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DYNAMIC BEHAVIOR OF VINYL CHLORIDE IN AQUATIC ECOSYSTEMS

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DYNAMIC BEHAVIOR OF VINYL CHLORIDE IN AQUATIC ECOSYSTEMS

by

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ABSTRACT

To evaluate the behavior of vinyl chloride in aquatic ecosystems, best estimate and worst case models of lake and stream ecosystems were analyzed through the use of mathematical simulation. The characteristics of the chemical, biological, and physical transformations of vinyl chloride indicated in the models were determined by laboratory experimentation and extrapolation of reaction data for similar compounds. These transformations included oxidation, substitution, elimination, hydrolysis, and free radical reactions; complexation; direct and indirect photochemical reactions; microbial degradation and toxicity; bacterial, algal, and fungal sorption; and volatilization. Loss of vinyl chloride from the aquatic environment by volatilization appeared to be the most significant process in its distribution.

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CONTENTS

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SECTION I

CONCLUSIONS AND RECOMMENDATIONS

A worst case system analysis of vinyl chloride behavior in aquatic systems suggests that unrealistically high levels of vinyl chloride inputs would be necessary to maintain significant concentrations in these systems. However, given extreme environmental conditions, aquatic sediments could exhibit long-term storage of low levels of vinyl chloride.

Chemical degradation of vinyl chloride under pH's, reactant concentrations, and temperatures common to the environment should not be significant. Neither auto-oxidation nor degradation by free radicals is important in most natural waters at low vinyl chloride concentrations. Increased persistence of vinyl chloride due to complexation with Ag^+ and Cu^+ should be minimal. Data are not available for consideration of other metal species.

Experiments with distilled water, water from the effluent of a PVC plant, and two natural waters indicate that photolysis of vinyl chloride is probably a slow process under environmental conditions.

Vinyl chloride does not appear to be sorbed by microorganisms, as indicated by laboratory experiments with five mixed bacterial populations, three mixed fungal populations, two axenic bacterial cultures, and one alga. The five mixed bacterial populations did not degrade the vinyl chloride to any detectable extent. Also, at vinyl chloride concentrations up to 900 mg l^{-1}, no toxic effects on the bacterial cultures could be detected.

The rate of bulk exchange of gaseous vinyl chloride between atmosphere and water is about twice that of oxygen. Loss of vinyl chloride by volatilization from water is therefo[illegible]ably the most significant process in its distri[illegible]

The [illegible]ptions and consequently the conclusions of this analysis may be invalid when vinyl chloride enters a receiving water as a component of a tar or sludge or when large concentrations of surface active agents are present with the vinyl chloride in water. Further study is necessary for specific situations where these conditions exist.

SECTION II

INTRODUCTION

Vinyl chloride ($CH_2 = CHCl$), a colorless, highly flammable gas, is used primarily in the production of the resin, polyvinylchloride (PVC). The PVC is then used in the manufacture of many synthetic plastics and rubbers. Vinyl chloride monomer (VCM) is therefore present in many manufacturing operations and, because water is used as a medium in the polymerization reaction, it is also a possible contaminant of waste water discharged from these plants.

In recent studies, chronic exposure to VCM has resulted in liver injury to laboratory rats and rabbits. Also, some workers in PVC plants have contracted angiosarcoma of the liver (1). Because of its possible harmful effects on humans and other living organisms and the ubiquitous nature of vinyl chloride in the manufacturing industry, the behavior of VCM in aquatic ecosystems has come under critical study.

The present study was undertaken to investigate the behavior of vinyl chloride in aquatic systems under conditions simulating large inputs of VCM from industrial sources. The study involved the use of a conceptual model of vinyl chloride interactions in aquatic systems; physical, chemical, and biological experiments with vinyl chloride; mathematical models; and system analysis. The relationships among the various facets of the study are represented in the diagram in Figure 1.

The physical, chemical, and biological interactions of vinyl chloride with the components of aquatic systems determine the behavior of vinyl chloride in the system. The individual interactions can be characterized quantitatively by laboratory experimentation and the behavior of VCM within an aquatic system can be approximated by simulation of a system model. An initial conceptual model of the interaction of vinyl chloride in an aquatic environment, developed and described by Gillett et al. (2) is represented by the compartment diagram in Figure 2. In the diagram the boxes represent storage of vinyl chloride or its reaction products and the arrows represent transport or transformation processes.

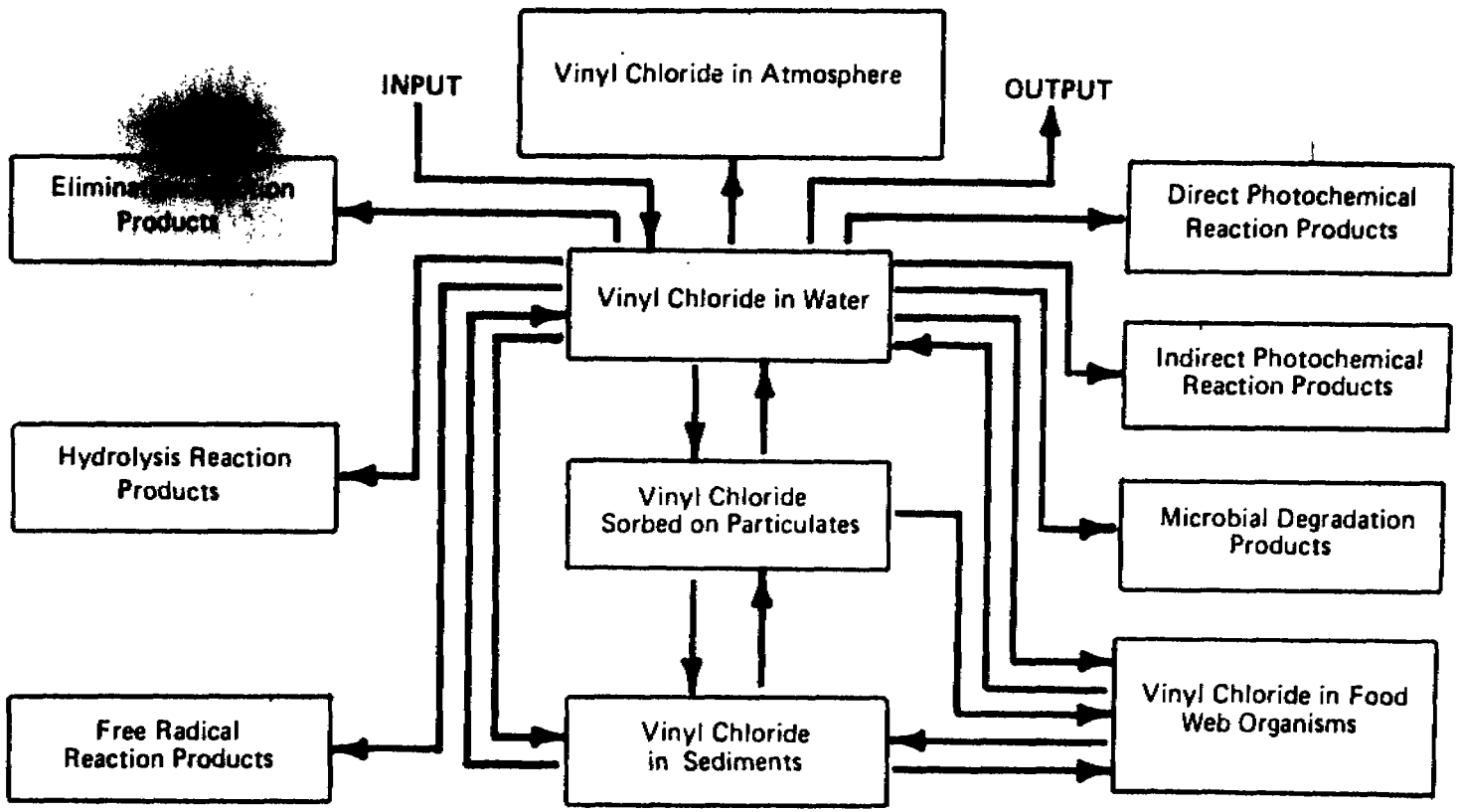


Figure 2. Initial conceptual model of vinyl chloride interactions in an aquatic environment.

SECTION III

SYSTEM ANALYSIS

For the purposes of the present study the behavior of vinyl chloride in an aquatic system may be assumed to be a function of four aspects of the system:

- the components of the system with which vinyl chloride may associate or react (e.g., water, organisms, other chemical species);
- the interactions or coupling pathways among these components;
- the characteristics of the interactions (e.g., magnitude, rate, saturation); and
- the rates of vinyl chloride inputs to the system.

The conceptual model of Figure 2 was used to organize the facts and assumptions into an initial system hypothesis as described by Gillett et al. (2). This model represents the components and interaction pathways considered to be important in a study of vinyl chloride in an aquatic system. This initial conceptual model was transformed to the conceptual model of Figure 3 through consideration of preliminary studies of vinyl chloride (3), available data on vinyl chloride and analogous compounds, and constraints on the scope of the investigation as defined by the nature of the problem.

The working conceptual model (Figure 3) indicated the need for quantitative characterization of the chemical, biological, and physical interactions between the components. The transport process dynamics have been evaluated in published descriptions of the behavior of the transport media (e.g., particle, fluid, and trophic dynamics). The transformation process dynamics were evaluated by chemical, biological, and physical experimentation.

The qualitative conceptual model (Figure 3) and the associated quantitative interaction descriptions can be logically reduced or expanded to provide a hierarchy of system models. These system models can be represented mathematically and evaluated by simulation to provide descriptions of vinyl chloride behavior at various levels of abstraction or generality.

The quantitative aspects of the possible behavior of vinyl chloride in aquatic systems may be approximated by simulation and analysis of a system model of a sample lake and stream. The conclusions resulting from these hypotheses, however, are only as good as the assumptions made in their formulation. These assumptions may be changed to incorporate new information or to apply the analysis to a particular aquatic system.

ASSUMPTIONS

The most significant assumption in this type of analysis is the model itself. The choices of components and their couplings represent a mixture of logical analysis, physical intuition, and personal biases. These choices affect the parameters, inputs, outputs, and responses of the model.

A best estimate approximation of the behavior of vinyl chloride in a sample lake or stream was obtained assuming the most reasonable estimates of the rates of transformation processes as determined from laboratory results. Experiments indicated that rates for all processes except volatilization are essentially zero (Section IV, V, VI, and VII). This assumption results in the simplified model of Figure 4.

To evaluate the boundaries of possible vinyl chloride behavior, two additional system models were derived describing extreme behavior at two levels of resolution. In these worst case analyses, all chemical and biological transformation processes were assumed to proceed at a rate that is just below the level of measurement in the experimental procedures used for their determination. Conditions in the aquatic environment (e.g., turbulence, stratification, sediment scouring) were assumed to be at the extreme of the environmentally realistic range that would cause worst case system responses. The system models of Figures [redacted] and 6 were analyzed subject to these worst case assumpt[redacted]

A [redacted] of linear, first-order ordinary differential equatio[redacted] assumed to be a reasonable mathematical approximation of the dynamic behavior of vinyl chloride in the hypothesized structures. This is justified by recourse to the theory of linearization about an operating path (4) and assumes that vinyl chloride input represents a small system perturbation.

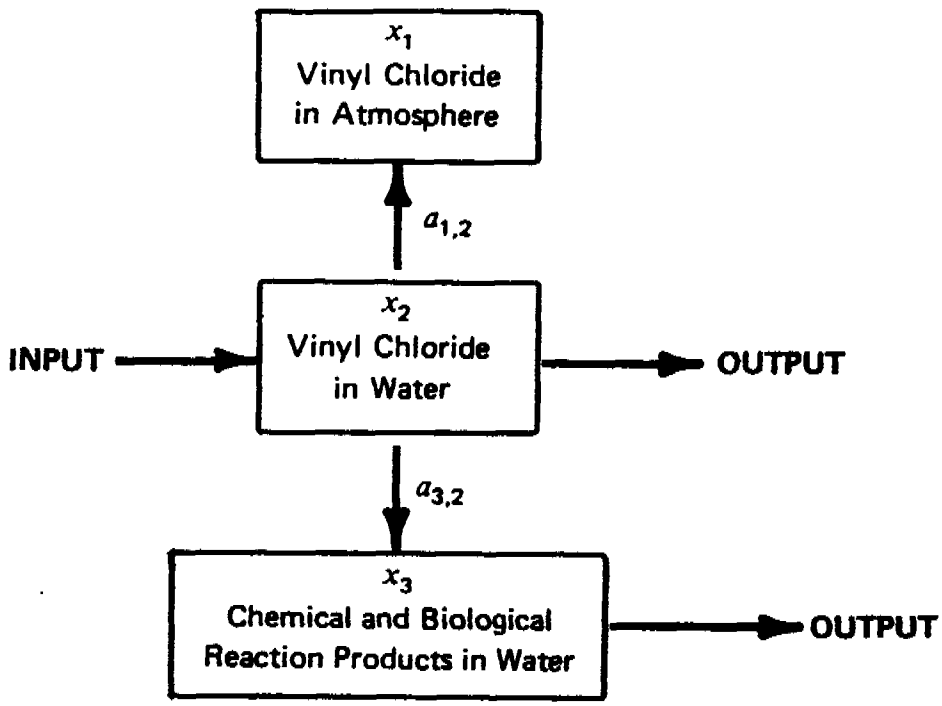


Figure [illegible] System model with worst case chemical and [illegible]gical transformation reaction rates.

The system diagrams of Figures 4 through 6 therefore were directly translated to a set of equations that can be written in vector form as

$$\frac{dX}{dt} = AX + BU \qquad (1)$$

where the x_i represent the variable quantities stored in the boxes; the a_{ij} represent the rate coefficients for transfer from box j to box i; and the u_i represent the inputs to box i.

The typical or sample lake is assumed to be 10^4 m^2 and 10 m deep. It has a residence time of 10 days and stratifies in summer with a metalimnion 0.5 m wide centered at a 5-meter depth. It is completely mixed above and below the thermocline when stratified and completely mixed otherwise. The typical or sample stream parameters were derived from Tsivoglou and Wallace's (5) data on the Chattahoochee and Jackson rivers.

For the best estimate model, equation (1) reduces to

$$\frac{dx_2}{dt} = a_{1,2}\, x_2 + u_1 \qquad (2)$$

The rate coefficient value, $a_{1,2}$, of the best estimate model of the [redacted] a bulk gas exchange coefficient between water and atm[redacted] of 0.436 day^{-1} (6, Section VII of this report). [redacted] input was set at 1 mg l^{-1} vinyl chloride in the infl[redacted] water as a reference value.

The gas exchange coefficient, $a_{1,2}$, in the best estimate stream model is 0.96 day^{-1} (5, Section VI of this report), and the input is again 1 mg l^{-1} vinyl chloride.

Table 1. WORST CASE MODEL PARAMETERS

Symbol	Interactions	Value (day^{-1})
$a_{1,2}$	Volatilization of vinyl chloride	0.436
$a_{3,2}$	Chemical and biological degradation	0.115
$a_{11,4}$	Chemical and biological degradation	0.115
$a_{2,4}$	Transport across thermocline	0.0178
$a_{4,2}$	Transport across thermocline	0.0178
$a_{6,2}$	Uptake by filter feeding organisms	0.000292
$a_{7,4}$	Uptake by filter feeding organisms	0.000292
$a_{8,5}$	Uptake by benthic organisms	0.000292
$a_{9,6}$; $a_{9,7}$ $a_{9,8}$	Uptake by predator	$9.73\ (10^{-5})$
$a_{10,6}$; $a_{10,7}$ $a_{10,8}$; $a_{10,9}$	Uptake by omnivore	$7.3\ (10^{-5})$
$a_{5,6}$; $a_{5,7}$ $a_{5,8}$; $a_{5,9}$	Turnover rate of organisms	0.1
$a_{5,4}$	Water to sediment transport	$0.107\ (10^{-2})$
$a_{4,5}$	Sediment to water transport	$3.45\ (10^{-4})$
$a_{i,i}$	Loss from compartment	$-\sum_j a_{ji}$
u_2	Input to water	1 ppm
u_4	Input to water	1 ppm

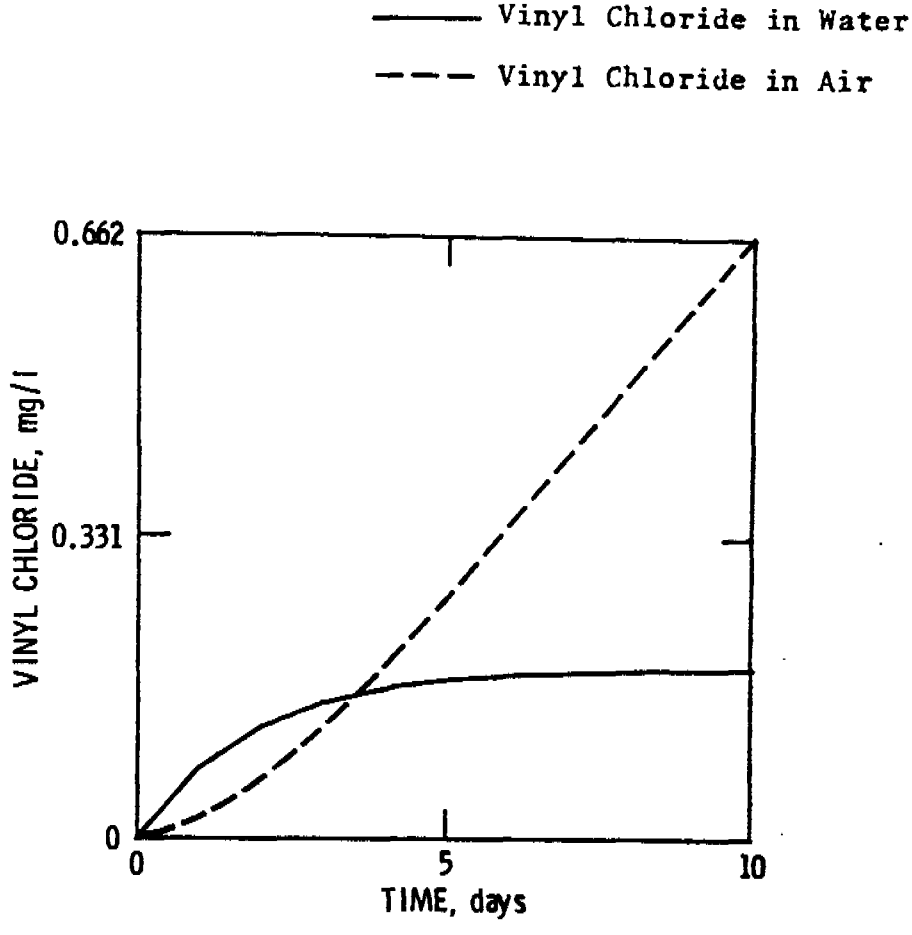


Figure [illegible] Lake simulation with best estimate model.

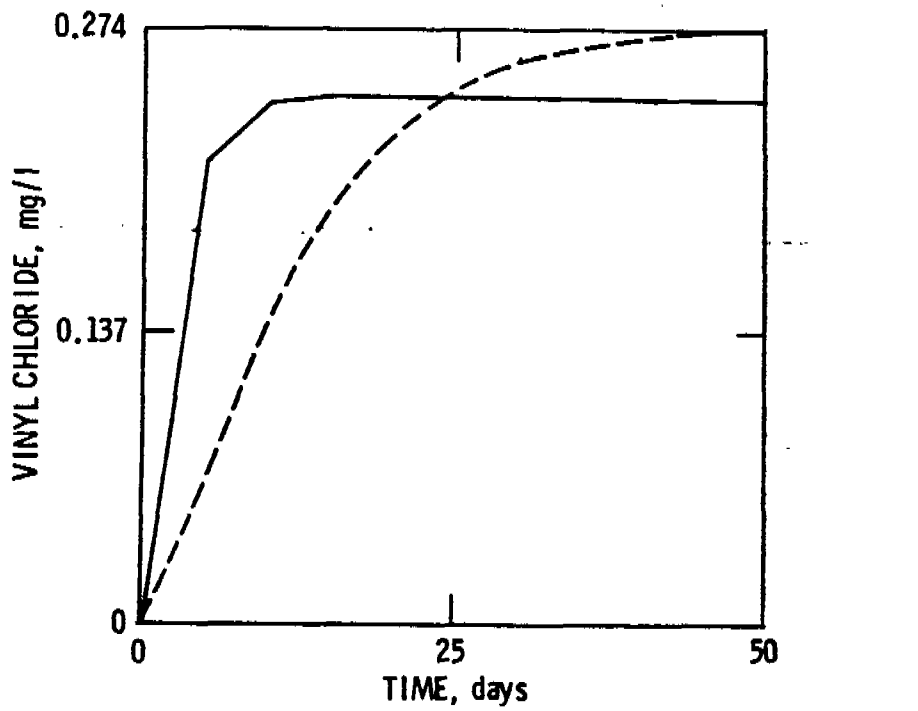


Figure [redacted] Lake simulation of the model of Figure 5.

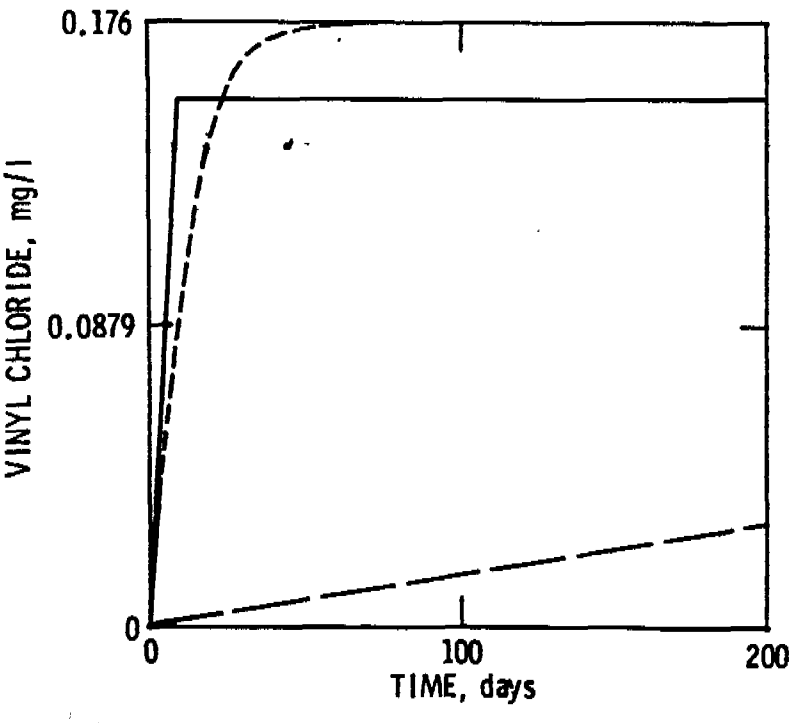


Figure 11. Stratified lake simulation of the model in Figure 6.

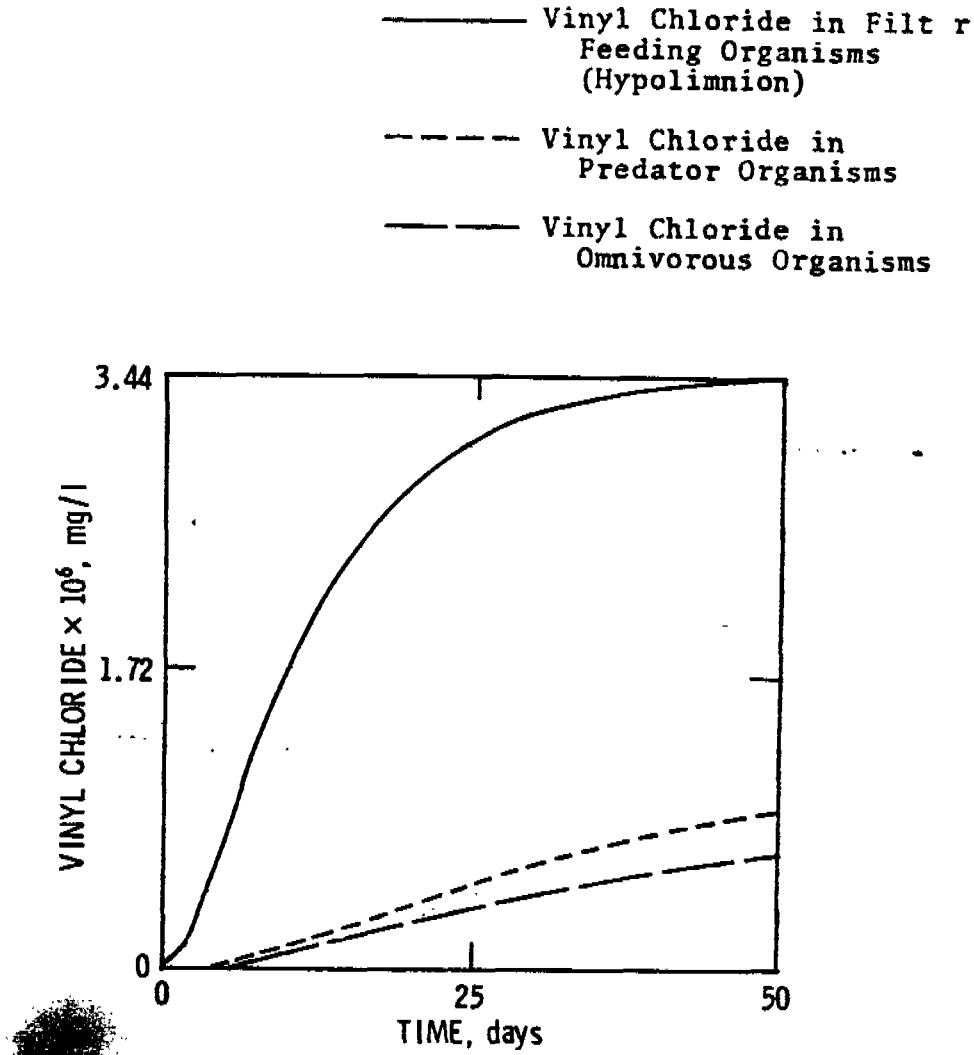


Figure 13. Stratified lake simulation of the model in Figure 6.

A diagnostic input consisting of a pulse of vinyl chloride can produce a characteristic response for each component. This response is a very concise way of demonstrating the behavior predicted by the system hypothesis. The total response to a pulse input contains all the information necessary to characterize the system (10). Figures 15 through 17 show the component responses to a pulse input of 1 mg l^{-1} vinyl chloride to the epilimnion waters for the model of Figure 6. In Figure 18, the beginning of the slow loss of vinyl chloride from the sediments can be seen aft r about 60 days.

The results of a pulse input of 1 mg l^{-1} vinyl chloride to the sediments are shown in Figures 19 through 21. The slow but continuous loss of vinyl chloride from the sediments is evident. This loss occurs to the air (rate $\pm$ 7 x 10^{-6} mg l^{-1} day^{-1}) and to downstream waters (rate $\pm$ 3.9 x 10^{-6} mg l^{-1} day^{-1}).

All of the results assume steady-state levels of biomass components and particulates and do not include any low level toxic effects or biomagnification (i.e., selective retention of vinyl chloride). From the results of these model simulations it appears that vinyl chloride should not remain in an aquatic ecosystem under most natural conditions.

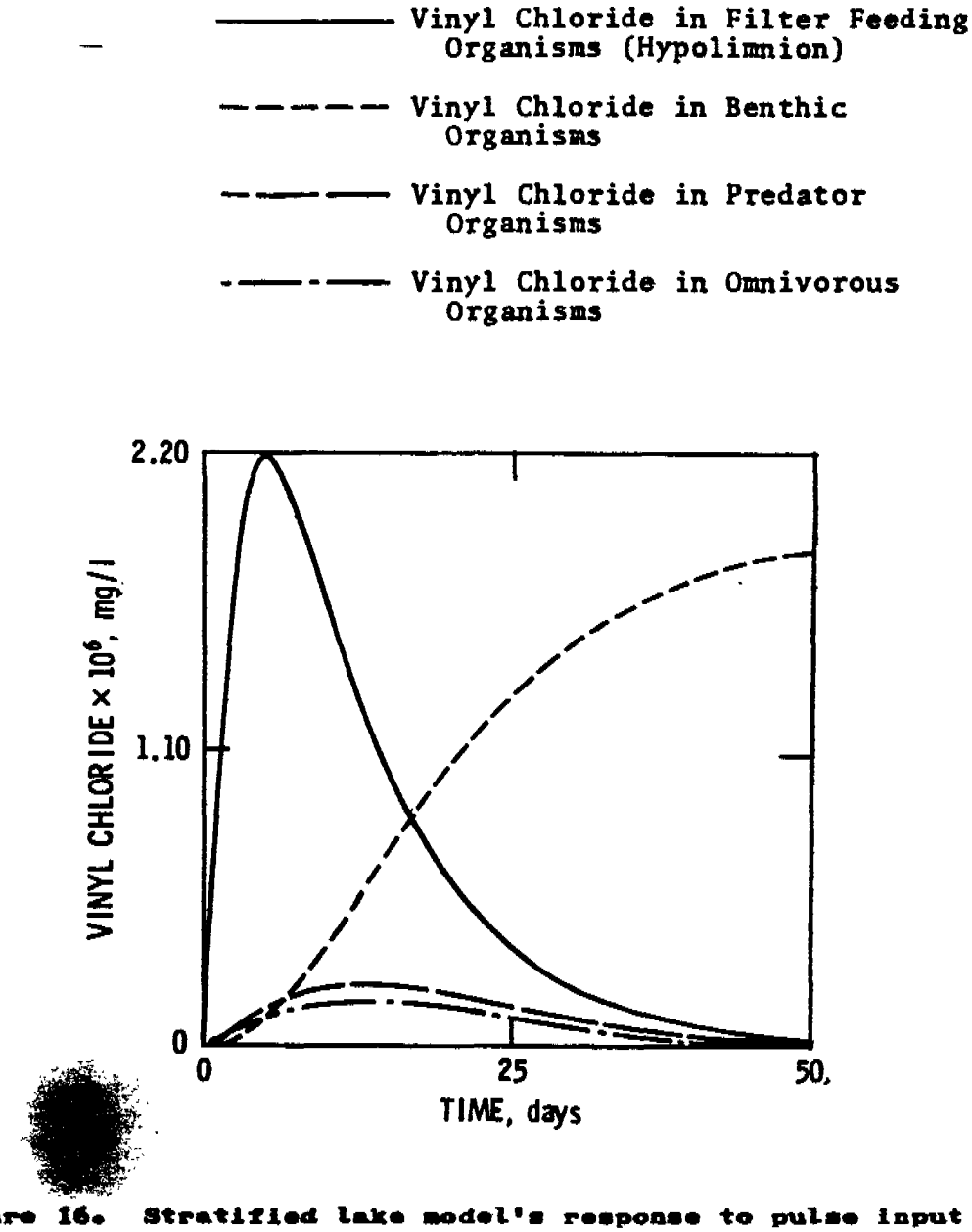


Figure 16. Stratified lake model's response to pulse input of vinyl chloride to epilimnion water.

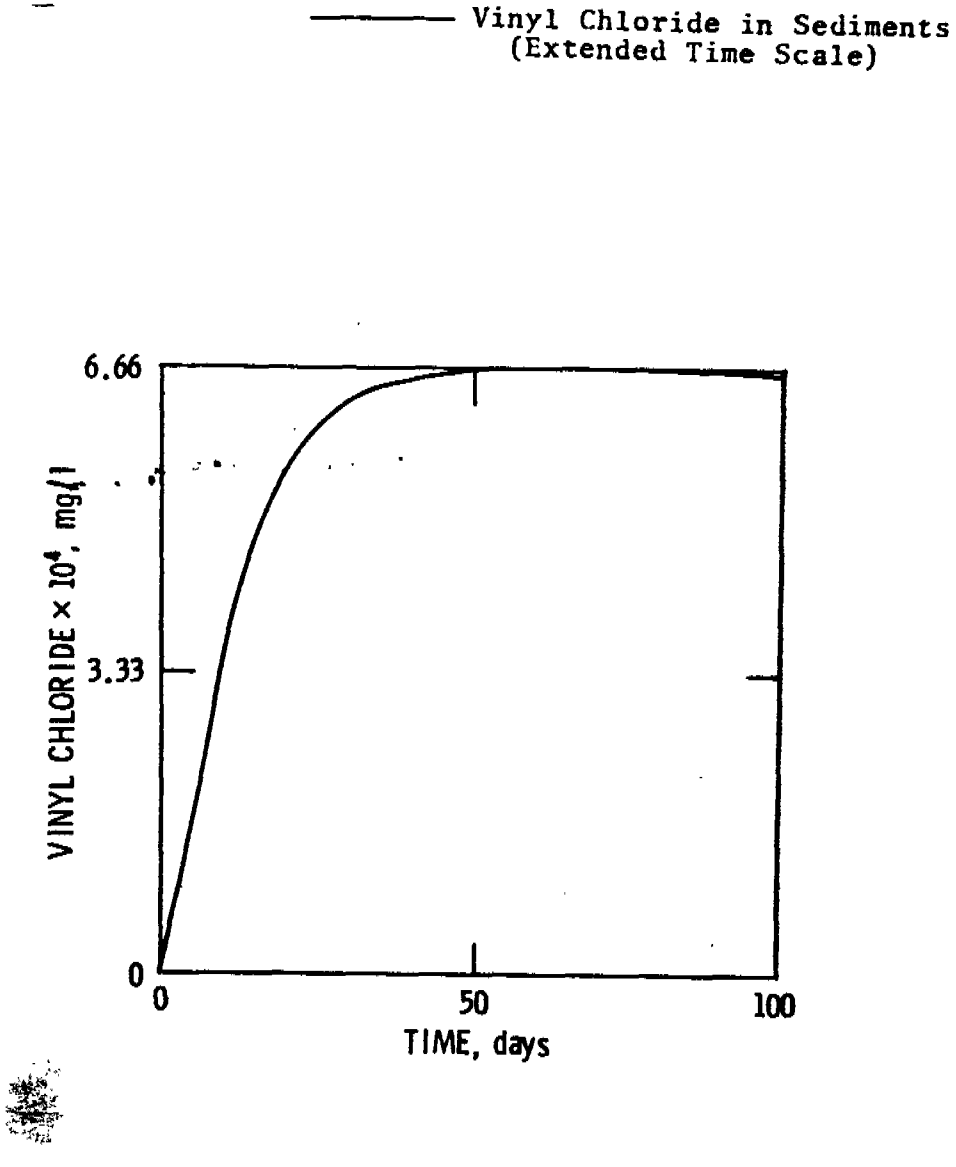


Figure 18. Stratified lake model's response to pulse input of vinyl chloride to epilimnion water.

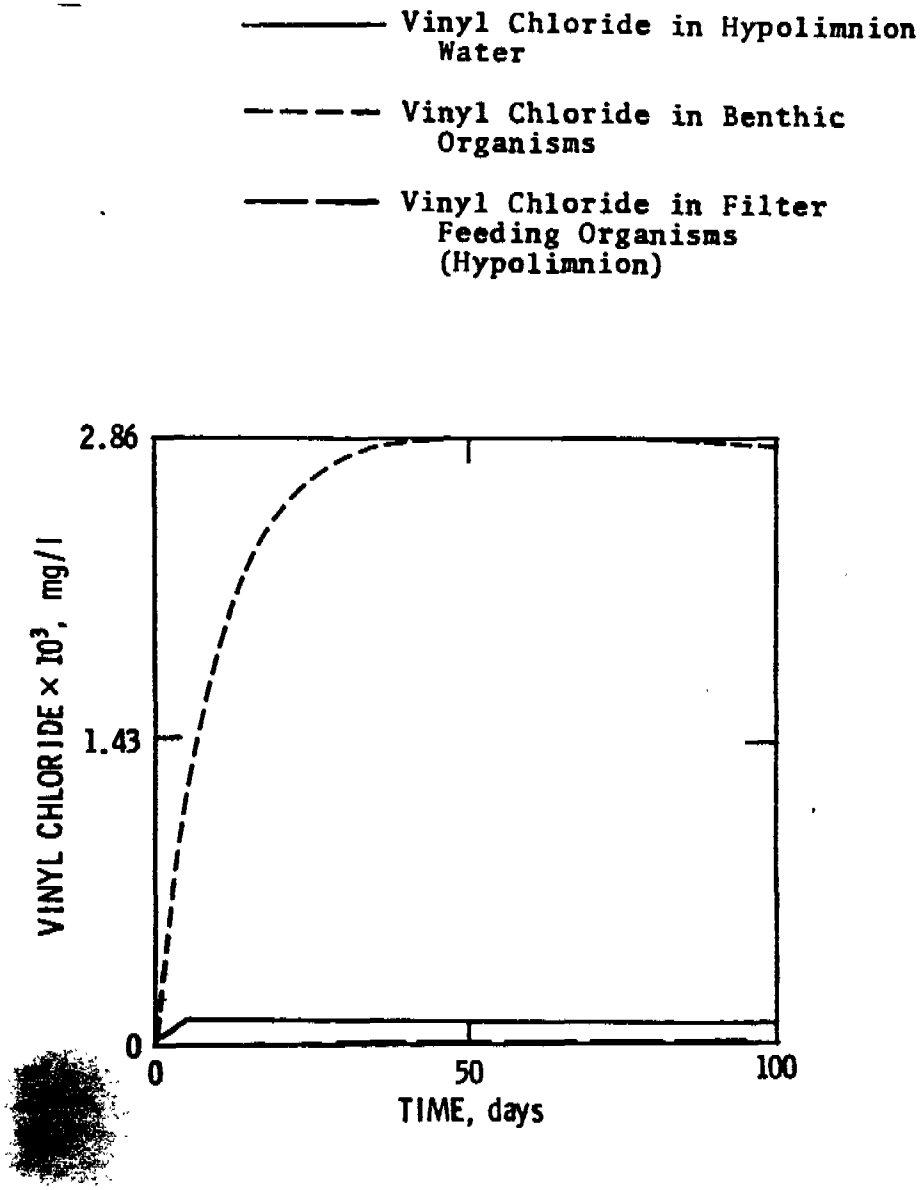


Figure 20. Stratified lake model's response to pulse input of vinyl chloride to sediments.

SECTION IV

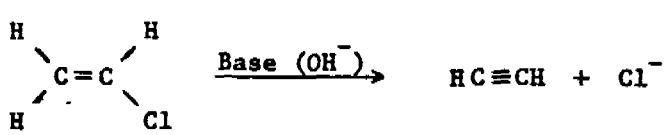
CHEMICAL INTERACTIONS

No reference to studies of the degradation of vinyl chloride in water could be found in the literature. However, considerable data are available concerning the chemistry of vinyl chloride and related compounds that can be extrapolated to reaction conditions anticipated in the environment. Evidence supporting such extrapolations was obtained in a few preliminary experiments.

Four pathways were postulated as potential mechanisms for chemical degradation or alteration of vinyl chloride in the environment: substitution (11), elimination (12), addition (13), and oxidation (14).

In nucleophilic substitution, the chloride ion is displaced by a nucleophilic species (Nu) (11). Reactive nucleophiles common to the aquatic environment are amin s, thiols, water, and hydroxide ion. The reaction can be either first or second order depending on the specific mechanism.

The most probable elimination reaction in the environment is one in which hydrogen chloride is eliminated from vinyl chloride in the presence of base, producing acetylene (12). This is a second-order reaction and the rate is dependent upon the concentrations of both vinyl chloride and base. The most significant base present in natural water would be hydroxide ion:



The addition reaction most likely to occur to vinyl chlorides in the aquatic environment is the addition of water across the carbon-carbon double bond, catalyzed by acid (13).

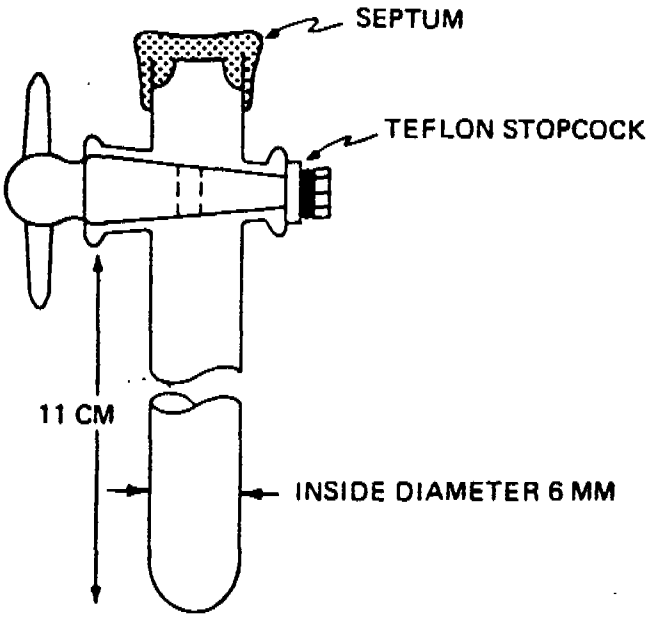


Figure 22. Vinyl chloride reaction vessel.

Table 2. ORDER OF MAGNITUDE ESTIMATES FOR HALF-LIVES FOR VINYL CHLORIDE REACTIONS

Reaction	Literature data			Estimated $t_{1/2}$ at 25°C[g]
	Temp. (°C)	Reactant	Maximum rate constant M^{-1} sec^{-1}	
Elimination[a]	95.53	Methoxide	10^{-7}	<10 yr
Substitution[b]	130	$C_2H_5S^-$	10^{-9}	<10 yr
Addition[c]	25	H_2O	10^{-4}	<1 yr
Addition[d]	25	Cl_2	10^{-1}	140 hr
Addition[e]	25	HOCl	10^{-2}	1000 hr
Hydrolysis[f]	120	H_2O	No RX	<10 yr

[a]Reference 17, methanol solvent, 10^{-3}M methoxide.
[b]Reference 18, reaction of 1-chloropropene in ethanol at 1 x 10^{-3}M thiol.
[c]Reference 19, acid catalyzed hydration at pH 3.
[d]Reference 20, 1,3,3-trichloropropene in aqueous acetic acid---1 mg l^{-1} chlorine.
[e]Reference 21, hypohalous acid addition to allyl alcohol at pH 4.5---1 mg l^{-1} hypohalous acid.
[f]Reference 15.
[g]Calculated assuming pseudo first-order kinetics.

A survey of the literature did not disclose any equilibrium constants for the formation of coordinate complexes between vinyl chloride and metal ions. However, data for the formation of complexes between structurally related olefinic compounds and Ag^+ and Cu^+ (Table 3) indicate that electron-withdrawing groups attached to the double-bonded carbon atom of the olefin decrease the equilibrium constant. Assuming a concentration of 10 mg l^{-1} for the silver-ethylene complex, equilibrium calculations show the complex to be greater than 99% dissociated. Similarly, the cuprous-β-chloro-allyl alcohol complex at 6.2 mg l^{-1} is also greater than 99% dissociated. The effect of other ligands common to the aquatic environment, which would be competing for the metal ions, are neglected in these calculations. Thus we conclude that at low metal ion and vinyl chloride ion concentrations, complexation by these metal ions is not important.

SECTION V

PHOTOCHEMICAL INTERACTIONS

Several possible mechanisms exist for the decomposition of vinyl chloride by light (Figure 23). Mechanism I, direct photolysis, involves direct absorption of light by vinyl chloride followed by reaction from its excited state (VCM)*. Several studies have indicated that vinyl chloride in the vapor phase decomposes when irradiated with very short wavelength ultraviolet light (< 200 nm) (20, 27, 28). The primary reaction processes are homolysis of the carbon-chlorine bond yielding a chlorine atom and elimination of molecular HCl. Twisting around the double bond, an undetectable reaction, may also occur.

Mechanism II, photosensitized reaction via energy transfer, involves absorption of light by a triplet sensitizer followed by energy transfer to vinyl chloride to form its first excited triplet state, (VCM)*. Studies by Bellas et al. (29), for example, indicated that photolysis of vinyl chloride can be sensitized in the vapor phase by mercury atoms. The authors concluded that in this case, the primary photochemical process for triplet VCM in the vapor phase involved elimination of molecular HCl. However, homolysis of the carbon-chlorine bond could not be ruled out by their data. In solution, the major photoreaction for triplet chlorinated olefins was found to involve twisting around the double bond (30).

Mechanism III, which we have called chemical sensitization, involves direct chemical reaction between sensitizer and olefin. Such reactions are known to occur in the condensed phase with simple olefins and electronically excited ketones (31).

Mechanism IV, free radical decomposition and polymerization of VCM initiated by photochemical homolysis of a species like a peroxide, is also a possible pathway. Examples of the light-initiated polymerization of vinyl monomers are discussed by Walling (32). Uri and co-workers found that polymerization of vinyl monomers can be "photosensitized" by chlorophyll (33) and by iron complexes (34, 35). The "photosensitization" in these cases clearly did not involve energy transfer, but rather the generation of free radicals followed by polymerization (Mechanism IV).

The photodegradation of vinyl chloride was studied to determine whether the above processes are possible in the aquatic environment, and whether their rates, if they occur, are sufficiently high to compete with other processes.

MATERIALS AND METHODS

Vinyl chloride gas from Matheson Company was used without further purification. Laboratory distilled water was redistilled from basic permanganate immediately prior to use.

Natural waters were obtained from the Oconee River in Athens, Georgia, and the Okefenokee Swamp (Big Water Lake) in South Georgia. Commercial humic acid was obtained from Aldrich Chemical Company.

Stock solutions of vinyl chloride were prepared in small bombs equipped with gas-tight Teflon stopcocks. Aliquants of VCM in gas-tight syringes were added to the bombs that were completely filled with known volumes of carbon tetrachloride; the gas rapidly dissolved into the CCl_4. Aqueous solutions were prepared following the same procedures; the concentration in water was then measured exactly by comparison to the CCl_4 stock solutions. Analyses for VCM were performed by gas-liquid chromatography on a 2 m x 0.32 cm glass column packed with 0.4% Carbowax 1500 on Carbopack A. The column was cured by heating at 200°C for 48 hours with slow purging by nitrogen.

Glc analyses were performed on a Tracor MT-220 Chromatograph using a flame detector. Photolysis studies were conducted on a rotating turntable apparatus, described in detail by Moses, Liu, and Monroe (36). A 450-watt high-pressure mercury lamp was the light source. The ultraviolet spectrum of VCM in water was obtained with a Perkin-Elmer 602 Digital Spectrophotometer using a specially constructed quartz cell equipped with a gas-tight Teflon stopcock. All photolysis studies were carried out in reaction cells equipped with gas-tight Teflon stopcocks. Controls established that no leakage of VCM occurred from these cells over a period of at least two weeks.

Kinetic studies were generally carried out at VCM concentrations of 10 to 20 mg l^{-1}. The light from the mercury lamp was filtered through a 3 mm-thick Pyrex sleeve (cutoff at 300 nm) for most of the studies. Singlet oxyg n

Indirect Photolysis

Although direct photolysis (Mechanism I) is immeasurably slow, the literature indicates that the light-induced transformations of vinyl chloride could occur through indirect pathways (Mechanisms II-IV). For example, substances found dissolved in certain natural waters wer found to greatly accelerate the photodecomposition of some pesticides (39, 40). Photolysis experiments were therefore conducted in natural waters and in distilled water containing model photosensitizers that absorb light of wavelengths > 300 nm.

Vinyl chloride was not readily degraded by singlet oxygen, an excited form of oxygen generated by methylene blue photosensitization. However, in the presence of acetone, a high-energy triplet sensitizer, or hydrogen peroxide, a free radical source, VCM decomposed rapidly when irradiated with ultraviolet light. The disappearance quantum yield (313 nm) for the acetone-sensitized reaction (3.0×10^{-2} M VCM) was 0.75. A colorless precipitate formed during photolysis, but it was not identified.

Since the major photochemical process for triplet 1,2-dichloroethylene and other mono-olefins involves isomerization (30), twisting about its carbon-carbon bond would be expected to be the primary process for triplet VCM. Other studies have indicated that reaction between triplet ketones and olefins (41) to form oxetanes is not particularly efficient. Therefore the high disappearance quantum yield for the acetone-sensitized photolysis of VCM was surprising. The photolysis may involve inefficient homolysis of the carbon-chlorine bond of triplet VCM, followed by free-radical polymerization of VCM, i.e., most of the VCM would be consumed by secondary thermal reactions.

The importance of photosensitization via energy transfer for the disappearance of VCM in the environment is difficult to predict. Such sensitization occurs efficiently only when the triplet state energy of the sensitizer equals or exceeds that of the acceptor, i.e., VCM. Since the triplet state energy of mono-olefins are very high (78-82 kcal $mole^{-1}$) (38), only high energy sensitizers such as acetone (triplet energy 80 kcal $mole^{-1}$) are effective. Unfortunately, little is known about the concentrations and distribution of high-energy sensitizers in the aquatic environment. The matter is further complicated by the fact that competing energy acceptors such as dissolved oxygen are also present in the aquatic environment.

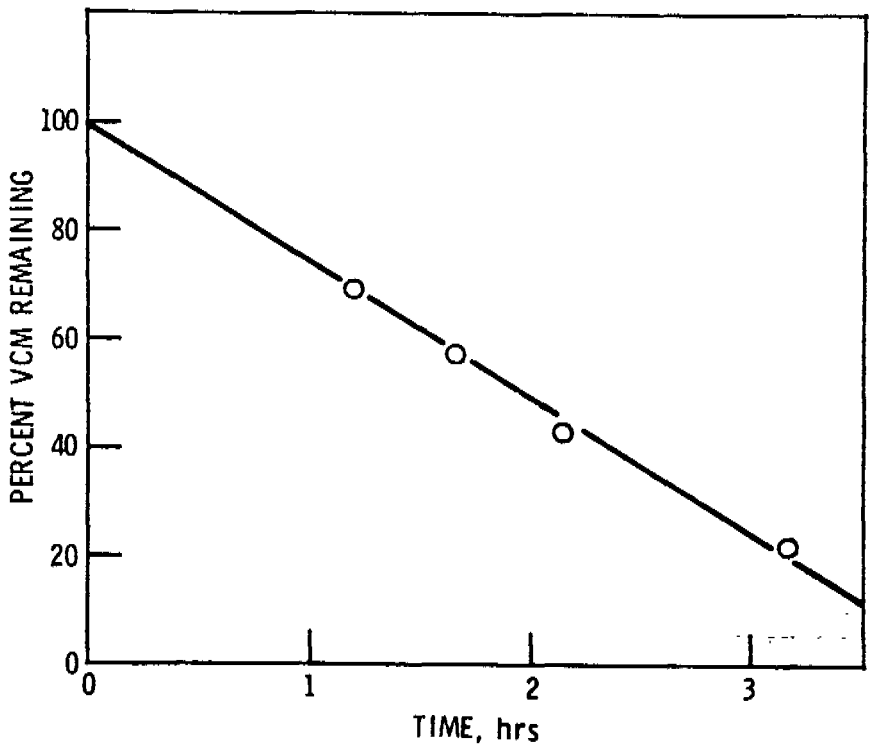


Figure 24. Decomposition of vinyl chloride in water by attack of free radicals generated by photolysis (300 nm) of hydrogen peroxide.

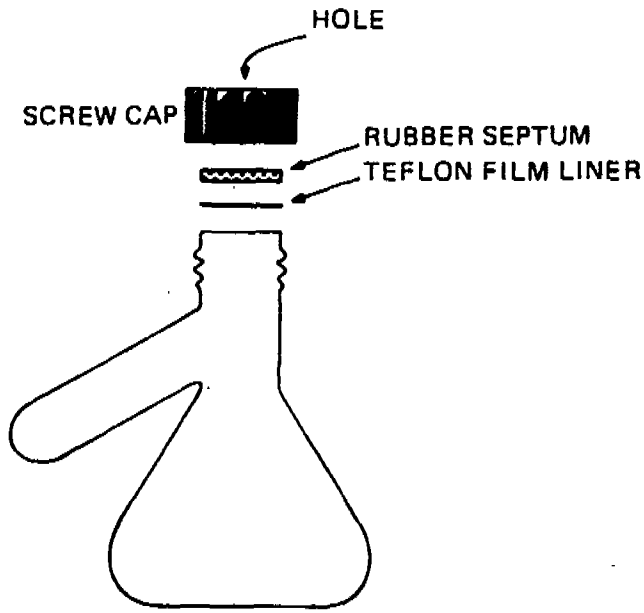


Figure [redacted] Apparatus for vinyl chloride degradation and toxicity studies.

medium containing 6.0 g glucose per liter. Medium was decanted and enough fungi were transferred to 5-ml graduated centrifuge tubes with ground glass stoppers to give approximately 5 g dry weight of fungi per liter of water.

Chlorella pyrenoidosa was grown in Bensen-Fuller medium containing 0.1% Hutner's trace element solution and incubated on a shaker at 15°C under 170 ft-c of continuous light. Cultures were centrifuged, washed three times, and transferred to 5-ml graduated centrifuge tubes with ground glass stoppers for sorption studies to give approximately 4 g dry weight of algae per liter of water. To eliminate corrections for volatilization of VCM to the air above the solution, tubes were filled to the top and all data were compared with data from control tubes (containing no organisms).

To determine dry weights of algae and bacteria used in sorption studies, cultures were centrifuged and the organisms were washed three times. The organisms were quantitatively transferred to tared beakers and dried to a constant weight at 90°C. Fungi were separated from test cultures for dry weight determinations by filtering, first through tared pre-filters, then through tared 0.22 micron Nucleopore filters, and by drying to a constant weight at 90°C.

RESULTS AND DISCUSSION

Sorption of Vinyl Chloride to Microorganisms

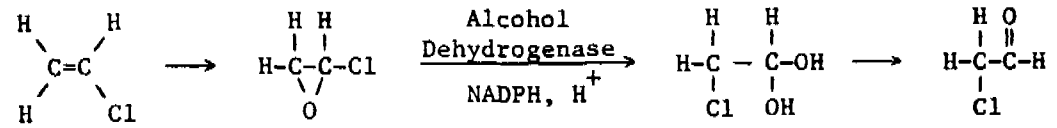
In systems in which sorption is linear (very low solute concentrations), the simple distribution coefficient (K_d) may be used to describe the extent of sorption of a compound to microorganisms

$$K_d = \frac{x/m}{c_e} \qquad (3)$$

where c_e = concentration (mg/mg) of solute in solution at equilibrium

containing only basal salts and 54 mg l^{-1} VCM without an additional carbon source. These cultures were monitored daily for one week. No degradation was detected at any time in any of the cultures.

Byington and Liebman (43) have shown that trichloroethylene was transformed to chloral hydrate by rat, rabbit, and dog liver microsomes in a reaction requiring NADPH and oxygen. Based on the structures of the compounds and the requirement of NADPH, alcohol dehydrogenase may be the active enzyme. If so, degradation of VCM by bacteria could be possible via the following pathway:



If the bacteria were capable of degrading VCM by this pathway, a system in which oxygen was not a limiting factor would be needed. The closed flask systems described earlier could limit the oxygen in the system. Therefore, six one-liter flasks containg the five bacterial populations in 1:40 nutrient broth and an uninoculated control were bubbled with 0.1% VCM in air for 96 hours and monitored for possible products by glc analysis at low column temperature using FID. No degradation products were detected in any of the cultures.

Toxicity of Vinyl Chloride to Bacteria

The toxicity of VCM to five actively growing bacterial populations was tested. Testing could not be done at VCM concentrations up to its solubility in water (1700 mg l^{-1}) because of the difficulty in supplying the bacteria with sufficient oxygen for growth above a VCM concentration of 900 mg l^{-1}. Because even at 900 mg l^{-1} VCM the oxygen concentration was low, a low nutrient broth concentration was used also (1:100) to insure that any differences in growth would be due to the presence of VCM rather than insufficient oxygen. No difference could be detected between bacterial growth in cultures and in test cultures containing up to 900 mg l^{-1} VCM. The VCM was therefore not toxic to bacteria at these concentrations.

rate of oxygen reaeration to eliminate the need for measurement of turbulence and to relate vinyl chloride volatilization to available environmental determinations of oxygen reaeration.

For comparison, the ratio of specific rates was also calculated using estimates of molecular diameter.

MATERIALS AND METHODS

Nitrogen-sparged, deionized water (900 ml) and saturated vinyl chloride solution (10 ml) were added to each of four beakers in an exhaust hood. The contents of beakers 1, 2, 3, and 4 were stirred to create vortices with depths of 0 (quiescent), 1.5 cm, 5 cm, and 10 cm, respectively. Oxygen and vinyl chloride concentrations were measured every 10 minutes for 180 minutes using a dissolved-oxygen meter and a gas chromatograph. Six replications of these experiments were performed.

RESULTS AND DISCUSSION

The gas exchange dynamics at the interface were represented as a first-order approach to equilibrium using the equation

$$\frac{dC}{dt} = K(C_s - C) \qquad (6)$$

where C = gas concentration
t = time
K = specific rate
C_s = saturation concentration

The concentrations of oxygen and vinyl chloride for each beaker in each replicate were used to determine the sums of squares for the best least squares fit to the logarithmic form of the solution to equation 6. The corrected sums of squares for all beakers stirred alike were pooled to

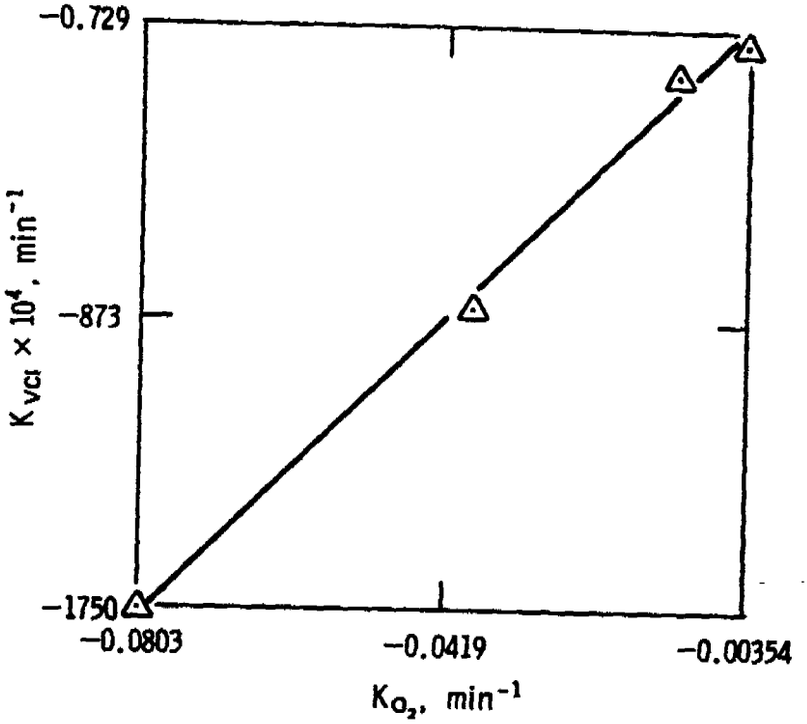


Figure [illegible] K_{VCM} versus K_{O_2} at four mixing levels.

specific rate of exchange of vinyl chloride gas between water and air is about twice that of oxygen.

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