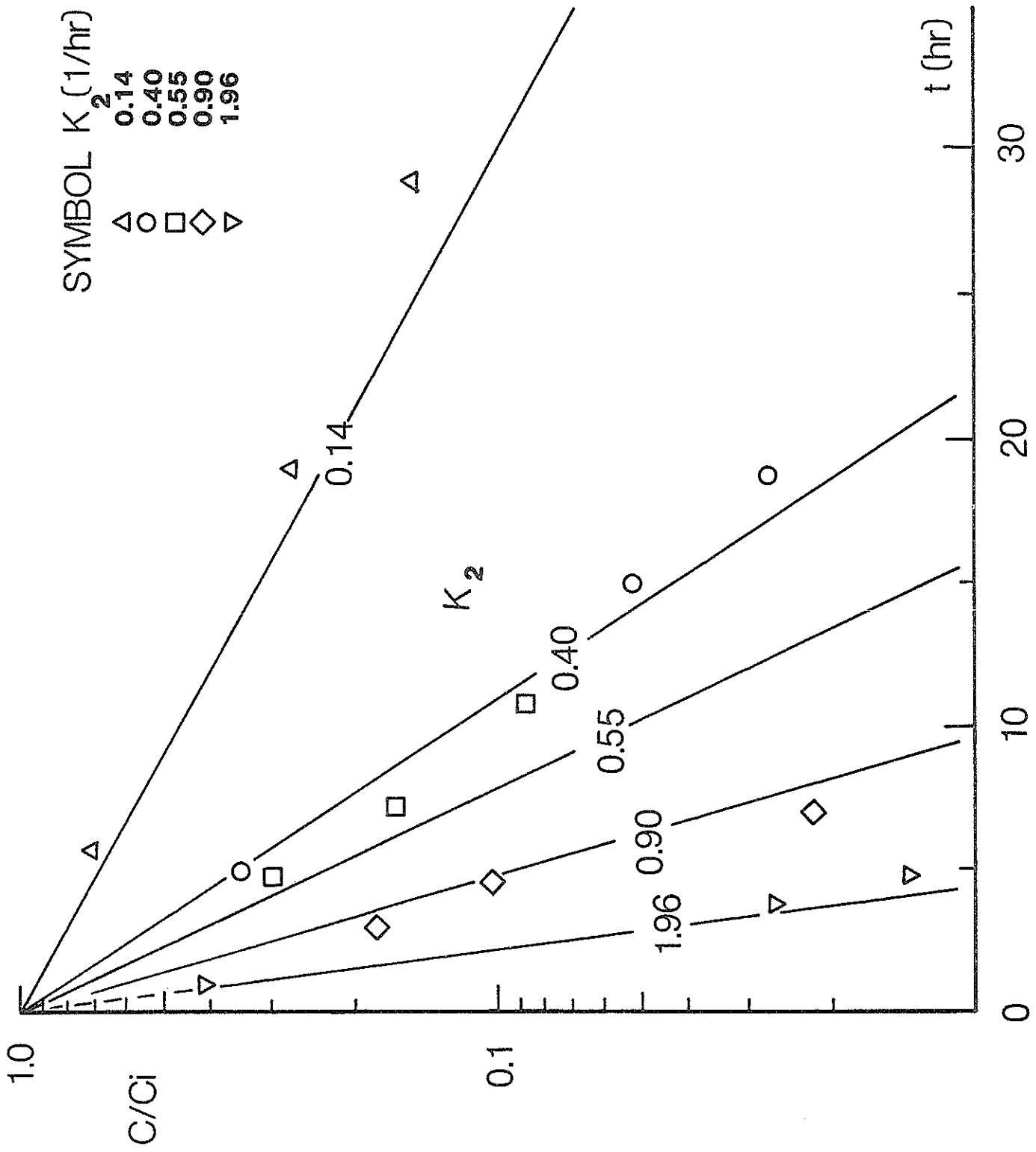


Figure 14. Volatilization kinetics of benzene in pilot studies.

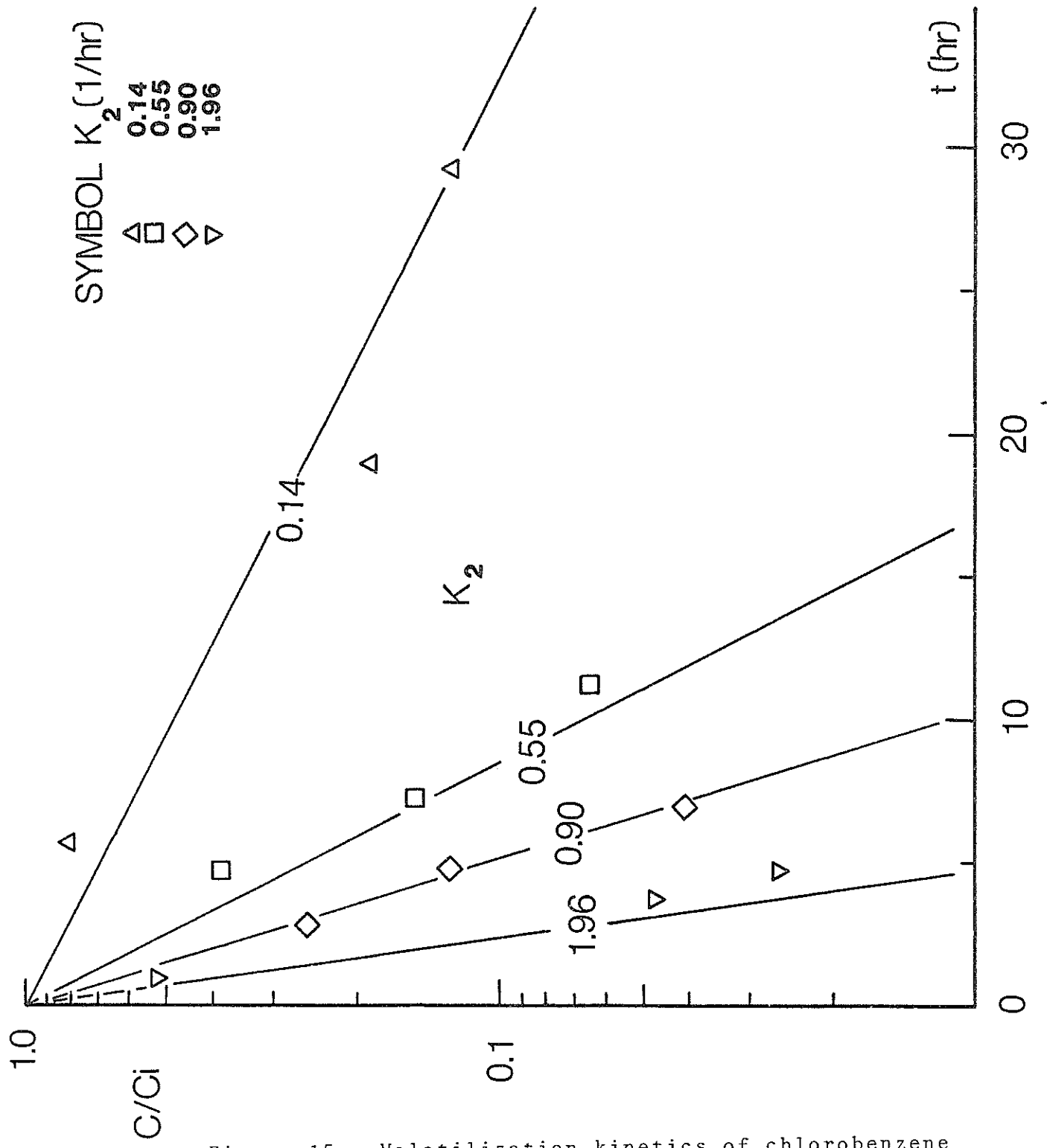


Figure 15. Volatilization kinetics of chlorobenzene in pilot studies.

between experiments and predicted values confirms the validity of the proposed value of  $n = 0.83$ .

The range of reaeration coefficients covered in this study varied from 0.14 to 1.96  $\text{hr}^{-1}$ . This range of  $K_2$  is typical of the many relatively rapid and shallow streams found in the western states. The VOC concentration range measured in volatilization experiments varied from approximately 1.0 mg/l to as low as 1.0  $\mu\text{g/L}$ .

Statistical analyses on the linear form (i.e., logarithmic) of equation (22), setting the intercept constant at  $C/C_i = 1.0$ , show that for a confidence interval of 95 percent, the experimental values of  $K_L/K_L^\circ$  vary from 0.48 to 0.57 for benzene and from 0.37 to 0.47 for chlorobenzene. The  $K_L/K_L^\circ$  values predicted from thermodynamic data for these compounds are 0.53 and 0.49, respectively. Even though the transfer coefficient ratio for chlorobenzene is slightly higher than the experimental confidence interval, the predicted benzene ratio coincides with the experimental mean. Thus, for the two compounds tested, the predicted  $K_L/K_L^\circ$  values are in agreement with the experimentally determined ones. This agreement between experimental results and theoretical predictions is shown in a visual way by comparing the experimental points in Figures 14 and 15 with the theoretically predicted concentration ratios represented by the solid lines. By extrapolation, implementation of the proposed model to actual streams should result in accurate estimates of the decay rate of various VOC.

Experimental Part D: Field Study. Results from a field study designed as a preliminary test of the model are also shown in Figure 4. This application was made using the Rio Grande near Albuquerque after repeated attempts to detect VOC in the Rio Grande near Las Cruces and



El Paso failed. Results from GC analysis of VOC in water in the Rio Grande north of the wastewater treatment plant and water at subsequent intervals downstream are shown in Figure 4.

Effects of volatility of VOC and pretreatment may also be seen in Figure 4. The water contained hexane and benzene which were identified using retention times and GC/MS techniques. Contribution to VOC from the Albuquerque wastewater treatment plant was small. Thus, to reduce the effect of dilution, the sample at Interstate 25 was chosen as the first sample. Results from actual quantification of VOC content versus distance (or time) are compared with theoretical curves in Figure 4. Experimental data for hexane are an excellent match with theory. However, results for benzene were erratic. This uneven behavior is similar to what may be expected if other sites of discharge were present downstream from Interstate 25. Although the presence of such sites is unknown to the authors, residential areas and small industries located downstream may be a source of such disturbances in the volatilization measurements.

## CONCLUSIONS

1. The most important self purification mechanism of low molecular weight organic pollutants in most agitated streams is volatilization to the atmosphere. Other less important mechanisms include biodegradation, adsorption and photolysis.

2. The volatilization kinetics of volatile and relatively insoluble substances are accurately predicted as a function of the volatilization of a reference. Oxygen may be used as a reference for this purpose because oxygen is ubiquitous, nontoxic and easy to detect. Also, several equations are available to calculate the reaeration of several types of reactors. Furthermore, effects of uncontrolled variables, such as temperature and the presence of surfactants and oils, are insignificant since both reference gas and the VOC interests are affected in the same manner.

3. The overall evaporation coefficients of volatile and relatively insoluble compounds may be computed from their respective diffusion coefficients or their molal volumes at their boiling point. These thermodynamic data are abundant and lead to precise estimates.

4. The volatilization of volatile and relatively insoluble compounds (which include a large number of priority pollutants) in rivers is an important self-purification mechanism. For example, our model may be used to predict that low molecular weight pollutants such as chloroform are reduced by three orders of magnitude within 100 km after the Albuquerque sewage treatment plant discharge. However, in slow moving streams such as the Tennessee River, similar results are obtained in more than 1000 Km from the point of discharge.

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