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THE OCCURRENCE AND BEHAVIOR OF HALOMETHANES IN THE AQUATIC ENVIRONMENT

by

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ABSTRACT

THE OCCURRENCE AND BEHAVIOR OF
HALOMETHANES IN THE AQUATIC ENVIRONMENT

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This study was conducted to determine the impact of the release of halomethanes produced during the chlorination of wastewater into the Red Cedar River. The levels of chloroform in sewage were monitored as it passed through the East Lansing sewage treatment plant: a decrease from 35.0 µg/ℓ $CHCl_3$ in raw sewage to <1.0 µg/ℓ following tertiary treatment was observed. The production of halomethanes during chlorination was demonstrated by an increase from <1.0 µg/ℓ to 16.0 µg/ℓ chloroform following chlorination of tertiary treated sewage.

The Red Cedar River was sampled and analyzed for the halomethanes ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$, $CHBr_3$). Levels above 1.0 µg/ℓ were found only near the sewage effluent discharge points of the cities of East Lansing and Williamston. The highest concentration detected (East Lansing) dropped from 14.0 µg/ℓ to <1.0 µg/ℓ $CHCl_3$ within 500 feet downstream to the discharge.

The development of a sewage tracer was investigated to provide a means by which to differentiate changes in haloform levels in the river due to dilution from those occurring as a result of volatization or adsorption. Methods researched were neutron activation

analysis of europium, dysprosium and bromine, as well as a fluorescence and chloride ion tracer. The neutron activation methods were found to be the most sensitive, with limits of detection of 1.0 µg/ℓ dysprosium and 35.0 µg/ℓ europium.

Laboratory controlled haloform/oxygen gas transfer and adsorption experiments were conducted to predict the persistence of haloforms in a river system. Oxygen to haloform gas transfer ratios of $CHCl_3$ (1.63), $CHCl_2Br$ (1,83), $CHClBr_2$ (2.40), and $CHBr_3$ (3.50) and a measured log sediment-water partition coefficient of 1.6 ($CHCl_3$) were used to calculate Red Cedar River haloform volatization half-lives of 31 hr ($CHCl_3$), 35 hr ($CHCl_2Br$), 46 hr ($CHClBr_2$), and 67 hr ($CHBr_3$).

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INTRODUCTION

During recent years concern has intensified over the environmental and toxicological effects of a variety of halogenated hydrocarbons that are widely used and discharged by industry. Previously, major research has emphasized establishing the occurrence and distribution of chlorinated pesticides in the environment. However, recently there has been a growing awareness of the extent to which the environment is being contaminated with the halogenated analogs of methane; primarily: chloroform, dichloromethane, dichlorobromomethane, chlorodibromomethane, and tribromomethane. These compounds, collectively known as halomethanes or haloforms, are widely distributed in the environment at the low parts per billion range. The halomethanes have been measured in drinking water (Bellar and Lichtenberg, 1974; Dowty et al., 1975; Kloepfer and Fairless, 1972; Novack et al., 1973; Symons et al., 1975; Kissinger and Fritz, 1976), in wastewater (Rook, 1974, 1976), and in natural waters (Murray and Riley, 1973). Low concentrations of halomethanes in marine sediments, air, rainwater, and foodstuffs were also detected by McConnel and Ferguson (1975). Since these compounds have no known natural source, the presence of halomethanes in the environment is assumed to reflect their input from human activities.

Aside from waterways that are directly loaded with halomethanes from industrial effluents, the highest concentrations of these compounds have been found in waters treated with chlorine for disinfection

(Bellar et al., 1974; Glaze and Henderson, 1975; Morris and McKay, 1975; Rook, 1974) or for bleaching paper pulp (Yung et al., 1975).

The halomethane content of drinking water and sewage increases markedly after chlorination. Where the halomethane concentration of raw drinking water originally contained less than 1.0 µg/ℓ it increased to more than 100 µg/ℓ after chlorination (Bellar and Lichtenberg, 1974). This increase is not unusual because the halomethanes are formed through an aqueous substitution reaction between chlorine (as HOCl) and organic matter in water (Bellar and Lichtenberg, 1974; Rook, 1974). Rook (1974, 1976, 1977) theorized that the halogenated methane compounds are produced according to the classical haloform reaction with polyhydroxy aromatic rings and diketo alicyclic rings which are degradation products of the fulvic acids.

In early studies of low levels of organic pollutants in drinking water, the existence of a mixture of chlorinated compounds, the halogenated methanes, was detected in drinking water whose source was the Ohio River at Evansville, Indiana. Initially, the compounds were believed to have originated from accidental industrial spills. Novack et al. (1973) also found halogenated methanes in drinking water and since they were not present in the source waters concluded that the only possible source of the halogenated methane compounds was their accidental introduction as reagent impurities during analyses.

During the summer of 1974, the New Orleans water supply was analyzed for volatile low molecular weight chlorinated hydrocarbons. Thirteen chlorinated compounds, including carbon tetrachloride and chloroform, were detected in the low µg/ℓ range of the water (Dowty et al., 1975). An attempt was made to correlate the presence of these

compounds in drinking water with their concentrations in the blood plasma of New Orleans residents. Since some of the halogenated compounds in the drinking water were known carcinogens and the incidence of cancer in the New Orleans area was well above the national average, Dowty et al. (1975) felt that the detection of carcinogens in blood plasma would suggest a cause for the high cancer rates. Three compounds: carbon tetrachloride, tetrachloroethylene, and dichlorobenzene were subsequently found in both blood plasma and drinking water. It was then concluded that the Mississippi River, the source of New Orleans' drinking water, also contained the chlorinated hydrocarbons. However, while analyses of both water supplies confirmed the presence of halogenated compounds in the finished drinking water, their concentration in river water was either less than the finished water or below the limit of detection. This indicated that the halogenated hydrocarbons were introduced during the water treatment process.

During this period, Rook (1974) and Bellar and Lichtenberg (1974) demonstrated that organohalides are produced during the chlorination of drinking water or wastewater. Both studies detected chloroform, dibromochloromethane, and bromodichloromethane as the volatile halogenated constituents of chlorinated waters. Rook postulated that the substances arise from a haloform type reaction between the chlorine and organic compounds in the water treated.

In December of 1974, the U.S. Environmental Protection Agency initiated the National Organics Reconnaissance Survey (NORS) to determine the concentrations at which volatile halogenated compounds occur in drinking waters throughout the United States (Symons et al., 1975). An additional objective of this survey was to also determine what effect

water treatment practices had on the formation of these compounds. Eighty water supplies were chosen to represent a wide range of raw water sources and treatment techniques. The results of this survey are summarized in Table 1. In the raw water supplies the levels of the 4 trihalomethanes were either below the limit of detection or in extremely low concentrations. Carbon tetrachloride and chloroform was found in only 5 and 13 percent of the raw and treated waters, respectively. The highest concentrations of carbon tetrachloride in treated water was 3 µg/ℓ.

In general, chlorinated water exhibited halomethane levels corresponding to the concentrations of non-volatile total organic carbon and suspended solids in the raw water. Since groundwaters are normally very low in dissolved organics, cities with this source of raw water had much lower concentrations of volatile chlorinated organics in their finished waters than those drawing water supplies from lakes or rivers. Treatment plants that disinfected the raw water by ozonation rather than by chlorination provided finished waters with the lowest concentrations of halomethanes.

Since the EPA survey, a number of studies have been conducted to measure halogenated organic compounds in drinking water and wastewater (Sturino and Gipple, 1977, Bunn et al., 1975; Nicholson and Meresz, 1975, 1976; Dowty and Laseter, 1975; Hammerstrand, 1976; Kissinger and Fritz, 1976; Suffet et al., 1976; Morris and Johnson, 1976). In all of them halomethanes were detected in water that had been chlorinated, and the researchers concluded that it was produced as a direct result of chlorination. Recent studies indicate that organics adsorbed into the particulate fraction of agricultural runoff can also be halogenated in modern water treatment plants during disinfection. Morris and Johnson

TABLE 1.

Concentration of Halomethane in Selected Finished Drinking Waters (After Symons et al., 1975).

	Concentration (µg/ℓ)	
Halomethane	Median	Range
$CHCl_3$	21	<0.1 - 311
$CHCl_2Br$	6	ND - 116
$CHBr_2Cl$	1.2	ND - 100
$CHBr_3$	ND in 68 percent	ND - 92

ND = None Detected

(1976) showed a direct correlation between increasing river turbidity and the halomethane concentrations, suggesting the need to reduce the suspended solids to low levels before chlorination.

The production of non-volatile chlorinated organic compounds as a function of water and wastewater chlorination has also been investigated (Pitt et al., 1975; Glaze et al., 1973, 1975; Jolley, 1975; Jolley et al., 1975; Grob and Grob, 1974; Carlson et al., 1975; Murphy et al., 1975; Reinhard et al., 1976). These studies detected numerous aqueous chlorination products at various concentrations. Many of these compounds, including the halomethanes, could not be accurately identified. Therefore, their significance is not yet known. However, as more water is recycled their formation and persistence is likely to become a serious problem. Thus, previous conclusions about the effectiveness of chlorine as a disinfectant may have to be revised as more research is conducted into the formation of undesirable halogenated organics.

REACTIONS OF AQUEOUS CHLORINE TO FORM HALOMETHANES

When chlorine disproportionates in aqueous solution at pH 7, the following species exist in order of decreasing relative mole fraction concentrations: HOCl (0.80), OCL^- (0.20), CL_2 (3×10^{-6}) and H_2OCl (10^{-8}) (Morris, 1975). The reactivities of these species relative to HOCl are: $OCL^- = 10^{-4}$, HOCL = 1, $Cl_2 = 10^3$, $H_2OCl^+ = 10^5$. Even though H_2OCl^+ and Cl_2 are more reactive, the relatively large concentration of HOCl effectively makes it the most reactive species. Therefore, the oxidation, electrophilic substitution, and addition reactions

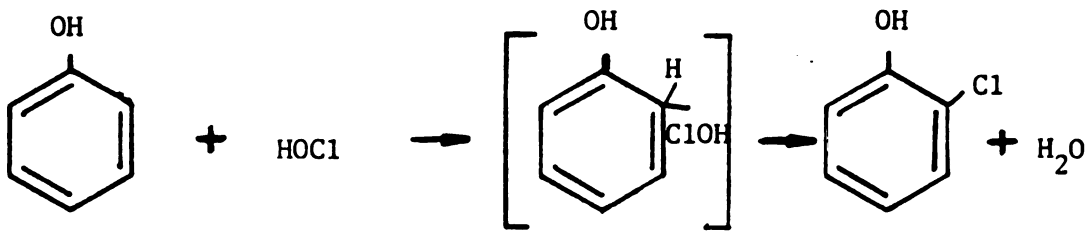
which occur in dilute aqueous solutions ($<10^{-3}$ M) at pH 6 to 8 are attributed to the electrophilicity of hypochlorous acid (Morris, 1975; Jolley, 1975).

Oxidation is the predominant reaction between the hypochlorous acid and organic matter. Oxidation reactions are responsible for the immediate chlorine demand during chlorination. Typical classes of organic compounds found in natural waters which can be oxidized by hypochlorous acid are the carbohydrates, polysaccharides, and the aliphatic organic acids. Chlorination of these compounds does not result in the formation of any chlorinated compounds. The result of oxidation is simply reduction in the total organic carbon content of the solution.

Electrophilic substitutions by hypochlorous acid are the major reactions responsible for the formation of non-volatile, stable chlorine-containing organic compounds during water treatment. The major classes of compounds in surface and wastewaters undergoing substitution by hypochlorous acid usually contain electron rich centers such as the unshared electrons of the nitrogenous bases (amides, amino acids, indoles, and pyridine as well as purine and pyrimidine derivatives) and the π electron systems of olefins and aromatic compounds (o-phthalic acid and the phenolic compounds catechol, p-cresol and phenol). Jolley (1975) compared the concentrations of chlorine substituted compounds in wastewater before and after chlorination and found a significant increase in stable chlorine containing compounds other than chloramine, indicating that substitution was taking place during treatment with chlorine.

Substitution of hypochlorous acid onto ammonia or amides proceeds by the attachment of the electrophilic acid molecule to the unshared electron pair of the nitrogen atom. As a result, a proton is released from the ammonia or amine molecule and a hydroxyl ion from hypochlorous acid to form chloramine and water.

Aromatic electrophilic substitution occurs in chlorinated waters according to the following reaction:



The reactivity of the aromatic molecule depends upon the presence of ring activating groups. Carlson et al. (1972, 1975) demonstrated that monosubstituted aromatics exposed to low concentrations of aqueous chlorine followed recognized trends for aromatic substitution by electrophiles. Ring activating groups such as hydroxyl, ether, amine or alkyl derivatives on the aromatic moiety accelerate substitution while the presence of electron deactivating groups such as nitro, chloro, and nitrile tend to prevent reaction.

Murphy et al. (1975) indicated that electrophilic aromatic substitution of phenol is inhibited by the presence of ammonia while Jolley (1975) reported lower yields of chlorinated compounds under conditions of high ammonia concentration. This could be due to

competition for active chlorine by ammonia to form chloramine which is an electrophile in aromatic substitutions. The mechanism of the reaction is unknown, but it is capable of rupturing the aromatic ring to form quinones which can be substituted to yield halomethanes.

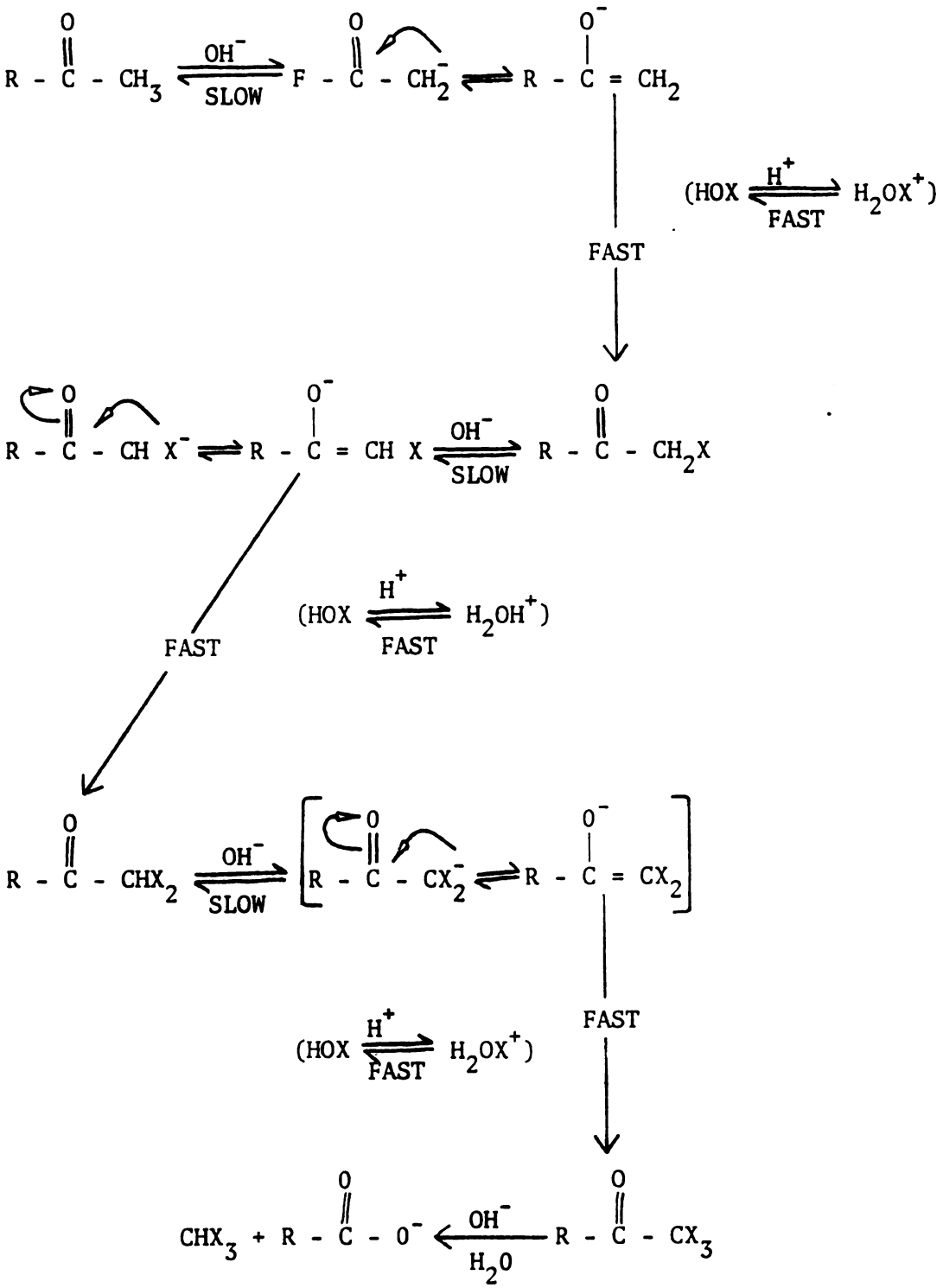
A study by Carlson et al. (1975) ruled out the possibility that significant levels of polychlorinated aromatic compounds are formed during water chlorination. Biphenyl was subjected to a wide range of aqueous chlorination conditions. However, polysubstitution was limited to disubstituted biphenyls and occurred only at very low pH and high chlorine levels (pH 2.2, 1350 mg/ℓ Cl_2).

Hypochlorous acid can attack double bonds to form chlorohydrins. This reaction involves the transfer of Cl^+ to the double bond to yield a chloronium ion. The reaction is completed by adding OH^- or other anions from the solvent at one of the chloronium bonds (Morris, 1975). Compounds susceptible to this type of electrophilic attack are terpenes, carotenoids, and the xanthophylls. Unless the double bond is strongly activated by substituent groups, reactions of this type would be too slow to be significant under normal water treatment conditions.

THE HALOFORM REACTION

During chlorination volatile halogenated organic compounds are formed primarily by the haloform reaction (Rook, 1974, 1975). In this classical reaction, aqueous hypohalites react with methyl ketones or compounds oxidizable to methyl ketones to yield halomethanes. The haloform reaction can proceed with an acid or base catalyst. In

dilute aqueous solution, the base catalyzed reaction is of primary concern and proceeds according to the following mechanism (Morris, 1975):



In this reaction, hydrogen is successively replaced by chlorine on carbon alpha to a carbonyl group followed by hydrolysis to produce the halomethane chloroform and a carboxylate ion. The mechanism of this reaction involves dissociation of a proton from the alpha carbon to form an enolate carbanion which can be attacked by electrophilic HOCl or OCl^-.

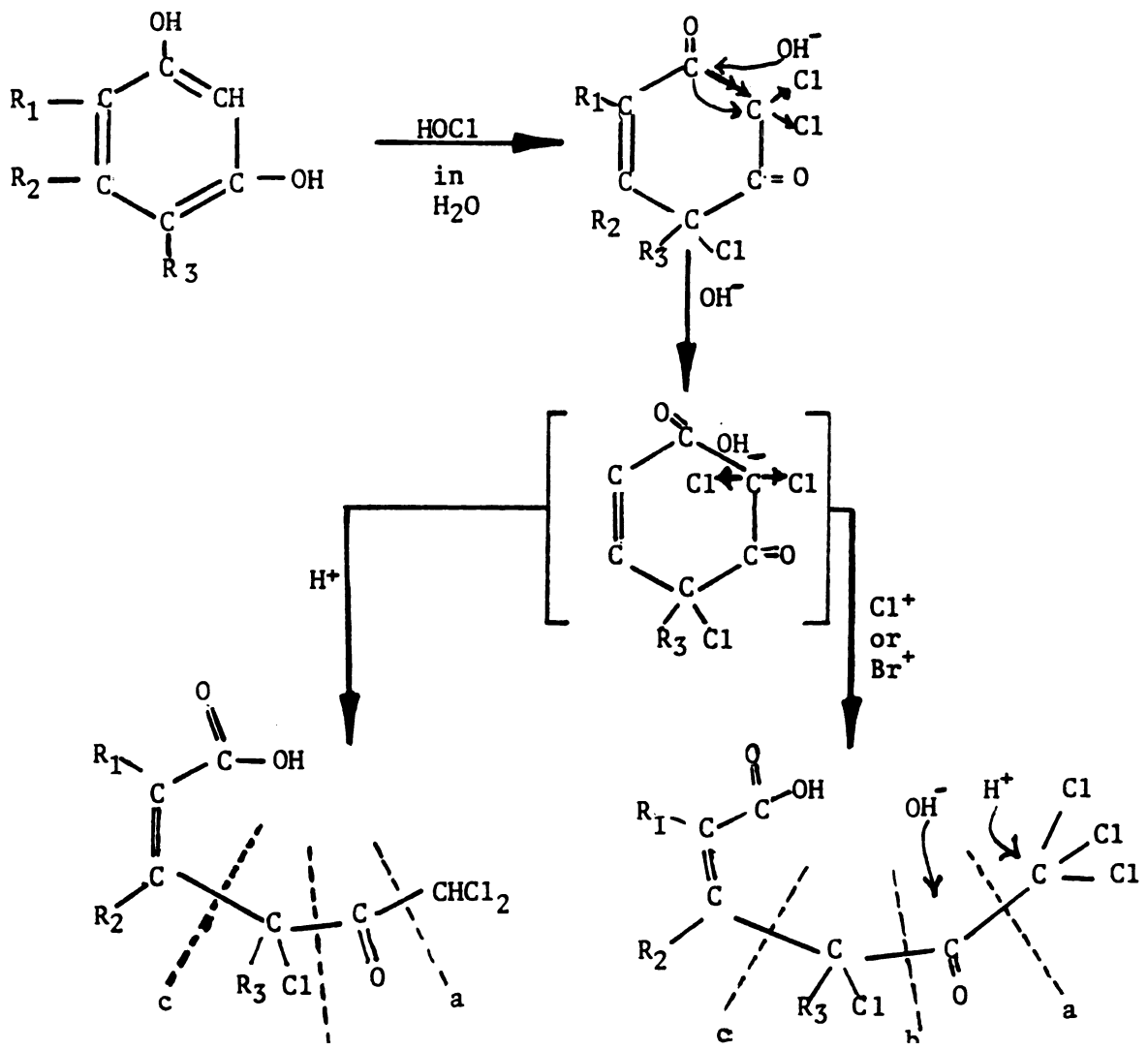
The reaction involving simple methyl ketones will form considerable yields of haloforms only at high pH. At the pH values normally encountered during water chlorination, chloroform formed from methyl ketones via this reaction mechanism is produced too slowly to produce significant amounts of halomethanes. Bellar and Lichtenberg (1974) explained the formation of chloroform by proposing the following reaction sequence:

$$CH_3CH_2OH \rightarrow CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}H \xrightarrow{HOCl} Cl_3\text{-}C\text{-}\overset{O}{\overset{\|}{C}}\text{-}H \xrightarrow{H_2O} Cl_3\text{-}C\text{-}\overset{H}{\overset{|}{C}}\text{-}(OH)_2 \rightarrow CHCl_3$$

In water, ethanol oxidizes to acetaldehyde which reacts with free chlorine to form chloral. Chloral can react with water to produce chloral hydrate which decomposes to form chloroform. In Bellar and Lichtenberg's study no experimental evidence was provided to indicate that chloroform was indeed being produced by this reaction sequence. This reaction scheme was based principally on the fact that acetaldehyde and chloral as well as chloroform were detected in the drinking water.

Rook (1975, 1976, 1977) contended that halomethanes were formed as a result of the haloform reaction involving the polydroxybenzene building blocks of the fulvic acids. These components of the fulvic acids are more highly activated than the methyl ketones of the simple

haloform reaction and are, therefore, much more reactive at pH values 6 to 8. They contain carbons which are more acidic than those alpha to single carbonyl groups. During laboratory controlled chlorination experiments at pH 7.5, Rook (1976) demonstrated the reactivity of resorcinol, a compound believed to be a common component of the fulvic acids. Following a 4 hr contact with 7 mM chlorine at 10°C, a 75 percent yield of chloroform was observed. Rook estimated the presence of one resorcinol ring per 200 carbons of the fulvic acids, and predicted a halomethane yield with fulvic acids of 0.4 percent on a carbon basis. The proposed mechanism for degradation of fulvic acids and resorcinol via free haloform is given below where the Cl^+ or Br^+ represents any



electrophilic halogenating species of the series: $X\ OH_2^+$, X_2, HOX and X_2O. Cleavage usually occurs at a, b, or c resulting in the major chlorinated compounds usually detected following chlorination (Rook, 1977). In tests with peat extracted fulvic acids, the halomethane yields ranged from 0.3 to 0.9 percent depending on the chlorination conditons.

The evidence for a fulvic acid precursor is reinforced by its high concentrations in water and wastewater and by the type of haloform reactive acidic groups it contains. Manka et al. (1974) surveyed the major classes of organic compounds in secondary sewage effluents. Fulvic acids comprised 26 percent of the total organics, followed by proteins (21 percent), anionic detergents (16 percent), and hymethanomelanic acids (7 percent). Of the humic compounds, fulvic acids are the most acidic and the only compounds which contain phenolic hydroxyl acidic groups. Suffet et al. (1976) identified the haloform reaction intermediate 1,1,1-trichloroacetone in Philadelphia drinking water but not in the new water strongly implying that the haloform reaction takes place during chlorination.

Brominated methanes have been detected in all analyses for the volatile halomethanes. Since they are believed to be produced by chlorination, some question exists as to the source of the bromine. Bellar and Lichtenberg (1974) reasoned that the brominated analogs came from bromine impurities in the chlorine which would react in the same manner as chlorine. This view contrasts with that of Rook (1974) and Morris (1975). They postulated that the source is bromide ion which is present in most natural waters in fractions of a part per million. However, bromide ion has a catalytic effect in oxidative

reactions of chlorine and also forms a stronger electrophile than hypochlorous acid. Bromide ion reacts with hypochlorous acid to form hypobromous acid and chloride ion. Because of its reactivity, HOBr

$$HOCl + Br^- \quad HOBr + Cl^-$$

undergoes haloform reaction at much faster rates than HOCl and, therefore, brominated organics are encountered.

The possibility of forming iodomethanes was demonstrated by Bunn et al. (1975). Potassium halides were used to establish the respective fluoride, chloride, bromide, and iodide ion concentrations which in turn could be oxidized to the respective hypohalous acid and reacted to produce halomethanes. Adding potassium fluoride and chloride to Missouri River waters treated with 7 mg/ℓ available chlorine had little effect on the production of trihalogenated methanes. The addition of potassium bromide, however, substantially reduced the chloroform concentration with a corresponding increase in the brominated halomethanes. Adding potassium iodide also decreased the chloroform with the production of iodine containing trihalomethanes: dichloroiodomethane, chlorodiiodomethane, and iodoform. No fluorinated compounds were found because hypochlorous acid is not a strong enough oxidizing agent to oxidize fluoride ion.

Kissinger and Fritz (1976) noted that storing water samples increases their halomethane content. This increase suggests that over time, organic matter in the sample reacts with residual chlorine or bromine to produce additional halomethanes. Therefore, it can be assumed that the concentrations of halomethanes change while water is in the distribution system of a city water supply. An exchange reaction may also take

place between chloroform and bromine. It was found that after three or four days, the chloroform concentration decreased with an increase in chlorobromomethane compounds and bromoform.

THE ENVIRONMENTAL THREAT FROM HALOMETHANES

In 1975 a Science Advisory Board Study Group (Anon., 1975) studied the potential carcinogenic and other health risks from ingesting selected organic compounds in drinking water and recommended that chloroform be considered a suspected carcinogen. They further recommended a continuous testing program to fully evaluate the effects of chloroform on human health. In 1978 a 100 μg/ℓ ceiling on total haloforms in drinking waters was established (Anon., 1978).

The amount of halomethanes produced during water chlorination does not seem to be significant as long as the concentrations remain in the low parts per billion range. However, if this release is viewed as occurring continuously, on a global scale, very large amounts of halomethanes are being introduced into the environment.

For example, the East Lansing sewage treatment plant processes about 14 million gallons of wastewater effluent daily with an average of 10 μg/ℓ of total halomethanes, thereby releasing approximately 0.53 kg (440 kg/yr) of these compounds into a small warm water stream each day. If all of the sewage and water treatment operations that practice chlorination in the United States are considered, 100,000 tons of halomethanes could be produced per year. In addition, the uses of chlorine in cooling waters and paper bleaching processes also result in extremely high halomethane losses. For example, it has been estimated that paper bleaching alone releases 300,000 tons of chloroform

to the environment per year as a result of the haloform reaction (Yung et al., 1975). This is more than twice the current American industrial production of chloroform, 130,000 tons per year (Fishbein, 1976).

Because significant amounts of halomethanes are currently being released to the environment as a result of water chlorination, it is important to determine the fate of these halomethanes in natural waters.

At present, there is no known natural process by which halomethanes are produced in the environment. Lovelock et al. (1973) suggested that chloroform, the halomethane most often encountered in natural systems at the highest concentrations, can be formed by atmospheric reaction between methane and chlorine. However, no experimental evidence was given for this reaction. Nevertheless, a study by Appleby et al. (1976) demonstrated that chloroform can be formed in the atmosphere as a product of the photochemical breakdown of trichloroethylene. The amount of chloroform formed by this reaction is not known, but presumably it is very small. Therefore, the major contribution of halomethanes into the environment is presently assumed to result from human uses of these chemicals and their production and release during the chlorination of water.

Background halomethane levels have been measured by a number of investigators. Murray and Riley (1973) measured the concentrations of chloroform and carbon tetrachloride in surface waters and in the air above the Atlantic Ocean. They detected average levels of 1.7 ppb chloroform and 0.3 ppb carbon tetrachloride in air and 8 μg/ℓ chloroform and 0.14 μg/ℓ carbon tetrachloride in surface water. McConnel and Ferguson (1975) measured up to 40 ppb chloroform and 70 ppb carbon tetrachloride in air and 0.2 μg/ℓ chloroform and 0.03 μg/ℓ carbon

tetrachloride in rainwater. Analyses of marine sediment revealed up to 4 µg/kg chloroform. Since the concentrations in the sediment were very similar to those in the overlying waters at half depth, it is presently assumed that the halomethanes do not tend to accumulate in sediments to any extent.

Chloroform and carbon tetrachloride levels in animal tissues and foodstuffs were measured by McConnel and Ferguson (1975). The chloroform content of foods was highest for dairy products (33 µg/kg in cheese, 22 µg/kg in butter) while the highest levels of carbon tetrachloride were found in oils (16 µg/kg in cod liver oil, 18 µg/kg in olive oil). Marine organisms contained chloroform levels ranging from below the limits of detection of 1 µg/kg to 180 µg/kg with an average of about 40 µg/kg. There was no indication that chloroform accumulates in the food chain. Organisms higher in the food chain contained the same and often lower concentrations of chloroform than their prey populations. The organisms reflected the general background concentrations of their environment. Laboratory accumulation studies revealed that aquatic organisms incorporated chloroform at the levels to which they were exposed, but as soon as they were placed into a low chloroform environment their chloroform levels decreased.

Post mortem analyses of human tissue revealed no significant accumulations of carbon tetrachloride and chloroform (McConnel and Ferguson, 1975). Chloroform was detected in tissue and fat samples of all 8 subjects tested (average age 70 yr). The levels ranged from 1 µg/kg in the liver to 68 µg/kg in body fat (average 51 µg/kg in fat). The low levels indicated that the amounts of chloroform ingested in food and water did not accumulate in the body tissue but were

metabolized and excreted. It is believed that most of the halomethanes are moderately to well absorbed from the gastrointestinal tract after oral administration (McConnel and Ferguson, 1975). A large proportion of the halomethanes are expired by the lungs either unchanged or are metabolized. Although mammals are capable of metabolizing chloroform and carbon tetrachloride, it is not known whether other organisms are able to do this. Indeed, microorganisms, which carry out the task of degrading almost all organic compounds, are not capable of breaking down halomethanes. However, the chloroacetic acids which can be products of vertebrate halomethane metabolism are microbially degraded.

Chemical degradation of halomethanes in aquatic systems is a slow process due to their low reactivity (Dilling et al., 1975). Since most of the volatile halomethanes end up in the atmosphere, any major degradation reactions must occur as atmospheric photochemical processes. Currently, it is assumed that aliphatic organochlorides in the environment are degraded in the troposphere through photochemical reactions. Pearson and McConnel (1975) measured the half-lives of some chlorohydrocarbons, including chloroform and carbon tetrachloride, in sealed quartz glass vials exposed to the diurnal and climatic variations of incident radiation and temperature. The measured experimental half-lives were 23 and 10 weeks for chloroform and carbon tetrachloride, respectively. The half-lives were dependent upon solar flux, temperature and air mixture composition. The half-life experiments indicated, however, that the halomethanes are more rapidly degraded in the atmosphere than are the chlorinated pesticides or PCBs, but they are more resistant to atmospheric reactions than the hydrocarbons and thus would not be expected to contribute to the formation of photochemical smog.

Tropospheric half-life experiments of chloroform and carbon tetrachloride were also conducted. Quartz ampules containing these halomethanes were exposed to radiation from a xenon arc. At low concentrations the photochemical reactions were of the first order, but their respective half-lives were not reported. The tropospheric breakdown products of chloroform were carbon dioxide and hydrochloric acid, along with some carbon monoxide and elemental chlorine. These were also the reaction products measured for carbon tetrachloride. Fishbein (1976) reports that the half-life for carbon tetrachloride is 37 hr and results in breakdown to chloroform. The halomethanes could play an important role in the destruction of the atmospheric ozone layers. This could prove to be a serious consequence of the indiscriminate release of these compounds into the environment. Yung et al. (1976) and Appleby et al. (1976) have established that chloroform is present in the atmosphere at concentrations high enough to cause a significant reduction in ozone levels. At this time, the ozone destroying potential of the halomethanes produced during water chlorination is difficult to assess because estimates of the total amounts of halomethanes released into the atmosphere are lacking.

Since all halomethanes are found at low concentrations, the major concern is not their acute toxicity, but chronic effects from continuous exposure to low levels. In addition, the mutagenic, carcinogenic, and teratogenic activities of these compounds are not fully understood and represent an additional area of concern. Relative to other halomethanes, chloroform is usually found at the highest concentration and, therefore, has the greatest potential for being a biohazard. Recently, Powers and Voelker (1976) showed that chloroform is

carcinogenic in Osborne-Mendel rats and B6C3F1 mice following long-term introduction at median toxic dose (MTD) and half MTD doses. The maximum dose the rats tolerated was between 180 and 200 mg/kg. For the mice the MTD's were 280 mg/kg for males and 480 mg/kg for females. The experiment was set up so that the animals were dosed for 5 consecutive days per week over 78 weeks. The results revealed benign primary kidney tumors in 20 percent of the male rats and 2 percent of the females. Chloroform treated mice showed significant incidences of hepatocellular carcinomas (63 percent of the males and 87 percent of the females). Metastasis occurred in some of the test animals.

Schwetz et al. (1974) studied embryo and fetotoxicity of inhaled chloroform in rats. The test animals inhaled 300 ppm chloroform for 7 hr per day on days 6 through 15 of gestation. This treatment resulted in a significant increase in the incidence of fetal resorptions, a decrease in fetal weight and length, and a reduction in conception rate. The incidence of resorption was dose related as was the increase in indicators of retarded fetal development. This study showed that inhaled chloroform was markedly embryotoxic but only showed that the effect of chloroform on rats and rabbits was limited to a mild fetotoxicity.

The toxicity of chloroform may be under multifactorial genetic control. Hill et al. (1975) has shown that mouse strain differences suggest intermediate or multifactorial genetic control of chloroform induced renal toxicity and death. The results showed that the chloroform dose lethal to 50 percent of the test animals was 4 times greater in C57BL165 males than in DBA/25 males while twice as much chloroform accumulated in the kidneys of the sensitive as the resistant strain.

First generation offspring were midway between parental strains for both parameters. The mode of action of chloroform and other halogenated hydrocarbons in producing pathological effects seems to localize in target tissues and bind covalently to cellular macromolecules (Ilett et al., 1973; Reid and Krishna, 1973; Brodie et al., 1971).

THEORETICAL DESCRIPTION OF RESEARCH CONDUCTED

The halogenated organic compounds produced during chlorination of water and wastewater are potentially dangerous substances and at this time, the dynamics of these compounds in a receiving water are not known. In order to assess the significance of the continuous release of low molecular weight halogenated hydrocarbons into the environment, some estimates of their persistence in an aquatic system must be established.

The three major modes by which low molecular weight halogenated hydrocarbons can dissipate from natural waters are volatization from solution into air, adsorption onto particulate matter followed by deposition into sediment, and by breakdown through chemical and biochemical reactions. Haloform degradation reactions in water occur very slowly, with a typical half-life of 15 months (Dilling et al., 1975). However, due to their volatility, haloforms partition out of the aquatic phase into the air relatively fast. Dilling et al. (1975), measuring the evaporation rates of selected C_1 and C_2 chlorinated hydrocarbons in water, reported experimental half-lives of 21 min for dichloromethane and chloroform and 20 min for 1,1,1-trichloroethane. The addition of various contaminants and adsorption substrates, such

as clay, limestone, sand, salt, peat moss and kerosine to the water imposed no significant changes on the evaporation rates of the compounds.

The results of the study by Dilling et al. (1975) suggest that chloroform and other low molecular weight hydrophobic compounds should evaporate from a stream in a relatively short period of time. These findings may be inconclusive because the volatilization rate measurements were conducted under only one given set of laboratory conditions. Variables affecting evaporation half-lives are extremely difficult to measure, standardize and reproduce and their values vary greatly among different natural aquatic systems as well as within the systems themselves. For this reason, a better method by which to predict evaporation behavior of volatile compounds needed to be devised.

A method investigated by Hill et al. (1976) and Smith et al. (1977), based on the theory of gas transfer across a two-film air-water interface introduced by Liss and Slater (1974), allows the extrapolation of laboratory volatilization measurements to natural systems. If one considers a body of water in contact with the atmosphere, a distinct region can be defined as in Figure 1. This model assumes that there exists a stagnant bilayer of water and air at the interface between the two phases which controls the rate at which a gas passes between the water and air bulk. Since the bilayers are static, passage across each layer occurs solely as a function of concentration gradients established by diffusive forces. On the gas side of the bilayer, there exists a partial pressure gradient while on the liquid side, the static layer exhibits a concentration gradient. The partial pressure of a gas, for example oxygen, at the

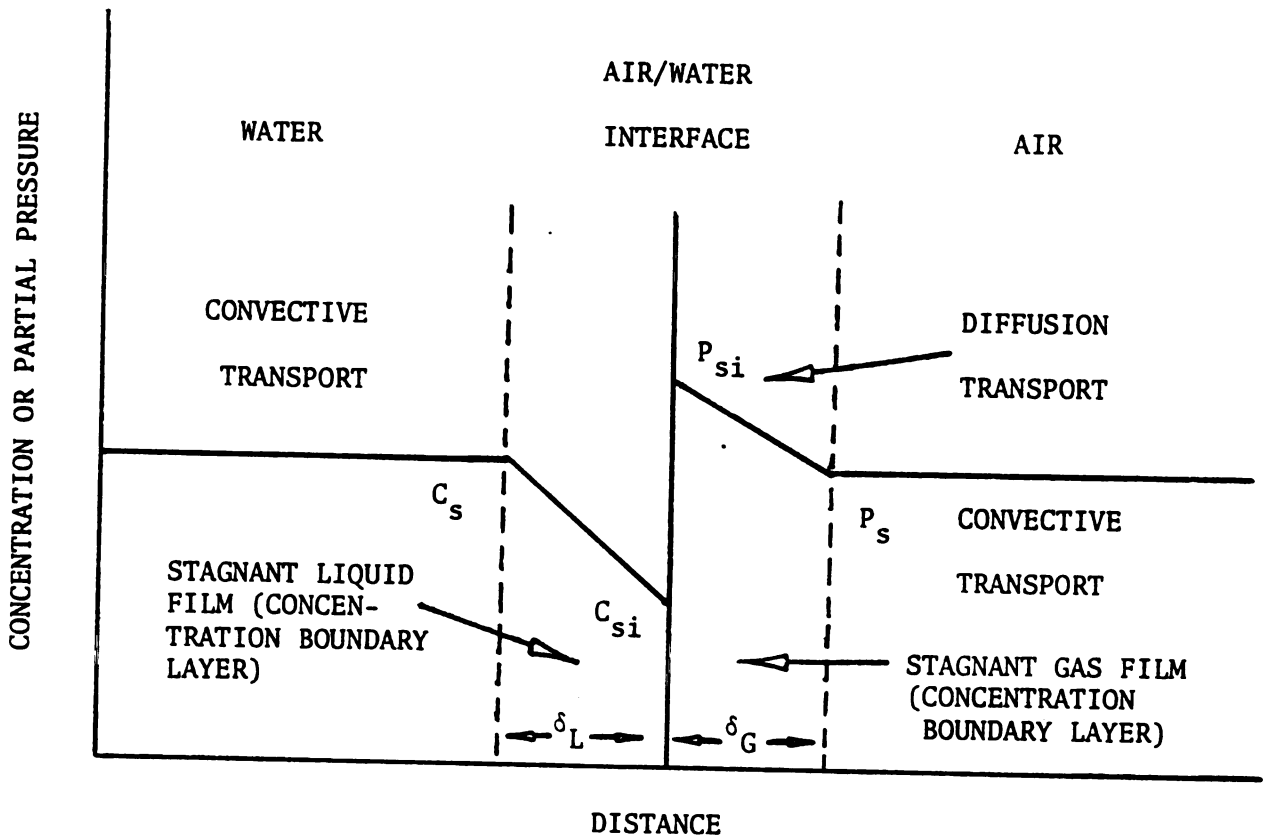


Figure 1. Diagram of the two layer air-water interface.

gas side of the interface between the two static layers is related to the gas concentration on the liquid side by Henry's Law:

$$P_{si} = H_c(S_i) \qquad (1)$$

P = gas partial pressure

H_c = Henry's Law constant

S_i = gas concentration in liquid

The rate at which passage across the bilayer takes place is a function of the degree of saturation of gas in the liquid phase with respect to the gas phase, the thickness of the interficial water layer and the thickness of the static air layer. The thickness of the individual water and air layers are in turn directly related to the amount of turbulence in the respective bulk layers. Thus, the more turbulent a body of water or air, the thinner it's stagnant layer, resulting in a more rapid transfer of gas molecules across the bilayer. Since the two stagnant layers are essentially independent of each other, passage will always take place across one of the layers at a faster rate than the other. The rate of transfer of gas between the two bulk phases is limited by the layer more resistant to mass transfer. In almost all natural water systems, with the exception of turbulent situations such as waterfalls or geysers, the rate of gas transfer is limited by the thickness and density of the stagnant liquid layer.

The rate expression

$$\frac{d(O_2)}{dt} = K_1 O_2 \quad \frac{A}{V} \left[(O_{2sat}) - (O_{2t})\right] \tag{2}$$

Where: O_{sat} = saturation concentration of O_2 in winter

O_t = concentration of O_2 in water at time t

A = surface area of air-water interface

V = volume of water bulk

K_1 = gas transfer coefficient

describing the transfer of a gas, for example oxygen, from the air to the liquid phase is a function of its saturation condition, the amount of liquid surface area and volume, and a rate constant K_1. The integrated form of this equation is:

$$(O_2)_t = (O_2)_{sat} - \left[(O_2)_{sat} - (O_2)_o\right] \quad e^{-\frac{A}{V} K_L t} \tag{3}$$

Where $(O_2)_o$ = initial conc. O_2

which is rearranged to yield:

$$\ln -\left[\frac{C_t - C_o}{C_s - C_o} - 1 \right] = - \frac{A}{V} K_L {}^{O_2} t \tag{4}$$

This equation can be used to determine the value of the gas transfer rate constant K_L if empirical values for C_o, C_t and C_s are known. A plot of $\ln - [\frac{C_t - C_o}{C_s - C_o} - 1]$ against time normally produces a straight line corresponding to the first degree polynomial equation $y = mx + b$ as in Figure 2.

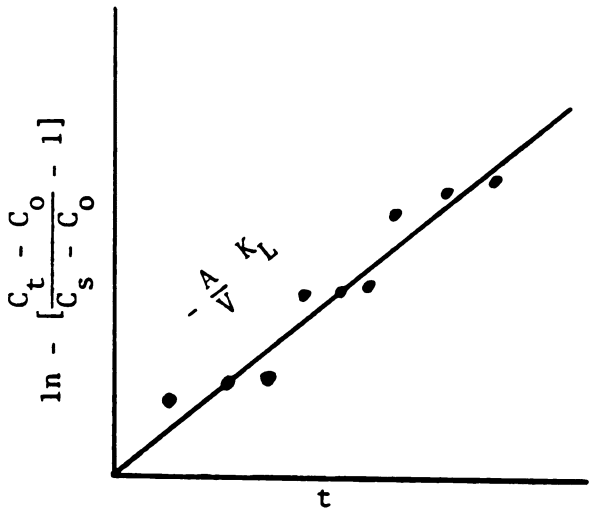


Figure 2.

The resultant slope of the straight line is equivalent to - A/V K_L, from which K_L is calculated.

The rate contant K_L changes with a change in water temperature or turbulence as well as by its ionic strength. Of these parameters, it is impossible to measure liquid turbulence accurately and extremely difficult to control reproducibly. Therefore, experimentally determined transfer coefficients will apply only under the conditions that the data used to calculate them was generated. Since liquid turbulence can vary a great deal, it is difficult to apply volatilization rates measured in single laboratory investigations.

An observation made by Tsivoglou (Tsivoglou et al., 1965; Tsivoglou, 1967) allows volatilization rates to be considered independent of turbulence conditions. Tsivoglou demonstrated that the ratio of the measured gas transfer rate constants (K_1), of two low molecular weight gases, remains constant over a wide range of turbulence conditions. Thus for the simultaneous measurement of two solution components A and B, the ratio (K_1^a/K_1^b) will remain a constant. Using a given gas or

solute as a reference substance, the relative volatility of any compound capable of gas transfer can be determined. This method is suitable for conducting laboratory predictions of the environmental volatilization behavior of low molecular weight halogenated hydrocarbons, such as chloroform.

A stirred beaker of water is sparged with nitrogen to remove the dissolved oxygen and spiked with chloroform. As the solution gases reach equilibrium with the atmosphere, chloroform is volatilized and the water becomes re-saturated with oxygen. The solution is monitored for chloroform and oxygen as a function of time. The data generated is analyzed with equation 4, resulting in a pair of transfer coefficients K_L^{O} and $K_L^{CHCl}3$ from which the ratio $K_L^{CHCl}3/K_L^{O}2$ is calculated. Since this ratio is independent of turbulence and other effects, it applies to most natural water systems. This ratio may now be used to estimate the chloroform transfer constant for a given aquatic system. If the oxygen reaeration constant of the system is known, the following equation is used.

$$(K_L^{CHCl_3})_{\substack{\text{Water}\\\text{Body}}} = \left(\frac{K_{CHCl_3}}{K_L^{O_2}}\right)_{\text{Measured}} \times (K_L^{O_2})_{\substack{\text{Water}\\\text{Body}}} \qquad (5)$$

The ultimate variable is the oxygen reaeration constant of the water body. Values for many streams, rivers and lakes can be found in the literature (Langbein and Durum, 1967; Grant, 1976; and Bennet and Rathbun, 1972

If it becomes necessary to formulate a more accurate model of the gas transfer relations of a particular body of water, the O_2 transfer coefficient for that particular system must be more closely estimated. Many different theoretical approaches to the determination of O_2

reaeration in rivers and streams have been attempted (Bennet and Rathbun, 1972). Tsivoglou (1967) has developed a very accurate technique which measures the reaeration coefficient of streams with a radioactive tracer gas, but is complicated and time consuming. Foree (1976) used this method to formulate an empirical relationship between the oxygen reaeration constant, $K_1^{0_2}$ and stream bed slope. Data was taken from reaeration studies performed following the method of Tsivoglou conducted on 20 different streams. The streams studied covered a wide range of drainage areas (between 1 and 1850 square miles) and low-flow discharges (0.45 410 c.f.s.). With this data, the following relationship was established:

$$K_{0_2} = 0.30 + 0.19\ S^{1.2} \qquad (6)$$

Where: K_{0_2} = 0_2 reaeration coefficient at 25°C ($days^{-1}$)

S = slope of stream bed in ft/mi

$S = \frac{dE}{L}$ = change in elevation (ft) / length of stream (mi)

This equation suggests that the value of the reaeration coefficient is a direct function of the slope of the stream since surface turbulence, the limiting factor in gas transfer, increases with an increase in stream slope. Equation 5 can now be re-written in terms of equation 6:

$$K_{L\ (Water)\ Body}^{CHCl_3} = \left(\frac{K_L^{CH_3Cl_3}}{K_L^{0_2}}\right)_{(Measured)} \times (0.30 + 0.19\ S^{1.2}) \qquad (7)$$

According to equation 7, in order to predict the volatilization behavior of a certain compound in a given stream, it is only necessary

to perform laboratory measurements of the transfer rate of that compound with respect to oxygen and to know the average slope of the receiving stream. The resultant value for the transfer coefficient of the compound studied will be an estimate from which the following information can be derived:

(a) The evaporation half-life of the compound in the stream:

$$t\ ½ = \frac{0.693}{\frac{CHCl_3}{K_L}} \qquad (8)$$

(b) The length of the stream required to volatize 80 percent of the initial concentration of the compound:

$$V_r t = \ln - \frac{(.8-1)}{\frac{CHCl_3}{-K_L}} \quad V_r = \text{Length} \qquad (9)$$

Where: V_r = stream velocity met/min

IN SITU MODEL

A haloform gas transfer rate coefficient can be determined by in situ measurements of haloform levels. In order to perform the measurement it is necessary to isolate a river or stream section which contians an established haloform plume of a constant initial concentration C_a. The river bed affected by the plume should be relatively homogenous and flow at a given measured velocity V_r. An idealized situation is diagrammed in Figure 3, which depicts a stretch of stream of velocity V_r, whose haloform concentration is being reduced by evaporation, solely as a function of residence time in the stream.

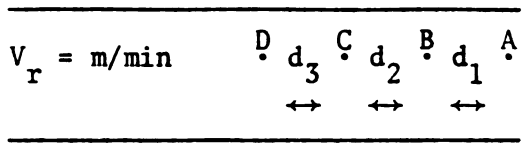


Figure 3. Idealized representation of a river plume.

Samples are collected at measured distances downstream from point A and analyzed for haloforms. Distances from A are converted to units of time by dividing by stream velocity.

For sample "d"

$$t_d = \frac{(d_1 + d_2 + d_3) \text{ meters}}{V_r \text{ meters/min}} = \text{min} \qquad (10)$$

The haloform concentrations measured, with their corresponding time values are used to determine a haloform transfer coefficient by equation 4 where $C_0 = C_a$ and $C_s = 0$.

Unfortunately, an ideal situation as pictured in Figure 3 does not exist. For most rivers receiving waste effluent, a dilution factor must be taken into account until the wastewater has become completely mixed with the river water. Since the concentration of haloforms present in the river decreases as a function of dilution as well as volatilization, it is necessary to differentiate between the two processes. The concentration of tracer is measured in each sample collected for haloform analysis. Because of variations in dilution, it is important that the same sample be used for both the haloform and dilution analyses. A dilution correction factor is determined for each sample by dividing the concentration of tracer in the sample by the tracer concentration of the original, undiluted effluent. Haloform values are corrected for dilution by multiplying by the corresponding

dilution factor. The corrected values can now be used as in the previous model to determine the haloform gas transfer coefficient K_g.

There are a number of methods which can be used to trace dilution of an effluent plume. One method commonly employed is the salt dilution technique. This method is based on the fact that a greater amount of Cl^- ion is present in sewage effluent than is normally present in the receiving stream. Upstream and wastewater effluent samples are analyzed to establish initial chloride levels. An instantaneous dilution factor for plume samples can be calculated by solving the two simultaneous equations:

$$XA + YB = C \tag{11}$$

$$X + Y = 1 \tag{12}$$

Where: X = fraction of A in mix

Y = fraction of B in mix

A = upstream Cl^-

B = effluent Cl^-

C = sample Cl^-

This method is easy to perform since it is adaptable to automated wet-chemical analysis methods such as the Technicon Autoanalyser^R, and because it does not require the addition of any tracer material.

Another method commonly employed is the dye tracer technique (Baumgartner et al., 1969; Stewart et al., 1969). A fluorescent dye such as Rhodamine, Fluorescein or Rhodamine B is added to effluent to a desired dye concentration. The dye is released with the effluent and its concentration following dilution is measured by fluorescence spectrophotomentry. Since the fluorescent dyes follow Beer's Law,

dilution can be monitored accurately by this method. A problem which sometimes arises during wastewater applications of this technique is the bleaching or oxidative breakdown of the dye by sunlight or residual chlorine present in the effluent. Problems also tend to arise in the metering of the dye solution into the effluent at a constant rate.

An interesting fluorimetric method is one developed as a tracer of Kraft mill effluent (Braumgartner et al., 1971). This method simply scans the fluorescence spectrum of paper mill effluent and that of the dilutent water. A fluorescence peak not present in the receiving water, but exhibited in the effluent spectrum is used to trace the effluent dilution. This method could be applied to the tracing of sewage effluent, which contains many naturally fluorescing substances as well as strongly fluorescing compounds such as optical brighteners added to laundry detergents.

While radioactive tracers have been used in limnological investigations, their application is severely limited by expensive equipment, handling problems, the need for highly trained technicians, and the reluctance of state and federal authorities to permit the release of radioactive substances into the environment. The disadvantages of this tracer technique can be overcome with neutron activation analysis techniques. The method involves measuring the dispersion of water soluble non-radioactive rare earth element such as europium or dysprosium which would not normally be present in the wastewater effluent or the Red Cedar River. The water samples collected at each sampling station are activated in a nuclear reactor, and the concentration of the tracer element is measured radiochemically.

The activation reactions which take place can be described as follows:

$$^{151}Eu + {}_{o}n^{1} \longrightarrow {}^{152}Eu + 1.40 \text{ MeV } \gamma \text{ Ray, } T_{1/2} = 9.3 \text{ hr} \qquad (13)$$

$$^{164}Dy + {}_{o}n^{1} \longrightarrow {}^{165}Dy + 0.32 \text{ MeV } \gamma \text{ Ray, } T_{1/2} = 2.3 \text{ hr} \qquad (14)$$

Since the chemical characteristics of europium and dysprosium are very similar to those of metals alkaline earth such as magnesium and calcium, they should exist in aqueous solutions as uncomplexed ions. Very little is known, however, about the adsorptive tendencies of these elements with respect to sediments, soils, and geological materials. Therefore, before these elements can be used as tracers preliminary studies must be carried out in the laboratory to establish their adsorptive capacity on the suspended particulate matter in the effluent and river.

While atomic absorption spectroscopy sensitivity of europium and dysprosium are about 0.6 and 0.8 mg/ℓ, respectively, the corresponding absolute sensitivity of these elements by neutron activation analysis is in the order of pg/ℓ (10^{-12} g). However, because of chemical interferences, the optimum operational sensitivities are probably in the order of 1.0 ng/ℓ. Thus, the sensitivity of radioactive tracer techniques is realized with very few of its disadvantages with the possible exceptions of interfering elements and the high cost associated with neutron activation analysis.

Bromide ion has also been used successfully as a neutron-activable tracer (Jester and Uhler, 1974). Bromide ion is activated and behaves according to the reaction:

$$^{79}Br + {}^{1}_{0}n \text{ ---- } ^{80}Br + 0.617 \text{ MeV} \qquad (15)$$

The limit of detection of the .617 MeV gamma peak of Br 80 is reported as 20 µg/ℓ. This limit is close to that of europium or dysprosium. The use of $Br^{=}$ ion has an advantage over Eu or Dy because bromide ion is already present in sewage and its plume could be traced without requiring the addition of tracer. In the event of the necessity of tracer addition, the use of Br^{-} would be much more economical than europium or dysprosium.

MATERIALS AND METHODS

Analysis of Haloforms by Gas Chromatography

Instrument: Varian 1800, Tritium foil electron capture detector.

Column: 2 m x 3 mm i.d. nickel column packed with 10 percent Squalane on Chromosorb W-AW.

Column Temperature: Isothermal at 70°C.

Injection: On-column injection at port temperature of 130°C.

Detector Temperature: 170°C.

Carrier Gas: Pre-purified Nitrogen passed through a molecular sieve gas purifier.

Nitrogen Flow Conditions: 30 lbs/in^2 head pressure.

Confirmatory Column: 6' x 1/8" 3 percent OV-1 on Chromosorb WHP. Column temperature - 23°C.

Extraction Procedure: A modification of the direct aqueous extraction method proposed by Mieure (1977) and Richard and Junk (1977) was used. Five ml of water sample was added to 1 ml of Fisher certified

methylcyclohexane. The mixture was shaken for 1 min and the layers were allowed to separate. Two µℓ of the methylcyclohexane layer was injected into the gas chromatography.

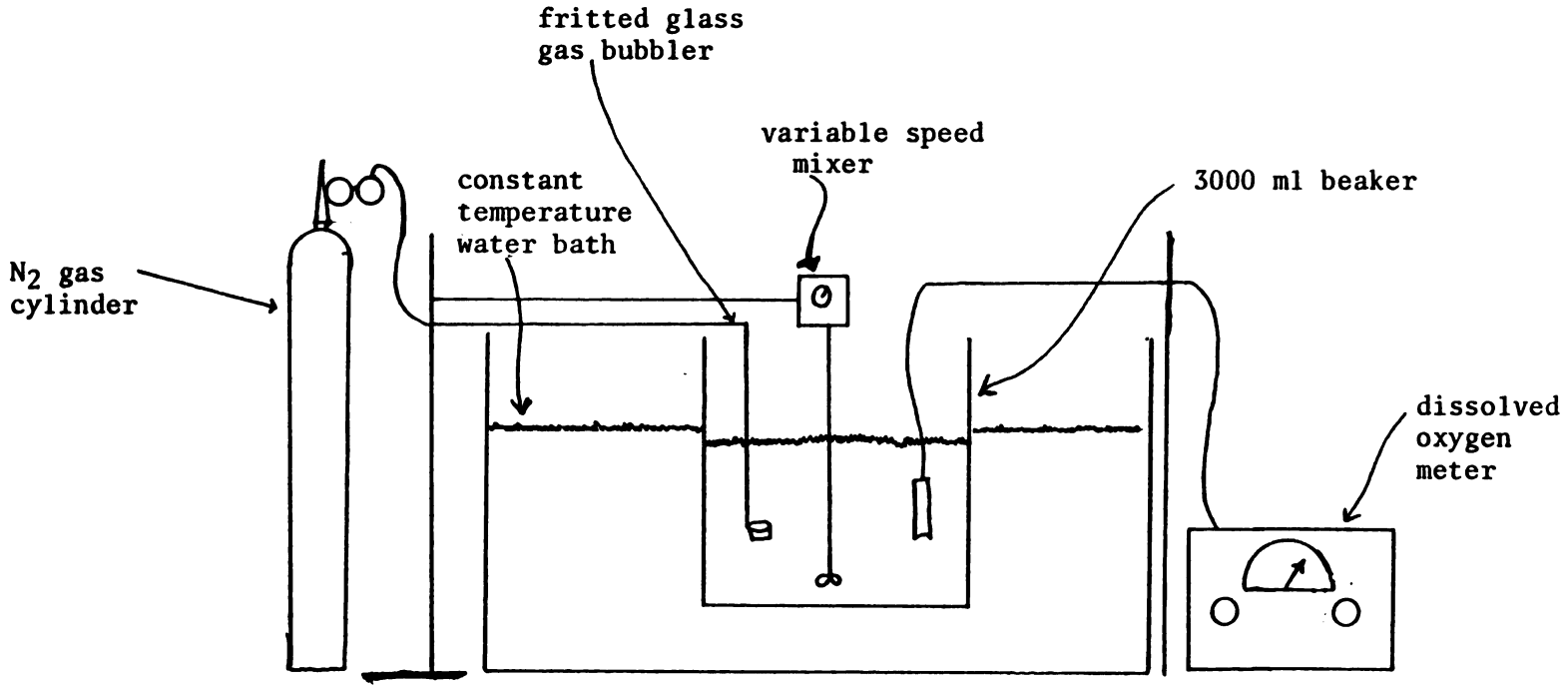
Standards: Stock chloroform solutions of 1.0 and 0.1 µg/ml were made by dilution of a chloroform solution containing 0.670 ml of Burdick and Jackson, pesticide grade $CHCl_3$ in 100 ml of methylcyclohexane. Standard $CHCl_3$ solutions in the range of 5 to 500 µg/ℓ were made by dilution of $CHCl_3$ stock solutions.

A stock mixed standard solution containing the four haloforms: $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ was prepared by diluting 0.5 ml of a mixed analytical standard of volatile organics obtained from the Quality Assurance Branch, U.S.E.P.A., Cincinnati, Ohio, in 50 ml of methylcyclohexane. Standard solutions were made from this stock.

Quantitation of Peaks: Analog output from the gas chromatograph was applied to a Sargent-Welch model SRG strip chart recorder operating at 1"/min. Areas of peaks were estimated by multiplying the height of the peak (mm) by its width at half height. The peak areas corresponding to solutions of standards were used to construct a standard curve from which unknown sample concentrations could be determined by graphical interpolation.

Field Sampling for Haloforms: River samples were collected using a disposable, graduated 20 cc syringe fitted with a 12 in, 13 guage stainless steel needle. A 10 ml sample is drawn at 12 in depth, and 5 ml transferred to a Teflon^R stoppered 8 ml test tube containing 1 ml of methylcyclohexane. Sample extraction is performed immediately by shaking for 1 minute.

Figure 4. Diagram of apparatus used in volitization studies.



Volatilization Studies

The apparatus diagrammed in Figure 4 was used to measure volatilization of $CHCl_3$ (and the other haloforms). Organic-free distilled water (2200 ml) was placed into a 3,000 ml beaker and brought to the desired temperature in a Forma Scientific model 2341 constant temperature bath. During temperature equilibriation, the dissolved oxygen was sparged from the water by bubbling nitrogen gas through the mixed water for a period of two hr or until an O_2 reading of less than 0.5 mg/ℓ was measured by use of a standardized Yellow Spring, Inc., model 57 dissolved oxygen meter.

After a methanol solution containing 200 µg of chloroform was introduced below the surface of the water and allowed to mix for three min, a 5 ml water sample, preceeded by a 2 ml rinse, was taken using a 20 ml, long-needled disposable syringe and immediately extracted into 1 ml of methylcyclohexane. Dissovles oxygen readings were simultaneously taken while the water samples were being drawn. The time each sample was taken was recorded as elapsed time from that of the first sample. Sampling was continued for 6 to 8 hours. Each set of samples was analyzed in the same run series by gas chromatography.

Tracer Studies

(A) Neutron Activation Analysis

Studies of the feasibility of tracing a wastewater plume by neutron activation analysis were conducted by determining the limits of detection of europium, dysprosium and bromide ion in river water and sewage. Stock solutions of Eu, Dy and Br^- were made in distilled water from which low concentration solutions (1 to 500 µg/ℓ) were made by appropriate

dilutions in tertiary treated sewage effluent or in Red Cedar River water. Five ml aliquots of the solution were transferred to polyethylene neutron activation vials. The samples were irradiated by fast neutrons at a neutron flux of 10^{12}/cm in the Michigan State University "TRIGA" nuclear reactor. The Dy, Eu and Br^- peaks of the irradiated samples were counted using a Nuclear Data large-memory pulse height analyzer and printed out on a teletypewriter. The gamma spectrum of each sample was standardized against the gamma spectrum of $Cobalt^{60}$. Sample activities were compared to background signals and to the activities of sewage, river water and distilled water blanks.

(B) Chloride "Salt Dilution" Method

A study into the feasibility of using chloride ion already present in sewage effluent as an internal tracer was conducted. A series of samples taken from the Red Cedar River were analyzed for chloride and chloroform concentrations. Dilution factors of East Lansing sewage effluent in the river water were calculated with respect to an upstream background chloride value and compared to drops of chloroform concentrations in the samples. Chlorides were determined with a Technicon "Autoanalyzer" while chloroform analyses were performed by gas chromatography employing the direct liquid extraction method.

(C) Fluorescent Internal Tracer Technique

A technique for determining the dilution of a wastewater effluent by fluorescence spectrophotometry was investigated using the method described by Baumgartner et al., 1971. Samples of water upstream and downstream to a wastewater discharge as well as a sample of the effluent were collected. The fluorescence spectrum of each sample was monitored between the emission wavelengths of 200 to 600 nm at an excitation

wavelength of 217 nm. The spectra were compared for characteristic emission bands originating from fluorescing components present in the effluent.

Adsorption Studies

(A) Sediment Characterization

Sediment was collected from the Red Cedar River 750 m downstream from the effluent outlet of the East Lansing sewage treatment plant with a pole-mounted Eckmann dredge. The sediment was screened through a series of standard sieves (#5, #10, #18, #30). Sediment passing through the #30 sieve was suspended in river water in a bucket by a strong mixing action and allowed to settle overnight. All but 2 cm of the water layer was decanted, and the soft top of the settled sediment was suspended by gently mixing by hand and poured off, leaving the heavier sand sediment behind.

The percent moisture of the sediment mixture was determined by drying a weighed sample of sediment suspension in an oven for 24 hr at 105°C and comparing the dry weight to the wet weight of the sediment.

Determination of Degree of Adsorption

A weighed aliquot of sediment suspension was introduced into a volumetric flask filled with distilled, deionized water. Two flasks, a sediment and a control, were sampled prior to addition of 100 µg of $CHCl_3$ in methanol to the sediment flask. The flasks were filled to the top and sealed to prevent evaporative losses. Twenty-four hours following addition of $CHCl_3$, 25 ml of samples were taken from each flask, centrifuged for 15 minutes at 12,000 rpm and analyzed by the liquid extraction method.

DESCRIPTION OF STUDY AREA

The study area is the Red Cedar River watershed. The Red Cedar River is a typical southern Michigan warm water stream located immediately east of Lansing, Michigan. The river originates as the outflow of Cedar Lake in Marion township, Livingston county, and flows northwesterly before entering the Grand River in the city of Lansing. The river has 12 major tributaries and drains approximately 1220 km^2 (472 mi^2) of both agricultural and residential land (Figure 5).

The main channel of the river is natural excpet for some areas which have been dredged and straightened for drainage. The width of the river varies from 8 to 25 m. The total length is 89 km (50.8), and the average gradient is 0.5 m/km (2.4 ft/mi) with elevations ranging from 263 to 301 m above sea level (817 to 934 ft)(Brehmer et al., 1968).

The chemical and biological characteristics of the Red Cedar River have been extensively studied (Ball et al., 1969; Brehmer et al., 1969). The stream is highly buffered and slightly alkaline. The turbidity is low but rises sharply during periods of heavy runoff until the erosion of stream deposits is exhausted (Grzenda et al., 1968). Dissolved oxygen pulses are common in the summer and occasionally the levels fall below 3.0 mg/ℓ. Nutrient loads are excessive although much of this material is flushed from the stream during spring floods (Ball et al., 1968).

The stream discharge varies from a few CFS in some dry years to upwards of 5000 CFS in the most serious floods. The flow of the river

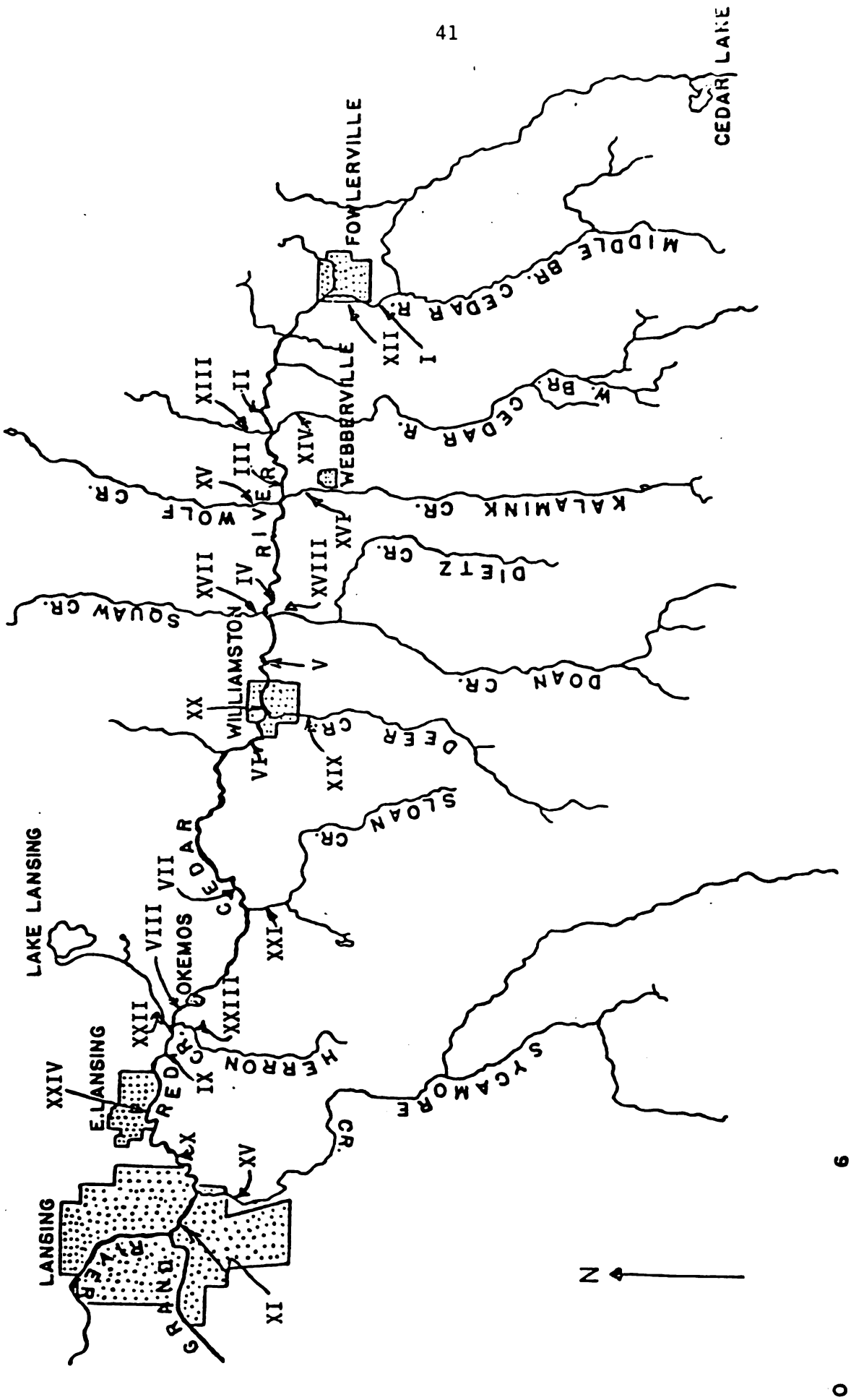


Figure 5. Red Cedar River and Principal Tributaries (including sampling sites).

is usually highest in the late spring when thawing frozen groundwater and melting snow contribute more to loading than heavy rains (Meehan, 1958). The flow is usually lowest in the late summer months before the fall rains. A steady decrease in discharge over the last 20 years has resulted in a critical summer flow. This decreased discharge can be traced to the increased well water usage and lowered water table in the river drainage area (Stevens, 1967).

Two artificial impoundments are located on the Red Cedar River. One is in Okemos at a picnic grounds and the other is at Michigan State University in East Lansing. This dam serves as a USGS stream discharge gauging station and also supplies cooling water for the university power plant. A third dam was located at Williamston, but recently one section collapsed and this has lowered the water level behind the dam considerably.

The Red Cedar River flows through or near 6 communities before its confluence with the Grand River (Figure 6). These communities are: Fowlerville, Webberville, Williamston, Okemos, East Lansing, and Lansing. Two of these communities, East Lansing and Williamston, chlorinate their wastewater before it is discharged into the Red Cedar River. Lansing's wastewater treatment facility also employs chlorination, but the effluent from this plant is discharged into the Grand River. Both Fowlerville and Webberville utilize sewage lagoons to treat the municipal wastes and the effluent is not chlorinated before discharge. Thus, the potential sources of halomethanes are the waste treatment facilities at Williamston and East Lansing.

Another potential source of halomethanes is the Utilex Manufacturing Company, the only industry located on the Red Cedar River. This

company performs zinc die casting and decorative plating, mainly of plumbing and automotive fixtures. During plating operation the process water is contaminated with toxic substances as: cyanide wastes, chromic acid, and sulfuric acid. Before 1972 this contaminated water was discharged directly into the Red Cedar River. In 1972 the Michigan Water Resources Commission required that facilities be installed to treat the contaminated process waters. Cyanide wastes are removed by adding sodium hypochlorite which oxidizes the cyanide ion to carbon dioxide and nitrogen. These wastes are retained approximately 1 day as they are discharged when the residual chlorine test is positive. The discharge enters a clarifier and then a system of settling ponds. The wastewater in the settling lagoons is discharged twice yearly (spring and fall) during periods of high river discharge. Harrington (1974) reports that 200 lb/day of sodium hypochlorite, caustic soda, and sulfuric acid are used to treat cyanide in this plant.

SAMPLING STATIONS

This research project was designed to provide information concerning 3 aspects of the problem of the occurrence of halomethanes in the Red Cedar River: background haloform levels, sources of halomethanes to the river, losses of halomethanes from the river to the atmosphere. To facilitate the quantification of background haloform levels, water samples were collected at selected points along the entire length of the river. These sampling sites are identified in Figure 5 by the numerals I-XI and listed in Table 2.

Since haloforms are not known to occur naturally in a river system, their presence indicates discharge at some point along the river. In

TABLE 2

List of Red Cedar River Sampling Points and Their Locations

Sampling Point Location	Site I.D. Number	Site Number (Figure 6)
Middle Branch, Red Cedar River at M-28, Fowlerville	1	XII
Middle Branch, Red Cedar River at Van Buren Road, Fowlerville	2	I
West Branch, Red Cedar River at M-28	3	XIV
Red Cedar River at Gramer Road	4	III
Kalamick Creek at Red Cedar River	5	XVI
Wolf Creek at Red Cedar River	6	XV
Coon Creek at Sherwood Road	7	
Squaw Creek at Rowley Road	8	XVII
Red Cedar River at Perry Road	9	IV
Doan Creek at M-28	10	XVII
Red Cedar River, 200 ft upstream to Williamston Sewage Treatment Works	11	XX
Williamston Sewage Treatment Plant, Final Effluent	13	XII
Red Cedar River, 60 ft downstream to outlet of sewage treatment plant	14	XII
Deer Creek at Linn Road	15	XIX
Sloan Creek at railroad bridge	16	XXI
Red Cedar River at Vanata Road	17	VII
Red Cedar River at Okemos Park	18	VIII
Wildlife Creek at Campus Hill Apartments	19	XXII
Red Cedar River at Grand River	20	XI

Table 2 (cont.).

Sampling Point Location	Site I.D. Number	Site Number (Figure 6)
Sycamore Creek at Mt. Hope Road, Lansing	21	XV
Red Cedar River at Potter Park, Lansing	22	XI
Red Cedar River, 500 ft downstream to East Lansing Sewage Treatment Works	23	XXIV
East Lansing Sewage Treatment Works, effluent	24	XXIV
Red Cedar River, 60 ft downstream to effluent outlet of East Lansing Sewage Works	25	XXIV
Red Cedar River at Kalamazoo Street, 200 ft upstream to East Lansing to sewage effluent outlet	26	XXIV

order to identify the major source of haloforms to the river, samples were collected at all points of introduction of significant amounts of water into the river. These stations were located upstream from the confluence of each major tributary to the Red Cedar River and directly below the points of introduction of sewage effluent at East Lansing and Williamston.

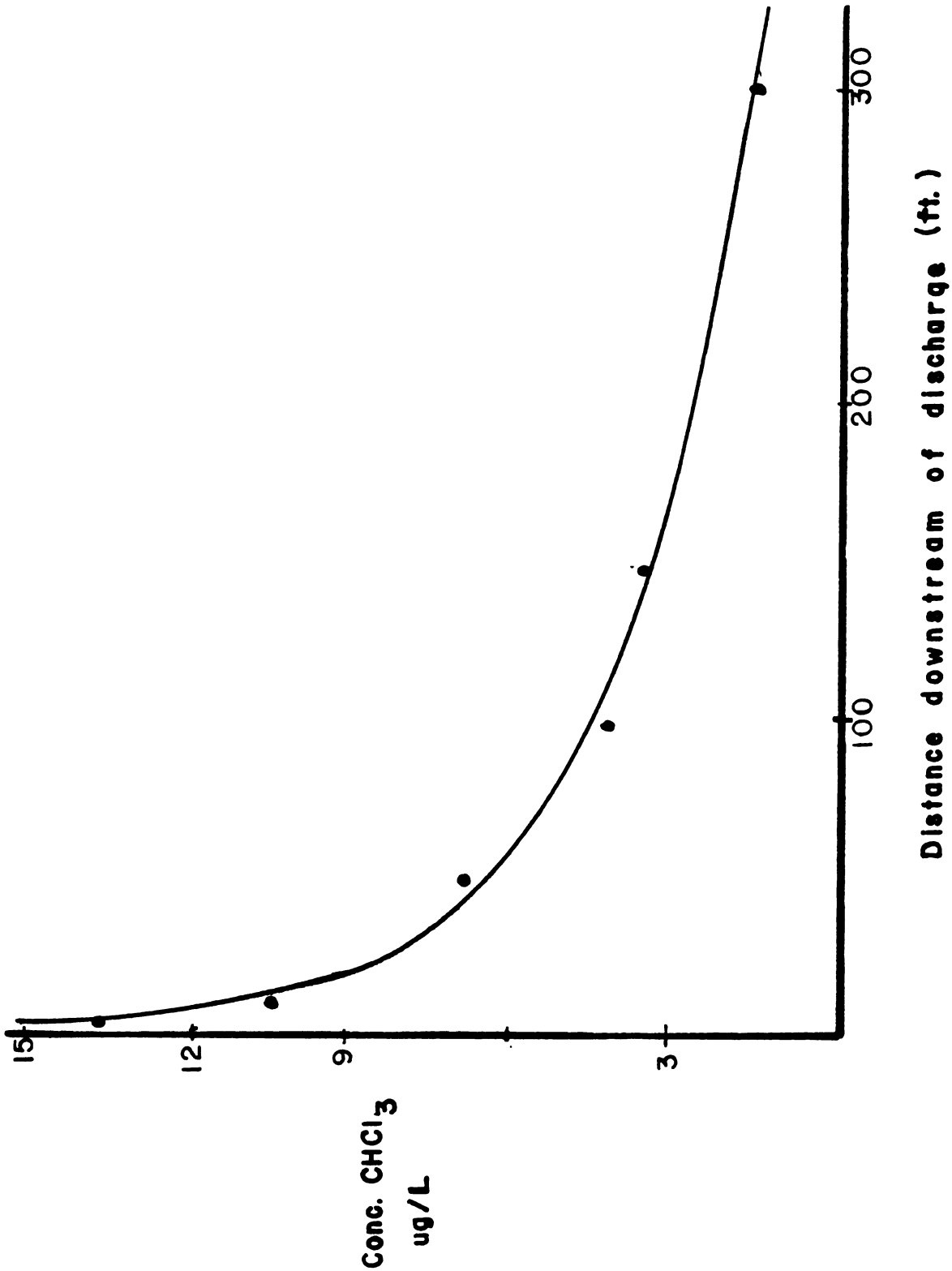
RESULTS

A. Survey of Chloroform Levels in Environmental Samples

The haloform levels of various samples analyzed in this study are given in Appendix C. Samples analyzed included sewage, potable water and water taken at various points along the Red Cedar River. The first set of samples (numbers 1-12) was collected from the East Lansing sewage treatment plant. Analysis of these samples indicated that raw sewage contained 35 µg/ℓ chloroform which was reduced to 20 µg/ℓ after primary treatment, 3 µg/ℓ after secondary and contained less than detectable levels prior to chlorination. Following chlorination, 16 µg/ℓ of chloroform was detected in the effluent. These results indicate that chloroform which enters the sewage treatment plant in sewage is volatilized during treatment. These results are predictable since secondary treatment at East Lansing consists of a strongly aerated biological digestion which would tend to remove volatile materials through sparging. The increase in chloroform levels from <1.0 to 16 µg/ℓ indicates that chloroform is being produced in sewage as a result of chlorination.

The second part of this survey was designed to measure levels of chloroform downstream to sewage discharge points. Samples 22 through 32 were collected at various points downstream from the point where East Lansing discharges treated sewage effluent into the Red Cedar River. Figure 6 depicts the chloroform levels in the Red Cedar as a function of distance from the point of discharge.

Figure 6. Graph of chloroform levels in Red Cedar River as a function of distance from point of discharge.


15
12
9
6
3
Conc. $CHCl_3$ ug/L
100
200
300
Distance downstream of discharge (ft.)

These data show that the original level of chloroform is reduced by 90% in the first 300 feet of the stream. This experiment is repeated in the Red Cedar River in samples 76 through 84, with the same results. The chloroform levels in Lansing sewage effluent near its discharge point into the Grand River were substantially lower, ranging between 1 µg/ℓ and 3 µg/ℓ.

The third portion of this study was an analysis of the Red Cedar River for haloforms. The survey began at the headwaters of the Red Cedar River and ended at its point of confluence with the Grand River. The major tributaries of the river were also sampled (Figure 5). The results are represented by samples 314 through 345 which indicate that background concentrations of the haloforms: $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$ are below the limits of detection of the analytical technique used in this tudy for most portions of the river and in all of its tributaries. Measurable levels were present only below the point of discharge of sewage effluent from the cities of Williamston and East Lansing.

CONCLUSIONS

The findings of this portion of the study indicate that the brominated analogs of chloroform: dichlorobromomethane and dibromochloromethane, are produced during chlorination of water and wastewater. However, levels of the haloforms in most reaches of the river are below their limits of detection of 10 µg/ℓ.

The concentrations of the respective haloforms in the Red Cedar decrease rapidly within a short distance from their release point. This reduction in chloroform levels is the result of dilution in the

effluent stream. The results of the spring analyses (samples 76 through 84) exhibit a much faster concentration decrease than samples analyzed during the summer (335 through 341) which is consistent because the total flow of the Red Cedar is much lower in the summer than during the spring, when the effect of dilution becomes much more pronounced.

B. Tracer Studies

1. Neutron Activation Tracer Studies

The feasibility of using a neutron activatable element as a dilution tracer was investigated by irradiating Red Cedar River water containing between 1 μg/ℓ and 1 mg/ℓ of europium and dysprosium for 36 min in the M.S.U. "TRIGA" nuclear reactor. The resulting gamma spectra are presented in Figures 7, 8, and 9. The gamma spectrum of irradiated river water (Fig. 7) exhibits a Compton edge at low gamma energies and two peaks of intermediate intensity at about 600 and 800 KeV, neither of which interferes with the europium (Fig. 8) or dysprosium (Fig. 9) spectrum. The limits of detectability for the 130 KeV peak of europium and the 368 KeV peak of dysprosium appear to be approximately 35 μg/ℓ because these peaks could not be resolved from background activity below this value. The number of gamma disintegrations counted in 400 sec at each concentration monitored is given in Tables A-1 through A-5 of the Appendix. Solutions of 1000 μg/ℓ and 50 μg/ℓ europium, whose relative concentrations were 20:1, had an activity ratio of 17.4:1, while 500 μg/ℓ and 50 μg/ℓ dysprosium solutions (concentration ratio 10:1) exhibited an activity ratio of 10.5:1.

Figure 7. Gamma spectrum of irradiated Red Cedar River water.

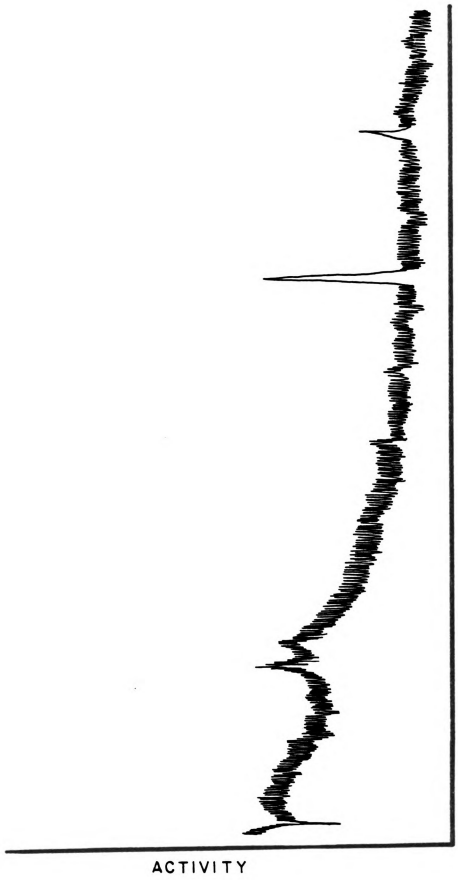

GAMMA ENERGY
ACTIVITY

Figure 8. Gamma spectrum of 1000 ug/L and 50 ug/L Europium in river water.

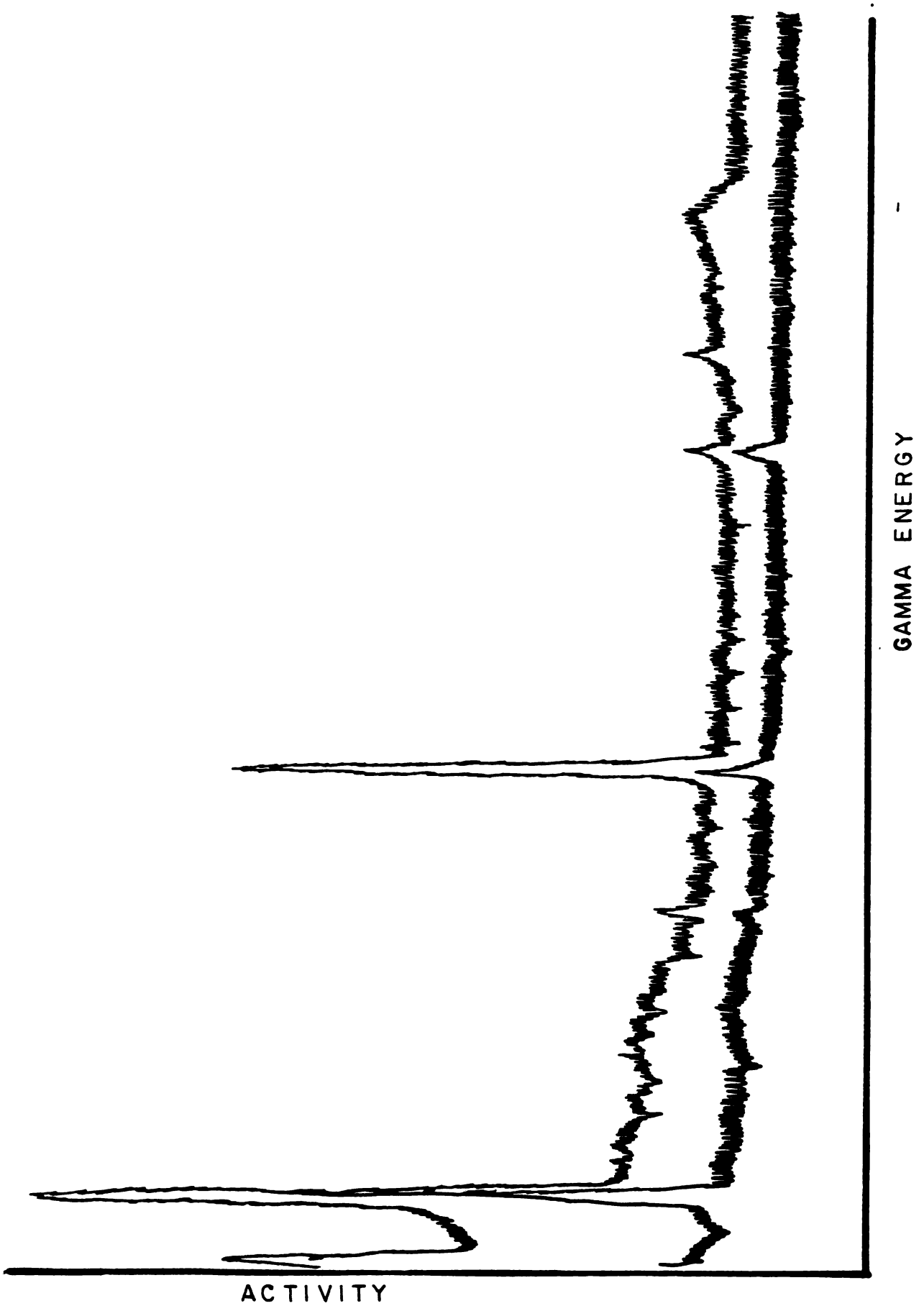

ACTIVITY
GAMMA ENERGY

Figure 9. Gamma spectrum of 500 ug/L and 50 ug/L Dysprosium in river water.

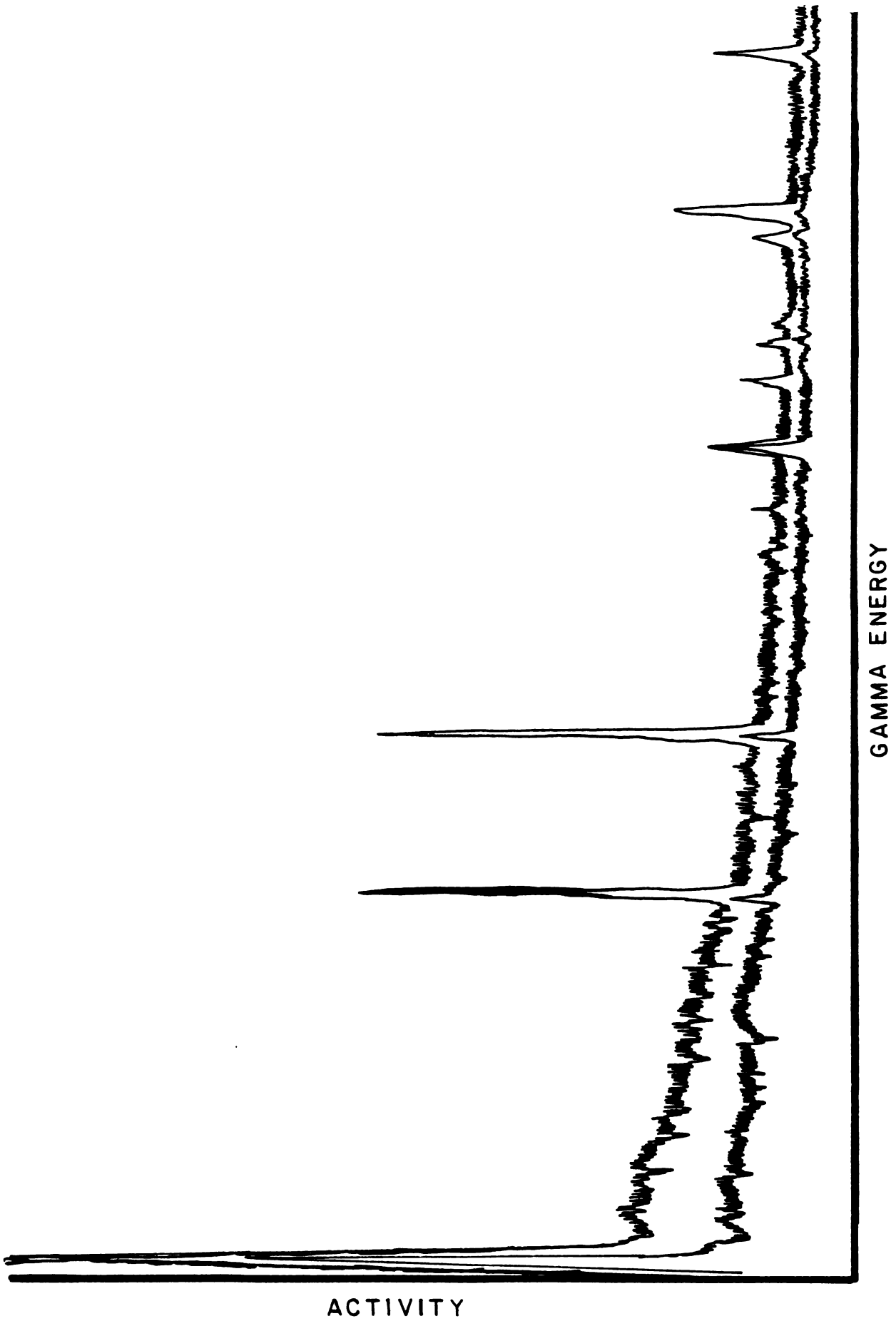
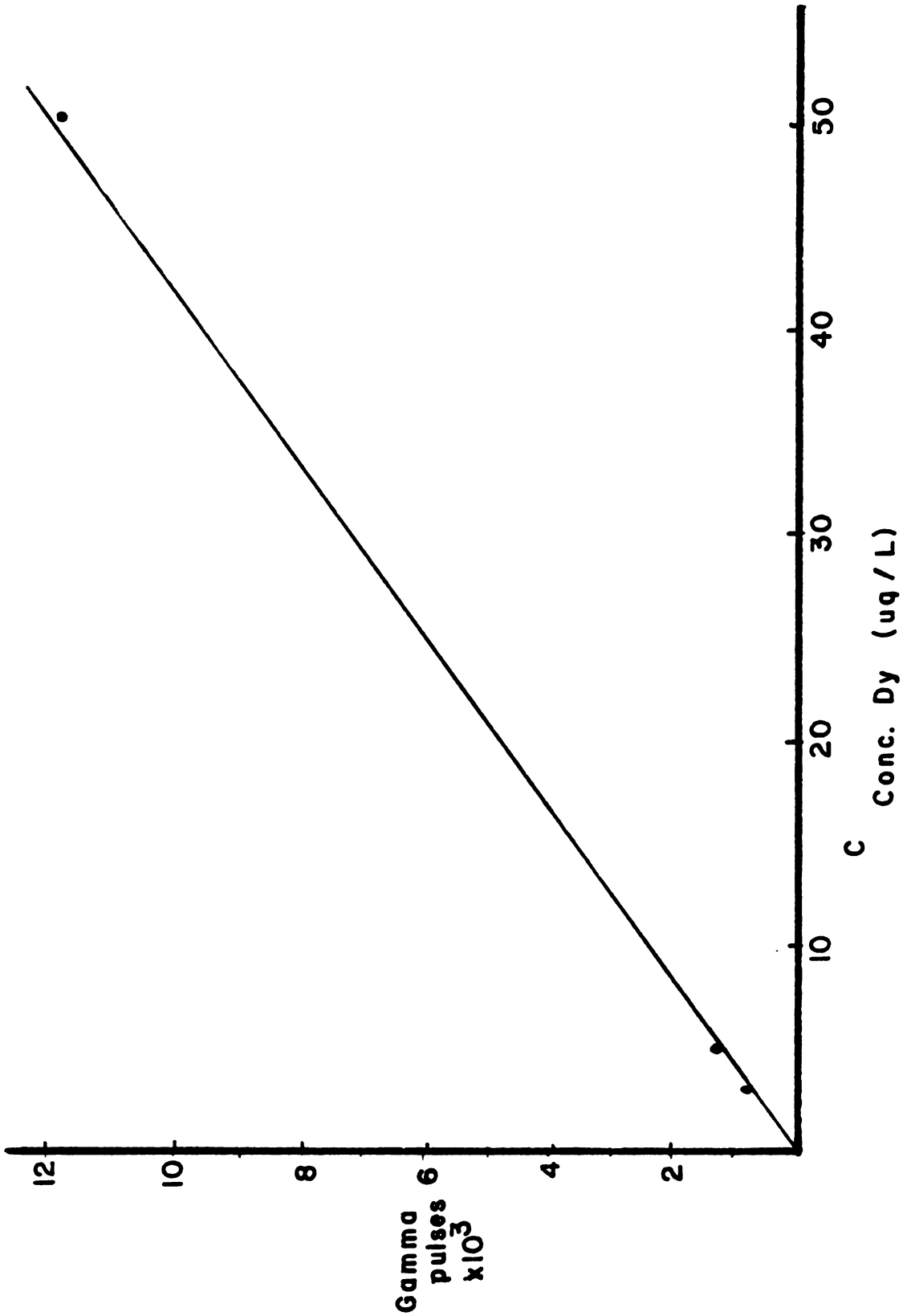

GAMMA ENERGY
ACTIVITY

Figure 10. Graph of the gamma activity of the 94.6 KeV peak of Dysprosium solutions as a function of concentration.


Gamma pulses x10^3
12
10
8
6
4
2
10
20
30
40
50
C Conc. Dy (uq / L)

A second neutron activation experiment was performed by irradiating solutions of dysprosium in river water for 40 min. This time the 94.6 KeV gamma peak was monitored. The results contained in Tables A-5 through A-11 of Appendix A and presented graphically in Figure 10 demonstrate a close linear relationship between dysprosium concentration and gamma activity of the 94.6 KeV peak of each sample. Samples in this trial were only counted for 100 sec, not 400 sec as previously, yet the lower limit of detectability was 1 μg/ℓ, which is much less than the 35 μg/ℓ limit of the former run.

From these experiments, it was concluded that dysprosium at concentrations about 1 μg/ℓ could be used as a neutron activable tracer in river water by monitoring its 94.6 KeV gamma peak.

2. Bromide Ion Internal Neutron Activation Tracer

The use of bromide ion as an internal neutron activable sewage tracer was investigated by collecting East Lansing sewage effluent and Red Cedar River water samples upstream and downstream to the East Lansing sewage drain. The samples were irradiated for 30 min; however, a bromide gamma emission expected at 617 KeV was not observed. The gamma spectrum of each of the samples was essentially identical, indicating that if bromine was present in the samples, its concentration was below the limit of detection of this method. This experiment also demonstrated that there were no neutron activable elements at detectable concentrations in the sewage which were not also present in the Red Cedar River.

3. Chloride Ion Internal Dilution Tracer

The purpose of this portion of the study was to determine if the chloride ion normally present in sewage effluent could be used

as a dilution tracer. Values listed in Table 1 of Appendix B indicate that the concentration of chloride ion present in sewage (86 mg/ℓ) is about twice the amount detected in effluent-free upstream samples (43.5 mg/ℓ). These values were used in calculating sewage dilution factors by the following simultaneous equations:

$$A(X) + B(Y) = C \tag{16}$$

$$X + Y = 1 \tag{17}$$

Where: X = fraction of sewage in sample

Y = fraction of upstream water in sample

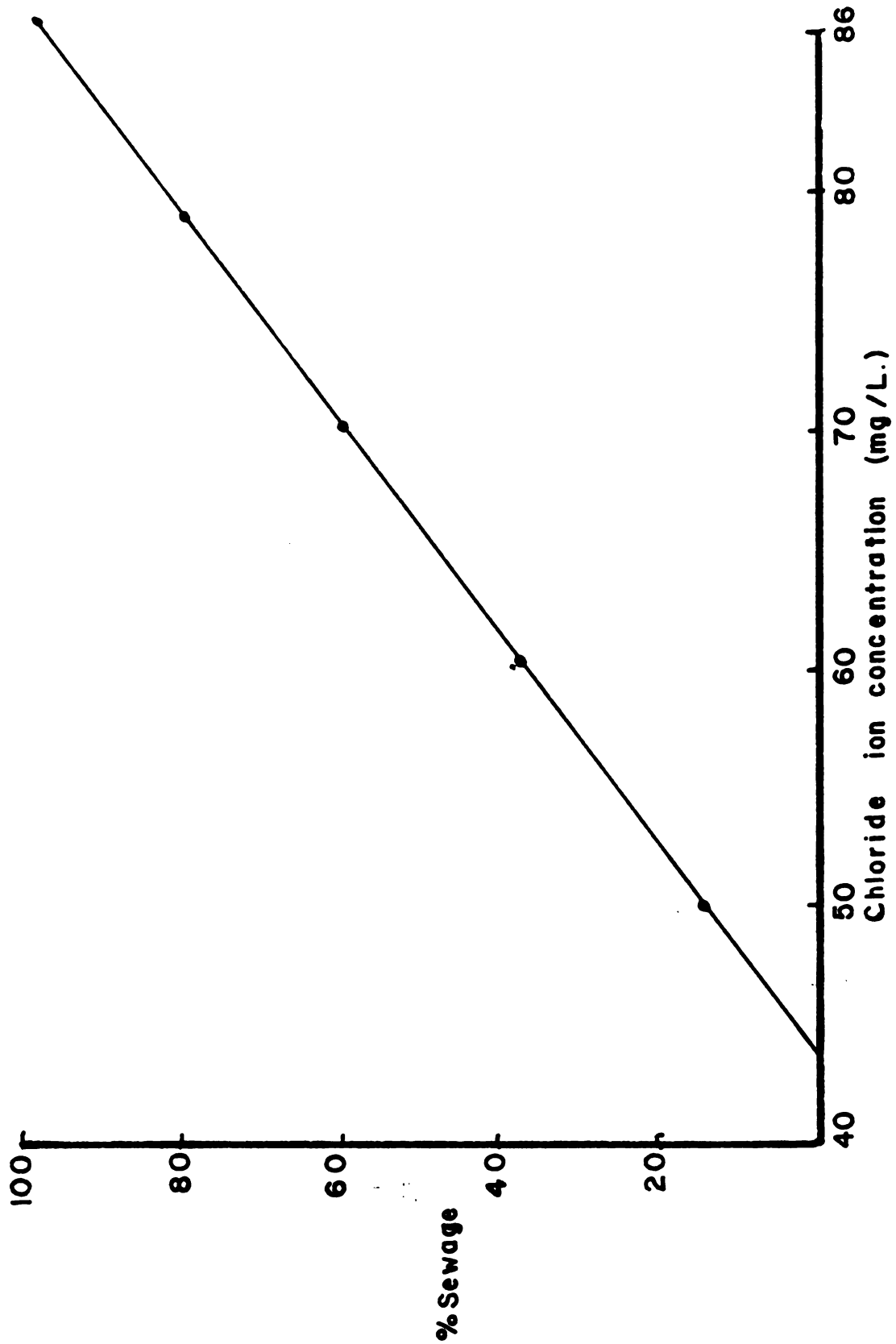
A = concentration of Cl^- ion in sewage (86 mg/)

B = upstream concentration of Cl^- ion (43.5 mg/)

C = concentration of Cl^- ion in downstream sample

Figure 11 represents a solution for the simultaneous equations for any downstream chloride concentration. The percent of sewage in any water sample taken downstream from the East Lansing sewage treatment plant effluent discharge can be read directly from this graph. It should be noted that at dilutions greater than about 2 to 1, a small change in measured chloride ion concentration represents a large change in dilution. For example, the difference of 5 mg/ℓ between chloride concentrations of 55 mg/ℓ and 50 mg/ℓ represents a change from 27% sewage (2.7:1 dilution) to 15% sewage (5.6:1 dilution). Therefore, a very small error in a chloride assay of 1 mg/ℓ can introduce a very large error in the determination of dilution factors. A larger difference in chloride ion concentration between effluent and the river or the absence of chloride ion from dilution water would result in less potential error. Table B-2 compares the chloride dilution method to dilution factors observed for chloroform in sewage.

Figure 11. Graph of percent sewage contained in samples as a function of chloride ion concentration.


100
80
60
40
20
% Sewage
40
50
60
70
80
86
Chloride ion concentration (mg/L.)

The calculated values do not agree well, with greater than 200% deviation between the two methods.

Another factor which would tend to increase errors in calculating dilution ratios using chloride ion is the introduction of chlorides from other sources. A sample taken from a storm drain emptying into the river 400 ft downstream to the sewage outlet (Sample 15, Table B-2) contained a significantly higher level of chloride (78 mg/ℓ) than present in the river (51 mg/ℓ, Sample 16), immediately upstream. This discharge causes an increase in chloride concentration in the river, resulting in an apparent decrease in the sewage dilution factor. Such localized inputs of chloride can occur at many points along the course of a river, making accurate determinations of dilution factors of a particular chloride ion discharge very difficult.

4. Internal Fluorescence Tracer

An investigation into the feasibility of monitoring a wastewater effluent for a fluorescing compound which could ultimately be used as an internal effluent dilution tracer was conducted in Squaw Creek. This small creek, which runs through the city of Kalamazoo and receives effluent from a paper processing plant, was sampled and analyzed by fluorescence spectrophotometry. The emission spectrum of creek samples and the paper plant effluent scanned at an excitation wavelength of 217 nm contained a peak of 326 nm. Fluorescence intensities (Table 3) were smallest in the sample taken upstream of the effluent discharge and largest in the effluent samples collected from the clarifier. In addition, a reduction as a function of distance downstream from the point of effluent discharge was also observed.

TABLE 3

Fluorescent Internal Tracer Data

Sample	Location	Fluorescence at 326 nm (Peak Height)
1	Squaw Creek, 400 ft upstream to point of discharge of Mead Paper Company effluent	3.8
2	Final Clarifier - Mead Paper Company	39.0
3	Squaw Creek, 2 mil downstream of effluent discharge	10.0
4	Squaw Creek, 4 mil downstream of effluent discharge	6.0

Excitation Wavelength = 217 nm

Bandpass = 4 nm

Sampling Location = Squaw Creek, Kalamazoo, Michigan

All samples centrifuged for 10 min at 2500 r.p.m. prior to fluorescence measurements.

This data strongly suggests that reduction of fluorescence with distance from discharge is a function of dilution of the clarifier effluent, and can be quantified by the formulation of a standard curve using upstream water as the diluent. This method could be adapted to selected effluents, including sewage, provided that a suitable fluorescing substance is present in the effluent and not in the receiving water. In applying this tracer technique a number of factors which would tend to introduce error must be considered. Many fluorescing materials are highly labile compounds which photodecompose readily; therefore, the photodecomposition behavior of the particular fluorescing peak must be determined. Another factor requiring consideration is the chemical oxidation of fluorescing material by chlorine added to sewage for disinfection. This type of oxidation degradation can be measured by storing a sample in the dark and comparing fluorescence intensity with time.

CONCLUSIONS

Of the four tracer techniques investigated in this study, the bromide internal standard neutron activation technique and the chloride dilution method gave the poorest results. The levels of bromide ion in sewage were not high enough to be detected and, therfore, could not be quantified. In water samples containing higher bromide concentrations, the neutron activation method should yield good results which are due primarily to the inertness of bromide ion and its extremely low environmental background level. The chloride dilution technique was considered unsuitable because

of the high background levels of chloride ion in the river relative to the concentration of chlorides released in sewage effluent. The inability to measure small differences beteen river and effluent chloride concentrations accurately results in potentially large errors being introduced into the determination of sewage dilution factors. This method also proved to be unsuitable because of a chloride discharge downstream of the sewage effluent discharge resulting in an elevated chloride concentration and causing an apparent reduction in the calculated effluent dilution factor.

The rare earth neutron activation tracer method was not practicable because the lower limit of detection was much higher than the 10^{-12}g originally anticipated. In the most favorable situation, a lower detection limit of 1.0 μg/ℓ (5×10^{-9}g) dysprosium was detected. The large discrepancy is primarily due to the reported detection limit actually being a theoretical value calculated with the following equation:

$$A = NT\emptyset(1 - e^{-\frac{0.693}{t_{\frac{1}{2}}}}) \qquad (18)$$

Where: N = number of dysprosium atoms present

T = nuclear cross section of dysprosium (Barns)

$\emptyset$ = neutron flux (cm^{-1})

t = irradiation time

$t_{\frac{1}{2}}$ = half-life of active isotope

According to this equation, 10^{-12}g of dysprosium, which has a nuclear cross section of 2100 barns, will have an activity of 2.33 disintegrations per second with a half-life 139 min when activated at a flux of 1.8×10^{12} cm^{-1} for 3 hr. A 100 second count should

result in 233 disintegrations. If all instrumental parameters were operating at 100% efficiency, the theoretical detection limit would be approached. In actual practice, this lower limit cannot be reached because the Ge Li detector cannot sense every gamma burst. The greatest factor affecting detector sensitivity is the geometric positioning of the sample with respect to the detector, which results in at least a 50% loss in sensitivity. Also, since the detector responds to peaks at all gamma energies, counts deleted due to coincident gamma bursts, especially in an environmental sample with many activable components, result in a further reduction in disintegrations counted. Other factors which could cause reduced sensitivity are quenching of the dysprosium gamma disintegration by secondary reactions and a reduction in activity caused by a short half-life with a longer period of time between activiation and measurement.

A lower limit of detection of 1 μg/ℓ is not low enough to make the addition of dysprosium to sewage effluent for use as a tracer element economically feasible. Assuming an effluent release of about 10 million gallons per day and a dysprosium cost of $3.00 per gram, it would cost over $1,000.00 to establish a 20 μg/ℓ level of dysprosium in sewage effluent.* The high chemical costs combined with problems associated with dispensing the dysprosium into effluent make this method less desirable than one utilizing a tracer already present in effluent.

The most promising technique considered was the internal fluorescent tracer method, which did not require the addition of

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*$\frac{10 \times 10^6 \text{ gal}}{\text{day}} \times \frac{1 \text{ day}}{24 \text{ hr}} \times \frac{12 \text{ hr}}{1 \text{ run}} \times \frac{20 \times 10^{-6} \text{g}}{\ell} \times \frac{3.78\ell}{\text{gal}} \times \frac{\$3.00}{\text{g Dy}} = \$1,135$

tracer and affords a reasonable sensitivity. However, since only a preliminary investigation was conducted, the importance of degradation, adsorption and interfering substances was not evaluated. Before this method can be used to confidently determine dilution, the effect of each of these factors must be considered.

C. Gas Transfer Kinetics Results

Results of gas transfer kinetics measurements conducted over a wide range of experimental conditions of temperature (3.8°C to 24.8° C) and turbulence are contained in Appendix D and Table 4. The primary purpose of thes experiments was to establish that the ratio of the transfer coefficient of any two volatile components of an aqueous solution is independent of changes in temperature and turbulence.

Overall, the rate of gas transfer increases with increasing temperatures (see Table 4). Although temperatures during each run were kept constant, it is not possible to quantify the relationship between temperatures and gas transfer because the turbulence in each case could not be standardized.

Turbulence was applied to the experimental gas transfer vessel by three different means: a magnetic stirrer, a variable speed motor with a small attached paddle (2 cm x 2 cm) and a fan type variable speed mixer. Mixing ranged from a gentle stirring action (Run No. 13) to highly turbulent swirling which created a large vortex (Run No. 14). The general trend observed was an increase in gas transfer rates with an increase in turbulence. Since there is no way to accurately quantify turbulence, this relationship could not be defined quantitatively.

TABLE 4

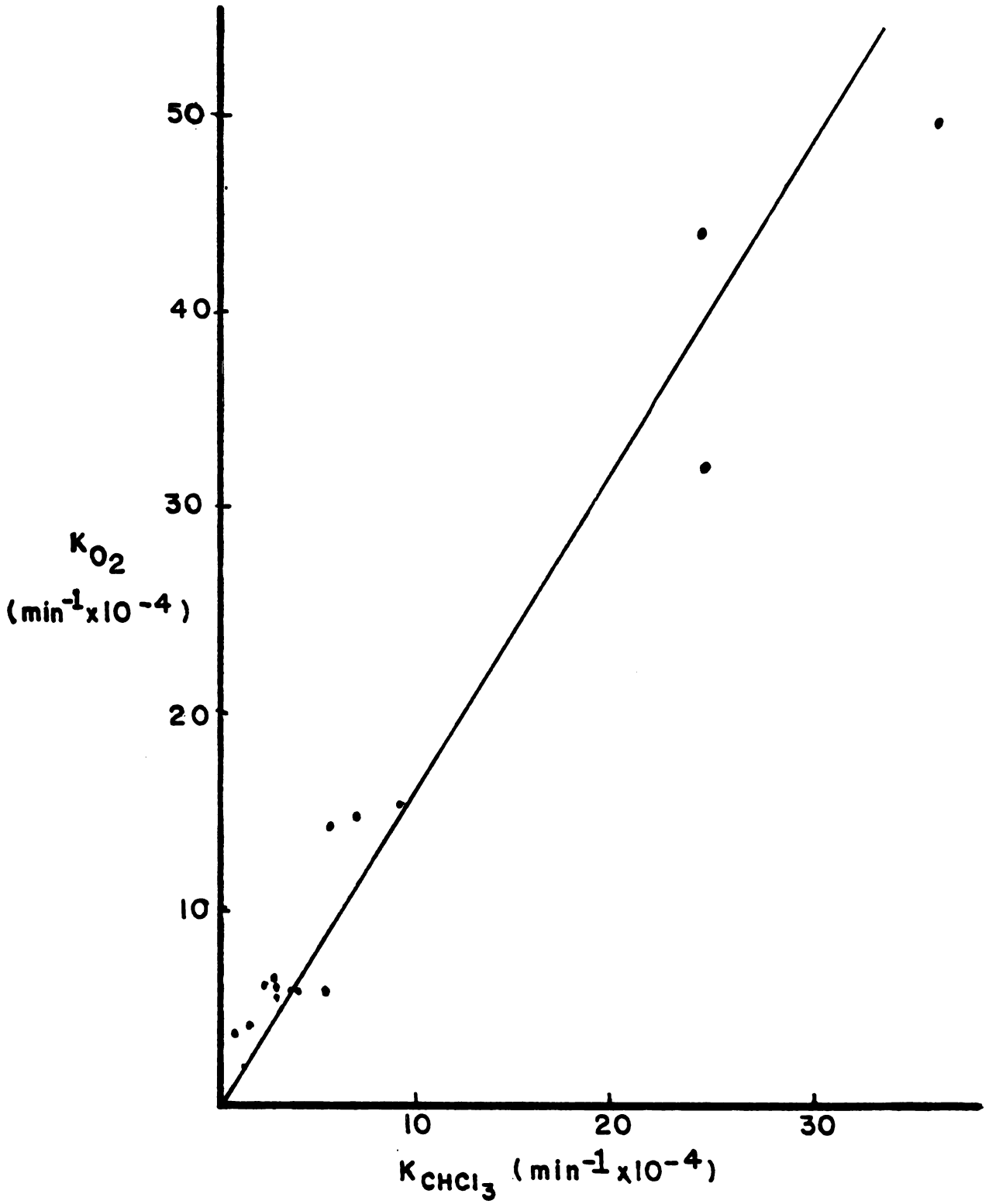
Experimentally Calculated Gas Transfer Rate Constants of Oxygen and Chloroform

Run No.	Date	Temperature °C	Stirring Rate	K_{O_2} (Min^{-1})	K_{CHCl_3} (Min^{-1})	$\frac{K_{O_2}}{K_{CHCl_3}}$
2	4-12-78	22.1	6	6.03×10^{-4}	3.04×10^{-4}	1.98
3	4-19-78	4.1	6	3.27×10^{-4}	1.05×10^{-4}	3.12
4	4-21-78	11.9	50	1.37×10^{-3}	6.22×10^{-4}	2.20
5	4-27-78	13.8	251	5.2×10^{-4}	2.87×10^{-4}	1.81
6	4-28-78	3.8	250	5.98×10^{-4}	2.61×10^{-4}	1.91
7	5- 1-78	24.7	255	5.63×10^{-4}	3.77×10^{-4}	1.49
8	5-17-78	24.5	265	5.94×10^{-4}	3.14×10^{-4}	1.90
9	5-31-78	23.2	455	1.54×10^{-3}	1.02×10^{-3}	1.51
10	6- 1-78	24.1	455	3.17×10^{-4}	2.01×10^{-4}	1.64
11	6- 2-78	24.5	145	5.17×10^{-4}	4.36×10^{-4}	1.19
12	6- 5-78	24.5	240	5.44×10^{-4}	5.86×10^{-4}	0.97
13	6-26-78	24.5	80	2.07×10^{-4}	1.54×10^{-4}	1.35
14	6-27-78	24.8	640	5×10^{-3}	3.62×10^{-3}	1.36
15	6-29-78	24.5	560	1.41×10^{-3}	7.68×10^{-4}	1.84
16	7-11-78	24.3	510	4.54×10^{-3}	2.33×10^{-3}	1.95
17	7-12-78	24.0	460	3.19×10^{-3}	2.40×10^{-3}	1.32

As an additional consideration, two runs (4 and 12) were conducted to establish the effect of wind on gas transfer. A high wind was directed at the solution surface by a fan positioned 3 ft from the gas transfer vessel. The results, however, are difficult to interpret because the measured oxygen/ haloform ratios are different from the other runs but do not exhibit any type of trend of their own. The ratio observed in run No. 4 was higher than all but one of the runs while the ratio calculated in run No. 12 was the lowest. Both runs were conducted under similar conditions of turbulence and wind. The chloroform volatization rate constant in run No. 12 was unusually high for the applied conditions while the oxygen rate constant in run No. 4 was higher than expected.

The ratios of the measured gas transfer coefficients of oxygen to chloroform ranged from a low value of 0.97 to a high of 3.12. These calculated ratios did not exhibit any trends with respect to changes in temperature, turbulence or wind effects. A plot of oxygen gas transfer constants vs. constants measured for chloroform is presented in Figure 12 and demonstrates that a linear relationship exists between the two coefficients over the range of conditions studied. Regression analysis about all of the data points in Figure 12 yields a line with a slope of 1.46 and a correlation coefficient of 0.95. The slope of this line represents a regression value of the oxygen to chloroform rate constant ratio. The mean value of all of the ratios determined individually is 1.75 with a standard deviation of ± 0.5. This value is close to the regression analysis value. If the obviously high value determined in run No. 3 is deleted, a value of 1.63 ± 0.35 results. Run No. 3 was deleted because it

Figure 12. Graph of Oxygen gas transfer rate constants versus chloroform gas transfer rate constant.


50
40
30
20
10
K_{O_2}
$(min^{-1} x 10^{-4})$
10
20
30
K_{CHCl_3} $(min^{-1} x 10^{-4})$

represents the results of one of the earliest runs performed, during which the method was in its initial stages of development and most prone to operator error.

In runs No. 16 and No. 17, the gas transfer rate constants of additional trihalogenated methanes ($CHCl_2Br$, $CHClBr_2$, and $CHBr_3$) were determined and the corresponding oxygen/haloform ratios calculated. The ratios measured in these two runs: $CHCl_2Br$, 1.83, $CHClBr_2$, 2.40, $CHBr_3$, 3.50, demonstrate that the gas transfer rate diminishes as chlorine atoms on chloroform are successively replaced by bromine. Although the oxygen/haloform ratios calculated do not agree between the two runs, the ratio of the chloroform rate constant to those of its brominated analogs agree very consistently.

Since the kinetics experiments involved a number of operations, errors could have been introduced at a number of points, with the major sources of error introduced during the measurement of oxygen and chloroform levels. In many of the runs, the saturation value of oxygen measured did not correspond to the value anticipated at that particular temperature. Two different oxygen meters were used; the first meter, a Horiba "Water Checker," produced less accurate saturation values than the Yellow Springs meter used in later runs (5 through 17) becuase there was no way to standardize the Horiba meter to a Winkler titration. However, it is assumed that the error introduced by the oxygen meters was determinate in nature because, regardless of the deviation of saturation values, the correlation coefficient calculated during each determination of the oxygen transfer rate constant was always greater than 0.98.

Errors introduced during the determination of the aqueous chloroform concentrations could have been caused by a number of

factors including errors due to standards, contamination, vaporization of stored samples, poor gas chromatographic technique or detector response and errors in volume of sample or extractant. The efficiency of extraction of chloroform from water, or percent recovery, was 98%. The error associated with analysis was ± 3 μg/ℓ at 50 μg/ℓ and the limit of detection was 1 μg/ℓ $CHCl_3$. In light of the sources of error involved in the determination of gas transfer rate constants, a standard deviation of ± 0.34 associated with the average oxygen/chloroform ratio of 1.63 is a reasonable value.

CONCLUSIONS

The gas transfer kinetics experiments of this study demonstrated that the ratio of the gas transfer coefficients of oxygen and chloroform remains constant as turbulence and temperature are varied. An increase in temperature or turbulence results in an increase in the gas transfer rates, but this increase occurs to the same extent in all volatilizable solution components. The effect of wind on the oxygen/chloroform gas transfer constant ratio could not be determined from the experiments performed. The value of the K_{O_2}/K_{CHCl_3} ratio calculated was 1.63 ± .63.

D. Results of Chloroform Sediment Adsorption Experiments

An experiment designed to measure the extent to which chloroform adsorbs to suspended sediment was conducted in order to determine whether the process of adsorption competes with volatization. Sediment collected from the Red Cedar River was standardized by seiving to below 30 mesh. The results of the adsorption experiment are given in Table 5. A total of four adsorption runs were

TABLE 5

Sediment Adsorption Data

Date	Sample Type	Sediment Weight (g dry wt)	Exposure Time (m)	Initial $CHCl_3$ (µg/ℓ)	Final $CHCl_3$ (µg/ℓ)	Δ CHCl (µg/ℓ)	Log Partition Coefficient ($\log \frac{\mu g/g\ sed}{\mu g/g\ sol}$)
5-23-78	Sediment	0.62	20	105	99	-6.0	1.2
5-23-78	Control	0.0	20	98	97.5	-0.5	--
5-30-78	Sediment	2.40	22	116	110	-6.0	1.18
5-30-78	Control	0.0	22	82	80	-2.0	--
6- 2-78	Sediment	1.85	21	104	102	-2.0	0.69
6- 2-78	Control	0.0	21	74	75	+1.0	--
6- 5-78	Sediment	1.54	20	140	125	-15.0	1.62
6- 5-78	Control	0.0	20	141	134	-7.0	--

conducted in which approximately 100 μg of chloroform was added to distilled water containing amounts of suspended sediment ranging between 0.62 and 2.40 g in a 1 liter flask. Adsorption of chloroform by the sediments over a 20 hr period ranged from 1.0 to 8.0 μg. The amounts of chloroform did not increase with increases in the weight of sediment in solution. The average sediment water log partition coefficient was 1.2, which is very low for a hydrophobic organic compound. Since the levels of suspended materials were much greater than normally encountered in the Red Cedar, and the exposure time longer than the evaporation half-life of chloroform expected in the Red Cedar, it can be concluded that adsorption by suspended materials is not a major chloroform sink.

DISCUSSION

The purpose of this study was to evaluate the partitioning between the atmosphere and the water and sediment of the Red Cedar River of haloforms formed during chlorination of treated East Lansing sewage effluent. It was originally proposed that the effluent of the East Lansing sewage treatment plant be analyzed for chloroform, and these levels monitored downstream as a function of distance from the point of release and its residence time in the river. These concentrations, after being corrected for dilution, would be used to determine a half-life and disappearance rate constant for haloforms in the Red Cedar. However, a number of factors made the problem of evaluating the persistence of chloroform in the Red Cedar much more difficult.

It was originally planned to devise a method by which dilution of sewage effluent by the Red Cedar could be quantified. However, the methods investigated proved to be either not sensitive enough or too complicated and expensive. Even if an accurate tracer had been developed, it probably would not have been utilized because levels of chloroform produced during the chlorination of wastewater were much lower than originally anticipated. When released into the river, the respective haloforms were rapidly diluted to levels that are below the limit of detection of the analytical method used in this study. It was also determined that volatization was responsible for the rapid decrease of the respective haloform concentrations from the water and the mechanism followed first order kinetics, which

cannot be corrected for random dilution effects. The measurement of an in situ volatization rate constant would have to be performed following complete dilution. Since the haloform levels following dilutions were generally too low to be quantified, the in situ experiments could not be performed. Therefore, it was decided that the partitioning dynamics of the haloforms would be measured in the laboratory with the methods described by Hill et al. (1976) and Smith et al. (1977) by which oxygen/haloform gas transfer ratios could be calculated and the results extrapolated to the Red Cedar River. The experimental results would be compared to values calculated using formulas devised to theoretically predict the environmental volatization rate constants of hydrophobic solutes (Liss and Slater, 1974; Mackay, 1977; Mackay and Wolkoff, 1973; Spacie et al., 1977; Spencer and Farmer, 1978).

The most widely accepted theoretical approach is that of Mackay (1977) which is based on the two layer air-water interface model. Mackay (1977) uses the following relationships to caluculate theoretical gas transfer rate constants:

$$N = K_L (C - P^o/H) \tag{19}$$

$$1/K_L = 1/k_L + 1/(Hkg/RT) \tag{20}$$

$$H = \frac{P^o \times M}{K R T} \tag{21}$$

Where: N = mass flux (moles/m^2hr)

C = liquid phase concentration (mole/m^3)

P^o = vapor phase partial pressure (atm)

H = Henry's Law Constant (atm - m^3/mole)

K_L = overall liquid phase mass transfer coefficient (m/h)

k_L = liquid film mass transfer coefficient (m/hr)

M = molecular weight of solute (g)

K = solubility in water at T°C (g/ℓ)

R = gas constant (.082054 ℓ·atm/°K mol)

Values of k_L and kg can be calculated for any solute by comparison to empirically determined values of the evaporation of water (which is 100% gas phase controlled, kg = 3000 cm/hr) and the flux of CO_2 (which is 100% liquid phase controlled, k_L = 20 cm/hr) with respect to relative molecular diffusion by the following relations:

$$kg = (3000 \text{ cm hr}^{-1}) \sqrt{18/M} \quad (22)$$

$$k_L = (20 \text{ cm hr}^{-1}) \sqrt{44/M} \quad (23)$$

Substitution of equations 22 and 23 into equation 20 results in a value which represents the total resistance of the stagnant air-water interficial bilayer to mass transfer. For most hydrophobic pollutants, liquid phase resistance is the rate controlling factor. The importance of gas phase resistance may be estimated from the calculated value for the Henry's Law constant. For H values below 2×10^{-5} atm m^3/moles, the pollutant tends to partition into the liquid, which results in the mass transfer being gas phase controlled, while above 10^{-3} atm m^3/mole the liquid phase is the controlling factor.

Values of the gas transfer rate constants for O_2, $CHCl_3$ and $CHBr_3$ calculated by the method of Mackay (1977) are listed in Table 6. While calculated values are at least an order of magnitude higher than experimentally observed values, the rate constant ratios agree very well. The theoretically determined rate constants should be lower than the

TABLE 6

Values of Gas Transfer Rate Constants Calculated by the Method of Mackay (1977)

Compound	Calculated Values (cm/hr)	Calculated Values min^{-1} (d = 14.5 cm)	Range of Experimentally Measured Values (min^{-1})	K_{O_2}/K_x Theoretical	K_{O_2}/K_x Observed
O_2	23.44	2.69×10^{-2}	5.94×10^{-4} - 5.0×10^{-3}	--	--
$CHCl_3$	11.40	1.31×10^{-2}	1.05×10^{-4} - 3.62×10^{-3}	2.06	1.6 ± .35
$CHBr_3$	5.88	6.76×10^{-3}	1.31×10^{-3}	3.99	3.5

experimental values because they represent gas transfer occurring at the surface of the ocean whereas the experimental values represent turbulent conditions. The utility of the theoretical calculation is that it can be used to predict the relative rates of gas transfer of two solution components.

Another theoretical approach to the prediction of relative rates of gas transfer is one investigated by Tsivoglou (1965) which suggests that the coefficients of molecular diffusion of two spherical molecules are inversely proportional to their molecular diameters. Therefore, the ratio of the gas transfer rate constants of any two compounds can be approximated by calculating the ratio of their molecular diameters. If molecular diameters are not available, the critical volume of the molecules can be used to estimate molecular diameter by the following equation.

$$\frac{V_c}{2N} \text{ or } \frac{V_c}{3N} = \frac{\pi d^3}{6} \qquad (24)$$

Where: N = Avogadro's number

V_c = critical volume

d = molecular diameter

The gas transfer ratio of K_{O_2}/K_{CHCl_3} determined by this method, using 2.98 $\mathring{A}$ as the molecular diameter of O_2 and solving Equation 24 given that the critical volume of $CHCl_3$ is 240 m^3/mole, results in gas transfer ratios of 2.68 (2N) and 2.12 (3N). This model works reasonably well for small spherical molecules, but it is not known how well it applies to larger, non-spherical compounds and should be used only to provide a first approximation for gas transfer rate constant ratios.

Once the ratio of the gas transfer rate constant of oxygen to a given pollutant is known, the volatization behavior of that compound can be predicted in any natural system for which the oxygen reaeration rate is available. This study was primarily concerned with the prediction of volatization behavior of compounds released into streams and rivers. Values of the oxygen reaeration constant range from 1.40×10^{-3} min^{-1} to 3.83×10^{-2} min^{-1} for small streams (Grant, 1976) and 6.94×10^{-5} min^{-1} to 6.46×10^{-3} min^{-1} for rivers such as the Mississippi, Allegheny and the Rio Grande (Langbein and Durum, 1967). Table 7 lists the expected range of the evaporation half-lives calculated for the trihalomethanes using these reaeration values and the experimentally calculated gas transfer ratios.

The range of half-lives listed in Table 7 is much too wide to be used to predict the half-life of a haloform released into a stream for which the oxygen reaeration constant is not known. In such a case it would be necessary to experimentally determine the oxygen reaeration constant of the particular stream or calculate it theoretically. There have been many theoretical approaches proposed (Churchill et al., 1962; O'Connor and Dobbins, 1958; Streeter and Phelps, 1925; Tsivoglou, 1967; Longbein and Durum, 1967; Foree, 1976; Tsivoglou and Neal, 1976). An excellent review of the theoretical approaches to prediction of reaeration has been prepared by Bennet and Rathbun (1972). The major disadvantage in the theoretical approach for predicting oxygen reaeration rates is the inability of a single equation to apply equally well to relatively quiescent large rivers and highly turbulent streams. Bennet and Rathbun (1972) have determined that the most reliable equation is:

TABLE 7

Expected Evaporation Half-Lives of the Trihalomethanes from Rivers and Streams

Compound	K_{O_2}/K_x (Empirically Calculated)	Half-Live Range
$CHCl_3$	1.63	29 min - 11.30 days
$CHCl_2Br$	1.83	33 min - 12 days
$CHClBr_2$	2.40	43 min - 16.6 days
$CHBr_3$	3.50	63 min - 24.2 days

$$k_{O_2} = 8.76 \frac{U^{0.607}}{H^{1.689}} \quad (25)$$

Where: k_{O_2} = O_2 reaeration constant (day^{-1})

U = mean stream velocity (ft day^{-1})

H = mean depth (ft)

Tsivoglou (1976) has developed an equation which relates the average slope of the stream to its oxygen reaeration constant:

$$K_{O_2} = \frac{0.0277\ \Delta h}{L} \quad (26)$$

Where: K_{O_2} = O_2 reaeration constant (hr^{-1}) at 20°C

Δh = change in elevation (ft)

L = length of stream (mi)

A similar equation has been developed by Foree (1976):

$$K_{O_2} = 0.30 + .19\ S^{1.2} \quad (27)$$

Where: S = slope of stream (ft mi^{-1})

K_{O_2} = O_2 reaeration constant ($days^{-1}$ at 25°C)

The equations of Tsivoglou (1976) and Foree (1976) may be used to predict the behavior of the haloforms in the Red Cedar, which has an average slope of 2.5 ft mi^{-1} (Table 8).

The experimentally calculated values listed in Table 8 indicate that the trihalomethanes have relatively short environmental volatization half-lifes, but are considerably longer than the 21 min chloroform half-life reported by Dilling et al. (1975) and values of 53 min ($CHCl_3$) and 102 min ($CHBr_3$) calculated by the method of Mackay (1977).

TABLE 8

Predicted Half-Lives of the
Trihalomethanes in the Red Cedar River

Compound	K_{O_2}/K_x	$T_{1/2}$ Tsivoglou $K_{O_2} = 1.15 \times 10^{-3}$ min^{-1}	$T_{1/2}$ Foree 6.04×10^{-4} min^{-1}
$CHCl_3$	1.63	16.37 hr	31.17 hr
$CHCl_2Br$	1.83	18.38 hr	35.0 hr
$CHClBr_2$	2.40	24.10 hr	46.0 hr
$CHBr_3$	3.50	35.15 hr	67.1 hr

The calculated water-sediment chloroform partition coefficient of 16 indicates that adsorption onto sediments is not a major chloroform sink in the Red Cedar River. An equation derived by Paris et al. (1978) was used to estimate the effect of sediment adsorption on the volatization rate.

$$\frac{-d\ C_{TOT}}{dt} = \frac{k}{1 + \frac{KM}{W}} \qquad (28)$$

Where: C_{TOT} = concentration of solute in water

k = volatization rate constant of solute

K = sediment-water partition coefficient of solute = $\left[\frac{\text{conc. in sed. (gm/gm)}}{\text{conc. in water (gm/gm)}}\right]$

$\frac{M}{W}$ = suspended solids in water (gm/gm) per unit weight of water

Assuming the Red Cedar River contains a maximum suspended sediment load of 150 mg/ℓ, the volatization rate of a compound with a partition coefficient of 16 will not be affected by sorption onto sediments.

CONCLUSIONS

Low part per billion levels (<30 μg/ℓ) of haloforms are produced as a result of chlorination of municipal sewage and released into the Red Cedar River; whereupon they become diluted to concentrations below 1 μg/ℓ within 500 feet. In the event of the discharge of higher levels, the haloforms would not be expected to persist due to their short volatization half-lives and extremely low sediment adsorption coefficients. However, the persistence of haloforms could become a problem if high concentrations were released into slow-moving quiescent systems.

The exact biological activity of the haloforms is not known at this time. Residue analyses of fish and sediment have indicated that haloforms do not accumulate in aquatic systems (McConnel and Ferguson, 1975). Since there is no evidence indicating that haloforms are microbially degraded, it is assumed that the major sink for haloforms introduced into the Red Cedar River is volatization to the atmosphere. Although the calculated half-lives for these substances are relatively short, indicating that their persistence in aquatic systems should not be a problem, and the levels at which they have been detected in the Red Cedar River are extremely low (<20 μg/ℓ), the aquatic toxicology of these common pollutants needs to be evaluated before the impact of their continued release can be evaluated.

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APPENDICES

APPENDIX A

NEUTRON ACTIVATION DATA

TABLE A-1

Neutron Activation Gamma Spectrum* of 50 μg/ℓ Dysprosium in River Water.

Cell Number	560	561	562	563	564	565	566	567	568	569
Counts	437	496	474	492	540	529	603	659	670	617
Cell Number	570	571	572	573	574	575	576	577	578	579
Counts	579	564	519	596	509	515	476	477	458	453
Cell Number	580	581	582	583	584	585	586	587	588	589
Counts	467	457	478	441	456	462	468	452	488	449
Cell Number	590	591	592	593	594	595	596			
Counts	462	437	459	461	397	450	495			

Cells assigned to Dy Peak = 560 - 579
Peak Area = Σ(560 - 579) = 10,763
Background = Σ(580 - 589/10 = 462
Corrected Count = 10,763 - 20(461.8) = 1,527
Counting Time = 400 seconds
Irradiation Time - 36 min.

*Only that portion of the gamma spectrum corresponding to the 368 KeV Dysprosium peak is listed.

TABLE A-2

Neutron Activation Gamma Spectrum of 500 μg/ℓ Dysprosium in River Water.

Cell Number	560	561	562	563	564	565	566	567	568	569
Counts	777	826	917	1022	1267	1523	1977	2337	2750	2881
Cell Number	570	571	572	573	574	575	576	577	578	579
Counts	2534	2218	1871	1561	1307	1206	1018	842	877	737
Cell Number	580	581	582	583	584	585	586	587	588	589
Counts	771	698	711	701	670	721	695	679	677	687

368 KeV Peak contained in cells 560 through 579
ΣCells 560 to 579 = 30,448
ΣCells 550 to 559 plus 580 to 589 = 14,444
Corrected count = 30,448 - 14,444 = 16,004

TABLE A-3

Neutron Activation Gamma Spectrum of 1 mg/ℓ Europium in River Water.

Cell Number	740	741	742	743	744	745	746	747	748	749
Counts	1377	1357	1352	1404	1471	1557	1657	1925	2106	2366
Cell Number	750	751	752	753	754	755	756	757	758	759
Counts	2865	3446	4222	5148	6133	6908	7072	6820	6137	5504
Cell Number	760	761	762	763	764	765	766	767	768	769
Counts	4722	3989	3477	3167	2761	2689	2450	2186	1943	1775
Cell Number	770	771	772	773	774	775	776	777	778	779
Counts	1629	1449	1406	1371	1358	1300	1247	1278	1203	1174
Cell Number	780	781	782	783	784	785	786			
Counts	1193	1219	1272	1170	1233	1227	1213			

Cells 750 to 775 correspond to the 130 KeV Gamma Peak of Eu
ΣCells 750 through 775 = 91,927
Background = ΣCells 776 through 786 = 12,182
Corrected Count = 91,927 - (12,182/11)(26) = 63,133

TABLE A-4

Neutron Activation Gamma Spectrum of 50 μg/ℓ Europium in River Water.

Cell Number	750	751	752	753	754	755	756	757	758	759
Counts	389	446	518	571	586	685	668	651	603	545
Cell Number	760	761	762	763	764	765	766	767	768	769
Counts	546	490	466	430	436	409	433	356	351	360
Cell Number	770	771	772	773	774	775	776	777	778	779
Counts	330	306	324	318	314	309	376	297	348	311
Cell Number	780	781	782	783	784	785	786	787	788	
Counts	325	317	299	324	302	308	308	284	309	

Cells 750 through 775 correspond to the 130 KeV Peak
Peak Area = Σ(750 to 775) = 11,840
Background = Σ(776 to 788) = 4,108
Corrected Count = 11,840 - (4108/13)(26) = 3,624

TABLE A-5

Neutron Activation Gamma Spectrum of 50 μg/ℓ Dysprosium in River Water.

Cell Number	210	211	212	213	214	215	216	217	218	219
Counts	608	746	1025	1527	2295	2886	2889	2381	1835	1214
Cell Number	220	221	222	223	224	225	226	227	228	229
Counts	940	700	567	568	534	498	494	462	478	456
Cell Number	230	231	232	233	234	235				
Counts	431	441	425	447	454	267				

Cells assigned to Dy 94.63 KeV Peak are 212 through 220.
Peak Area = Σ(212 to 220) = 16,992
Background = Σ(221 to 225) 15 = 573
Corrected Area = 16,992 - (573)(9) = 11,835
Counting Time = 100 seconds
Irradiation Time = 40 min.

TABLE A-6

Neutron Activation Gamma Spectrum of 5 μg/ℓ Dysprosium in River Water.

Cell Number	210	211	212	213	214	215	216	217	218	219
Counts	205	244	272	314	402	406	416	382	296	255
Cell Number	220	221	222	223	224	225	226	227	228	229
Counts	239	220	194	193	201	198	215	224	191	215
Cell Number	230	231	232	233						
Counts	178	192	210	234						

Cells 211 through 221 assigned to 94.6 KeV Dy Peak
Peak Area = Σ(211 to 221) = 3,446
Background = Σ(222 to 226) = (100,115) = 200
Corrected Count = 3,446 - 200 (11) = 1,246
Counting Time = 100 seconds

TABLE A-7

Neutron Activation Gamma Spectrum of 3 μg/ℓ Dysprosium in River Water.

Cell Number	210	211	212	213	214	215	216	217	218	219
Counts	237	282	290	329	352	373	353	304	286	260

Cell Number	220	221	222	223	224	225
Counts	294	280	217	269	212	230

Cells 211 to 221 assigned to 94.6 KeV Dysprosium Peak
Peak Area = Σ(211 to 221) = 3403
Background Count = Σ(222 to 225) = 232
Corrected Counts = 3,403 - (232)(11) = 851
Counting Time = 100 seconds

TABLE A-8

Neutron Activation Gamma Spectrum of 1 μg/ℓ Dysprosium in River Water.

Cell Number	210	211	212	213	214	215	216	217	218	219
Counts	266	239	214	235	249	223	210	217	208	212
Cell Number	220	221	222	223	224	225	226	227	228	
Counts	206	217	202	189	206	225	205	234	168	

Differences between background activity and Dysprosium Peak cannot be detected
94.6 KeV Dy Peak cannot be isolated
Counting time = 100 seconds

TABLE A-9

Neutron Activation Gamma Spectrum of 1 μg/ℓ Dysprosium in River Water.

Cell Number	210	211	212	213	214	215	216	217	218	219
Counts	205	244	272	314	402	406	416	382	296	255
Cell Number	220	221	222	223	224	225	226	227	228	229
Counts	239	220	194	193	201	198	215	224	191	215
Cell Number	230	231	232	234						
Counts	178	192	210	234						

Cells 211 to 221 assigned to 94.6 KeV Dy Peak
Peak Area = (211 to 221) = 3,446
Background = (222 to 226) = (1001)/5 = 200
Corrected Count = 3,446 - (200)(11) = 1,246
Counting Time = 400 seconds
Count corrected to 100 second counting time = (100/400)(1246) = 311

TABLE A-10

Neutron Activation Gamma Spectrum of 0.1 μg/ℓ Dysprosium in River Water.

Cell Number	210	211	212	213	214	215	216	217	218	219
Counts	207	180	215	169	214	194	198	188	201	219
Cell Number	220	221	222	223	224	225	226	227	228	
Counts	193	220	187	182	181	171	222	199		

No significant variation in background counts observed
94.6 KeV Peak cannot be isolated
Counting Time = 100 seconds

TABLE A-11

Neutron Activation Gamma Spectrum of 0.1 μg/ℓ Dysprosium in River Water.

Cell Number	210	211	212	213	214	215	216	217	218	219
Counts	680	622	662	677	685	697	666	672	685	684
Cell Number	220	221	222	223	224	225	225	227	228	229
Counts	654	627	661	617	651	631	634	653	617	644
Cell Number	230	231	232	233	234	235	236	237	238	239
Counts	643	685	649	618	671	696	649	648	653	651
Cell Number	240	241	242	243	244	245	246	247	248	249
Counts	601	594	644	644	616	676	672	670	643	658
Cell Number	250	251	252	253	254					
	647	632	615	609	630					

No significant variation in background counts observed
94.6 KeV Dysprosium Peak cannot be isolated
Counting Time = 400 seconds

APPENDIX B

CHLORIDE DILUTION

TRACER DATA

TABLE B-1

Chloride Tracer Sampling
Locations and Concentrations

Chloride Sample No.	Chloride mg/ℓ	Chloroform Sample No.	Chloroform µg/ℓ
1[a]	40	--	--
2[a]	44	76	<0.5
3[a]	59	--	--
4[a]	41	--	--
5[a]	39	--	--
6[b]	38	77	<0.5
7[c]	86	--	--
8[c]	72	78	7.8
9[c]	63	--	--
10[d]	79	--	--
11[a]	64	79	--
12[e]	73	80	3.4
13[f]	52	81	3.2
14[g]	48	82	<0.5
15[g]	51	83	<0.5
16[g]	51	84	<0.5
17[h]	78	--	--

[a]Sample 1 through 5, collected 300 feet upstream to Kalamazoo Street Bridge.

[b]50' upstream to Kalamazoo Street Bridge.

[c]Samples 7 through 9 and 78 were taken directly over E.L. Sewage outlet into the Red Cedar.

[d]10 and 11 plus 79 taken 100 feet downstream to sewage outlet.

[e]200 feet downstream to sewage outlet.

[f]300 feet downstream to sewage outlet.

[g]400 feet downstream to sewage outlet.

[h]Drain, 400 feet downstream to sewage outlet.

TABLE B-2

Chloride and Chloroform
Effluent Dilution Factors

Chloride Sample	Chloride Dilution Factor (Diluent:Sewage)	Chloroform Sample No.	Chloroform Dilution Factor* (Diluent:Sewage)	% Deviation
7	0	--	--	--
8	0	78	0	0
9	0	--	--	--
10	0.20	79		
11	1.08			
12	0.45	80	1.29	286
13	4.00	81	1.44	278
14	9.00	82	>15	>167
15	5.06	83	>15	>300
16	5.06	84	>15	>300

The values used to calculate the sewage dilution factor were:

1. UPSTREAM chloroform average = <0.5 µg/ℓ.
2. UPSTREAM chloride average = 43.5 mg/ℓ.
3. High value of 86 mg/ℓ chloride accepted as effluent value.

*4. Chloroform losses were neglected.

APPENDIX C

HALOFORM LEVELS OF ENVIRONMENTAL SAMPLES

TABLE C-1

Haloform Levels of Environmental Samples

Sample Number	Date	Location	($CHCl_3$) µg/ℓ
1	2- 1-78	East Lansing Primary Sewage	20.0
2	2- 1-78	East Lansing Primary Sewage	21.0
3	2- 1-78	East Lansing Raw Sewage	34.0
4	2- 1-78	East Lansing Raw Sewage	36.0
5	2- 1-78	East Lansing Secondary Sewage	2.0
6	2- 1-78	East Lansing Secondary Sewage	4.0
7	2- 1-78	East Lansing Final Unchlorinated	<1.0
8	2- 1-78	East Lansing Final Unchlorinated	<1.0
9	2- 1-78	East Lansing Final Chlorinated	14
10	2- 1-78	East Lansing Final Chlorinated	18
11	2- 1-78	East Lansing Primary - South	16
12	2- 1-78	East Lansing Secondary - South	10
14	2- 7-78	Air-Purged Distilled Water - Room 160, Natural Resources	<1.0
15	2- 7-78	Chlorinated Tap Water - U.S.D.A., Poultry Research	11
16	2- 7-78	Chlorinated Tap Water - U.S.D.A., Poultry Research	12
17	2- 7-78	Water Prior to Chlorination - U.S.D.A.	<1.0
18	2- 7-78	Water Prior to Chlorination - U.S.D.A., Poultry Lab	<1.0
19	2- 7-78	Distilled Water - Room 160, Natural Resources - Non-Purged	<1.0
21	2- 7-78	Solvent Blank	<1.0
22	2-26 78	East Lansing Sewage Outfall to Red Cedar	13.5
23	2-26-78	Upstream to Outfall	<1.0
24	2-26-78	5 Feet Downstream to Sample #22 - Right Bank	10.6
25	2-26-78	5 Feet Downstream to Sample #22 - Right Bank	10.5
26	2-26-78	50 Feet Downstream to Sample #22 - Right Bank	7.0
27	2-26-78	50 Feet Downstream to Sample #22 - Right Bank	5.3

Table C-1 (cont.).

Sample Number	Date	Location	($CHCl_3$) µg/ℓ
28	2-26-78	100 Feet Downstream to Sample #22 - Right Bank	4.4
29	2-26-78	100 Feet Downstream to Sample #22 - Right Bank	4.2
30	2-26-78	150 Feet Downstream to Sample #22 - Right Bank	3.65
31	2-26-78		3.40
32	2-26-78	300 Feet Downstream to Sample #22 - Right Bank	1.40
33	2-26-78	Snow Along Bank	1.0
76	4-26-78	Red Cedar River - 300 Feet Upstream to Kalamazoo St. Brigde	0.5
77	4-26-78	Red Cedar River - 50 Feet Upstream to Kalamazoo St. Bridge	0.5
78	4-26-78	Directly Over East Lansing Sewage Outlet to Red Cedar	7.8
79	4-26-78	100 Feet Downstream to Sewage Outlet	
80	4-26-78	200 Feet Downstream to Sewage Outlet	3.4
81	4-26-78	300 Feet Downstream to Sewage Outlet	3.2
82	4-26-78	400 Feet Downstream to Sewage Outlet	0.5
83	4-26-78	700 Feet Downstream to Sewage Outlet	0.5
84	4-26-78	900 Feet Downstream to Sewage Outlet	0.5
270	6-27-78	Lansing Sewage Chlorination Tank	3.0
271	6-27-78	Lansing Sewage Chlorination Tank	2.5
272	6-27-78	Lansing, Chlorinated Sewage Following Cascade Aeration	2.2
273	6-27-78	Lansing, Chlorinated Sewage Following Cascade Aeration	2.1
274	6-27-78	Grand River, 20 Feet Downstream to Sewage Effluent Drain	1.8
275	6-27-78	Grand River, 250 Feet Downstream to Sewage Effluent Drain	1.5
276	6-27-78	Grand River, 450 Feet Downstream to Sewage Effluent Drain	1.0
277	6-27-78	Grand River, 650 Feet Upstream to Sewage Effluent Drain	1.5

Table C-1 (cont.).

Sample Number	Date	Location	($CHCl_3$) µg/ℓ	($CHCl_2Br$) µg/ℓ	($CHClBr_2$) µg/ℓ	($CHBr_3$) µg/ℓ
315	7-16-78	Sampling Site #1	-	-	-	-
316	7-16-78	Sampling Site #2	-	-	-	-
317	7-16-78	Sampling Site #3	2.0	-	-	-
318	7-16-78	Sampling Site #4	-	-	-	-
319	7-16-78	Sampling Site #5	-	-	-	-
320	7-16-78	Sampling Site #6	-	-	-	-
321	7-16-78	Sampling Site #7	-	-	-	-
322	7-16-78	Sampling Site #8	-	-	-	-
323	7-16-78	Sampling Site #9	-	-	-	-
324	7-16-78	Sampling Site #10	-	-	-	-
325	7-16-78	Dry	-	-	-	-
326	7-16-78	Sampling Site #11	-	-	-	-
327	7-16-78	Sampling Site #12	-	-	-	-
328	7-16-78	Sampling Site #13	3.5	1.5	-	-
329	7-16-78	Sampling Site #14	-	1.5	-	-
330	7-16-78	Sampling Site #15	-	1.5	-	-
331	7-16-78	Sampling Site #16	-	-	-	-
332	7-16-78	Sampling Site #17	-	-	-	-
333	7-16-78	Sampling Site #18	1.5	-	-	-
334	7-16-78	Sampling Site #19	1.5	-	-	-
335	7-16-78	Sampling Site #26	1.5	-	-	-
336	7-16-78	Sampling Site #24	11.0	7.0	8.0	-
337	7-16-78	Sampling Site #23	5.0	2.0	3.0	-
338	7-16-78	Sampling Site #21	-	-	-	-
339	7-16-78	Sampling Site #22	2.0	1.5	1.5	-
340	7-16-78	Sampling Site #20	2.0	1.5	-	-
341	7-16-78	Sampling Site #25	9.0	3.2	7.0	-

- = Less than the least detectable concentration of 1.0 µg/ℓ.

APPENDIX D

GAS TRANSFER

KINETICS DATA

TABLE D-2

Oxygen and Chloroform Gas Transfer Kinetics
Date: Run 2, April 12, 1978

Sample Number	Elapsed Time (Minutes)	(O_2) mg/ℓ	($CHCl_3$) µg/ℓ	Temperature °C
34	2	0.9	72	22.2
	6	1.2		22.3
35	10	1.5	64.8	22.4
	12	1.7		22.4
36	20	2.1	63.0	22.5
	26	2.5		22.5
37	30	2.7	60.0	22.6
	35	3.0		22.6
38	40	3.2	48.0	22.7
	48	3.5		22.7
39	50	3.7	48.5	22.8
	54	3.8		22.8
40	60	4.1	46.0	22.8
	63	4.2		22.8
41	70	4.5	43.0	22.9
	75	4.6		22.9
42	80	4.8	41.5	23.0
	85	4.9		23.0
43	90	5.1	38	23.1
	95	5.3		23.1
44	100	5.4	37.5	23.2
	106	5.5		23.2
45	110	5.6	35	23.3
	116	5.7		23.3
46	120	5.8	33.3	23.4
	126	6.0		23.4
47	130	6.0	31.0	23.5
	140	6.1		23.5
48	150	6.4	26.4	23.5
	163	6.6		23.6
49	170	6.7	23.6	23.6
	178	6.8		23.7
50	188	6.9	21.8	23.7
51	361	8.0	9.6	24.2
52	390	8.0	8.6	24.2
53	420	8.0	7.3	24.3
54	450	8.1	6.6	24.3
55	480	8.1	6.2	24.3
56	510	8.1	7.2	24.3
57	540	8.1	4.4	24.3

Table D-2 (cont.).

Experimental Conditions

Initial O_2 = 0.9 mg/ℓ
Initial Temperature = 22.2°C
Initial $CHCl_3$ = 72.0 µg/ℓ
Saturation (O_2) mg/ℓ = 8.1 mg O_2/ℓ
Stirring Rate = 6 division of Corning Magnetic Stirrer

Oxygen/Haloform Ratio Data

Oxygen	Chloroform
b = 0.014	b = 0.17
k_{O_2} = m = -9.66×10^{-3}	m = 4.87×10^{-3}
r = 1.00	r = .99

$$\frac{k\ O_2}{k\ CHCl_3} = \frac{9.66 \times 10^{-3}}{9.87 \times 10^{-3}} = 1.98$$

TABLE D-3

Oxygen and Chloroform Gas Transfer Kinetics
Date: Rune 3, April 19, 1978

Sample Number	Elapsed Time (Minutes)	(O_2) mg/ℓ	($CHCl_3$) µg/ℓ	Temperature °C
58	5	1.2	91.0	4.2
--	11	1.7	--	4.1
--	15	1.8	--	4.1
--	19	2.0	--	4.1
59	24	2.2	83.0	4.1
--	29	2.3	--	4.1
--	32	2.4	--	4.1
--	36	2.6	--	4.1
--	39	2.8	--	4.1
60	44	2.9	86	4.1
--	49	3.1	--	4.1
--	54	3.3	--	4.1
--	59	3.5	--	4.1
61	64	3.7	85	4.1
--	69	3.9	--	4.1
--	74	4.1	--	4.1
--	74	--	--	4.1
62	79	4.2	78	4.1
--	80	4.3	--	4.1
--	84	4.4	--	4.1
63	99	4.8	79	4.1
--	104	5.0	--	4.1
--	109	5.2	--	4.1
64	119	5.4	82	4.1
--	120	5.5	--	4.1
--	124	5.6	--	4.1
--	134	5.8	--	4.1
65	139	6.0	75.0	4.1
--	154	6.3	--	4.1
66	159	6.4	67.4	4.1
--	161	6.5	--	4.1
67	179	6.8	68.0	4.1
68	199	7.1	71.4	4.0
--	201	7.2	--	3.9
69	224	7.5	66	3.9
--	226	7.6	--	3.9
70	239	7.8	66	3.9
--	251	7.9	--	3.9
72	259	8.0	62.4	3.9
73	439	9.7	48	4.1
74	469	10.0	--	4.1
75	499	10.2	--	4.1

Table 3 (cont.).

Experimental Conditions

Initial O_2 (mg/ℓ) = 0.6 mg/ℓ
Initial Temperature = 4.1°C
Initial $CHCl_3$ = L0.1 µg/ℓ
Saturation (O_2) mg/ℓ = 10.8 mg O_2/ℓ
Stirring Rate = 6 divisions on Corning Magnetic Stirrer

Oxygen/Haloform Ratio Data

Oxygen	Chloroform
$b = -8.7 \times 10^{-3}$	$b = 0.02$
$m = -5.24 \times 10^{-3}$	$m = -1.68 \times 10^{-3}$
$r^2 = 0.99$	$r^2 = 0.94$

$$\frac{k\ O_2}{k\ CHCl_3} = 3.12$$

TABLE D-4

Oxygen and Chloroform Gas Transfer Kinetics
Data: Run 4, April 21, 1978

Sample Number	Elapsed Time (Minutes)	(O_2) mg/ℓ	($CHCl_3$) µg/ℓ	Temperature °C
91	0	1.1	8.7	11.9
92	5	1.9	71.4	12.0
93	15	3.1	--	12.0
94	20	3.5	67	12.0
--	25	4.1	--	12.0
95	30	4.5	62	12.0
--	35	4.9	--	12.0
--	40	5.3	--	12.1
96	45	5.6	52.4	12.0
--	60	6.6	--	12.0
97	65	6.9	43	12.0
--	70	7.2	--	12.0
98	88	8.0	33.2	12.0
99	110	8.7	24	12.0
100	140	9.2	14	12.0
101	172	9.4	9.4	12.1
--	190	*9.5	--	12.1
102	207	*9.6	7.0	12.1
103	238	*9.6	6.4	12.1
104	271	*9.6	6.0	12.1
105	295	*9.6	5.8	12.1

Experimental Conditions

Initial O_2 (mg/ℓ) = 0.8
Initial Temperature = 12.9°C
Stirring Rate = 50 units on paddle blade mixer
Saturation Concentration of O_2 = 9.6 mg/ℓ
Wind Applied = high wind

Oxygen/Haloform Ratio Data

Oxygen	Chloroform
b = 0.14	b = -0.16
m = -0.022	m = -9.96×10^{-3}
r^2 = 0.99	r^2 = 0.96

$$\frac{k\ O_2}{k\ CHCl_3} = 2.20$$

*Values not used in calculation of rate constant due to closeness of values to saturation conditions.

TABLE D-5

Oxygen and Chloroform Gas Transfer Kinetics
Data: Run 5, April 27, 1978

Sample Number	Elapsed Time (Minutes)	(O_2) mg/ℓ	($CHCl_3$) µg/ℓ	Temperature °C
106	0.0	0.6	--	13.6
107	4.5	0.9	105	13.5
108	14.5	1.7	--	13.3
109	29.5	2.6	--	13.1
110	45.5	3.5	85	13.1
111	59.5	4.3	78	13.1
112	89.5	5.5	73	13.2
113	119.5	6.3	65	13.2
114	149.5	6.9	56	13.3
115	179.5	7.5	48	13.3
116	349.5	8.8	22	13.4
117	379.5	8.9	18	13.5

Experimental Conditions

Initial O_2 = 0.3 mg/ℓ
Initial Temperature = 13.8°C
Saturation O_2 Concentration = 9.5 mg/ℓ O_2
Turbulence Applied = 251 r.p.m. - Tri-R-Stir

Oxygen/Haloform Ratio Data

Oxygen

$b = -0.015$
$m = -8.32 \times 10^{-3}$
$r^2 = 1.00$

Chloroform

$b = 0.03$
$m = -4.60 \times 10^{-3}$
$r^2 = 1.00$

$$\frac{k\ O_2}{k\ CHCl_3} = 1.81$$

TABLE D-6

Oxygen and Chloroform Gas Transfer Kinetics
Data: Run 2, April 28, 1978

Sample Number	Elapsed Time (Minutes)	(O_2) mg/ℓ	($CHCl_3$) µg/ℓ	Temperature °C
106	0	0.5	125	3.8
107	10	1.3	125	3.4
108	19	2.1	94	3.6
109	30	3.0	94	3.5
110	60	4.8	85	3.5
111	90	6.1	76	3.5
112	120	7.0	0	3.5
113	150	7.7	60	3.5
114	180	8.2	54	3.5
115	222	8.9	48	3.5
116	250	9.1	39	3.5
117	280	9.4	36	3.5

Experimental Conditions

Initial O_2 = 0.3 mg/ℓ
Initial Temperature = 3.8°C
Saturation O_2 Concentration = 10.5 mg O_2/ℓ
Turbulence Applied = 250 r.p.m. on Tri-R-Stir

Oxygen/Haloform Ratio Data

Oxygen

$b = -0.05$
$m = -7.97 \times 10^{-3}$
$r^2 = 1.00$

Chloroform

$b = -0.09$
$m = -4.17 \times 10^{-3}$
$r^2 = 0.97$

$$\frac{k\ O_2}{k\ CHCl_3} = 1.91$$

TABLE D-7

Oyxgen and Chloroform Gas Transfer Kinetics
Data: Run 7, May 1, 1978

Sample Number	Elapsed Time (Minutes)	(O_2) mg/ℓ	($CHCl_3$) µg/ℓ	Temperature °C
130	0	0.9	103	24.8
131	10	1.8	100	24.8
132	20	2.4	89	24.8
133	31	3.0	86.4	24.9
134	45	3.7	86	24.9
135	60	4.5	85	24.9
--	70	4.9	--	24.8
136	95	5.7	64	24.8
137	121	6.4	54	24.6
138	172	7.3	36	24.6
139	204	8.0	38	24.8
140	234	8.3	24	24.8
141	264	8.6	21	24.8
--	294	8.8	--	24.7
142	300	8.9	18	24.7
143	330	*9.0	17	24.8
144	354	*9.1	--	24.8
145	395	*9.3	11	24.8
146	422	*9.3	7.6	24.8

Experimental Conditions

Initial O_2 = 0.7
Initial Temperature = 24.7°C
Saturation O_2 Concentration = 9.4
Turbulence Applied = 255 r.p.m. by Tri-R-Stir

Oxygen/Haloform Ratio Data

Oxygen

$b = 0.01$
$m = -9.014 \times 10^{-3}$
$r^2 = 1.00$

Chloroform

$b = .04$
$m = -6.028 \times 10^{-3}$
$r^2 = 0.99$

$$\frac{k\ O_2}{k\ CHCl_3} = 1.49$$

*Values not used in determination of rate constant due to proximity to saturation.

TABLE D-8

Oxygen and Chloroform Gas Transfer Kinetics
Data: Run 8, May 17, 1978

Sample Number	Elapsed Time (Minutes)	(O_2) mg/ℓ	($CHCl_3$) µg/ℓ	Temperature °C
158	0	0.9	95	24.5
159	10	1.9	96	24.5
160	20	2.6	73	24.6
161	30	3.3	66.5	24.6
--	40	3.75	--	24.6
162	50	4.27	63.4	24.6
--	60	4.60	--	24.6
163	70	4.95	62.4	24.6
--	80	5.30	--	24.6
164	90	5.53	54	24.6
165	200	6.9	28	24.7
166	230	7.1	19.5	24.7
169	260	7.3	18.7	24.8
170	290	*7.5	19.1	24.8
171	320	*7.5	16.4	24.8
172	350	*7.6	17	24.8
173	380	*7.6	13	24.8
174	580	*7.65	5	24.8
175	610	*7.75	* --	24.7

Experimental Conditions

Initial O_2 Concentration = 0.6 mg/ℓ
Initial Temperature = 24.5°C
Saturation 0 Concentration = 7.8 mg O_2/ℓ
Turbulence Applied = 265 r.p.m.

Oxygen/Haloform Ratio Data

Oxygen	Chloroform
$b = -0.14$	$b = -0.13$
$m = -9.50 \times 10^{-3}$	$m = -5.02 \times 10^{-3}$
$r^2 = 0.99$	$r^2 = -.98$

$$\frac{k\ O_2}{k\ CHCl_3} = 1.90$$

*Data not used in calculation of K values due to the closeness of the values to saturation.

TABLE D-9

Oxygen and Chloroform Gas Transfer Kinetics
Data: Run 9, May 31, 1978

Sample Number	Elapsed Time (Minutes)	(O_2) mg/ℓ	($CHCl_3$) µg/ℓ	Temperature °C
186	0	1.25	112	23.2
187	3	1.75	--	23.2
188	6	2.25	106	23.2
--	11	3.05	--	23.2
189	16	3.57	70	23.2
190	28	4.10	71	23.2
191	38	5.50	61	23.2
192	45	6.05	59	23.2
193	62	6.50	40	23.2
194	83	7.25	32	23.2
195	90	*7.40	28	23.2
196	139	*8.00	10	23.2
197	161	*8.00	8	23.2
198	200	*8.00	--	23.2
199	203	*8.00	5	23.2

Experimental Conditions

Initial O_2 Concentration = 0.80 mg/ℓ
Initial Temperature = 23.2°C
Saturation O_2 Concentration = 8.00
Turbulence Applied = 455 r.p.m. Tri-R-Stir

Oxygen/Haloform Ratio Data

Oxygen	Chloroform
b = 0.0181	b = 0.0022
$m = -2.47 \times 10^{-2}$	$m = -1.64 \times 10^{-2}$
$r^2 = 0.99$	$r^2 = 0.98$

$$\frac{k\ O_2}{k\ CHCl_3} = 1.51$$

*Values not used in calculation of rate constant due to closeness of values to saturation conditions.

TABLE D-10

Oxygen and Chloroform Gas Transfer Kinetics
Data: Run 10, June 1, 1978

Sample Number	Elapsed Time (Minutes)	(O_2) mg/ℓ	($CHCl_3$) µg/ℓ	Temperature °C
204(B)	0	1.45	121	24.1
205	5	2.25	--	24.1
206	11	3.20	103	24.0
207	15	3.95	97	24.0
208	25	5.65	75	23.5
209	40	6.80	40	24.0
--	50	7.20	--	24.0
210	60	7.40	21	24.1
211	85	7.50	9.6	24.1
212	115	7.60	3.4	24.6
213	155	7.65	2	24.6
214	185	7.62	1.2	24.7
215	1101	*7.70	0.5	24.7

Experimental Conditions

Initial O_2 Concentration = 1.4 mg/ℓ
Initial Temperature = 24.1°C
Saturation O_2 Concentration = 7.7 mg/ℓ
Turbulence Applied = 455 r.p.m.

Oxygen/Haloform Ratio Data

Oxygen	Chloroform
b = 0.160	b = 0.190
m = -0.0527	m = -0.0322
r^2 = 0.99	r^2 = 0.99

$$\frac{k\ O_2}{k\ CHCl_3} = 1.64$$

*Value not used in calculation of rate constant due to closeness of value to saturation conditions.

TABLE D-11

Oxygen and Chloroform Gas Transfer Kinetics
Data: Run 11, June 2, 1978

Sample Number	Elapsed Time (Minutes)	(O_2) mg/ℓ	($CHCl_3$) µg/ℓ	Temperature °C
216	0	1.85	131	24.5
217	5	2.28	130	24.5
218	10	2.52	128	24.5
219	20	3.00	115	24.4
220	30	3.56	115	24.4
221	50	4.55	100	24.5
222	70	5.10	85.6	24.5
225	90	5.46	74	24.5
226	175	6.60	40.4	24.5
227	196	6.80	33	24.5
228	225	7.00	29	24.3

Experimental Conditions

Initial O_2 Concentration = 1.8 mg/ℓ
Initial Temperature = 24.5°C
Saturation O_2 Concentration = 8.1 mg/ℓ
Turbulence Applied = 145 r.p.m. on Tri-R-Stir

Oxygen/Haloform Ratio Data

Oxygen	Chloroform
b = -0.0636	b = 0.0414
m = -0.00828	m = -6.98×10^{-3}
r^2 = 0.98	r^2 = 1.00

$$\frac{k\ O_2}{k\ CHCl_3} = 1.10$$

TABLE D-12

Oxygen and Chloroform Gas Transfer Kinetics
Data: Run 12, June 5, 1978

Sample Number	Elapsed Time (Minutes)	(O_2) mg/ℓ	($CHCl_3$) µg/ℓ	Temperature °C
233	0	1.90	140	24.2
234	5	2.25	132	24.2
235	10	2.72	119	24.2
236	20	3.32	106	24.2
237	35	3.92	91	24.2
238	60	4.80	67.4	24.2
239	95	5.65	48	24.1
240	125	6.25	44	24.1
241	155	6.60	32	24.1
244	185	6.82	23	24.1
245	283	*7.20	11	24.1

Experimental Conditions

Initial O_2 Concentration = 1.90 mg/ℓ
Initial Temperature = 24.5°C
Saturation O_2 Concentration = 7.20 mg/ℓ
Turbulence Applied = 240 r.p.m. on Tri-R-Stir
Wind Applied = High Wind

Oxygen/Haloform Ratio Data

Oxygen

$b = -0.06$
$m = -8.7 \times 10^{-3}$
$r^2 = 0.99$

Chloroform

$b = -0.07$
$m = -9.38 \times 10^{-3}$
$r^2 = 0.99$

$$\frac{k\ O_2}{k\ CHCl_3} = 0.975$$

*Value not used in calculation of rate constant due to closeness of value to saturation conditions.

TABLE D-13

Oxygen and Chloroform Gas Transfer Kinetics
Data: Run 13, June 26, 1978

Sample Number	Elapsed Time (Minutes)	(O_2) mg/ℓ	($CHCl_3$) µg/ℓ	Temperature °C
251	0	1.5	--	24.2
252	21	1.95	106	24.3
253	35	2.50	87	24.3
254	120	3.85	71.4	24.5
255	167	4.30	62	24.5
256	237	5.10	57.4	24.8
257	295	5.40	50.4	24.9

Experimental Conditions

Initial O_2 Concentration = 1.5 mg/ℓ
Initial Temperature = 24.5°C
Saturation O_2 Concentration = 7.8 mg/ℓ O_2
Turbulence Applied = 80 r.p.m. on Tri-R-Stir

Oxygen/Haolform Ratio Data

Oxygen

$b = -0.03$
$m = -3.32 \times 10^{-3}$
$r^2 = 0.99$

Chloroform

$b = -0.11$
$m = 2.46 \times 10^{-3}$
$r^2 = 0.94$

$$\frac{k\ O}{k\ CHCl_3} = 1.35$$

TABLE D-14

Oxygen and Chloroform Gas Transfer Kinetics
Data: Run 14, June 27, 1978

Sample Number	Elapsed Time (Minutes)	(O_2) mg/ℓ	($CHCl_3$) µg/ℓ	Temperature °C
258	0	1.7	95	24.8
259	2	2.6	82	24.8
260	4	3.4	71	24.8
--	5	3.8	--	24.8
261	6	4.1	77	24.8
--	8	4.5	--	24.8
262	10	5.2	53	24.8
263	13	5.8	--	24.8
264	15	6.2	41.2	24.8
--	18	6.5	--	24.8
265	21	6.8	31.4	24.9
--	24	7.1	--	24.9
266	29	7.3	26.4	24.9
267	36	7.6	19.4	24.9
--	40	7.7	--	25.0
268	52	*7.8	8	25.0
--	59	*7.9	--	25.0
269	68	*7.95	4	25.0

Experimental Conditions

Initial O_2 Concentration = 1.70 mg/ℓ
Initial Temperature = 24.8°C
Saturation O_2 Concentration = 8.0 mg/ℓ
Turbulence Applied = 640 r.p.m. on Tri-R-Stir

Oxygen/Haloform Ratio Data

Oxygen	Chloroform
$b = -8.3 \times 10^{-3}$	b = 0.48
m = -0.08	m = -0.058
$r^2 = 1.0$	$r^2 = .99$

$$\frac{k\ O_2}{k\ CHCl_3} = 1.36$$

*Values not used in calculation of rate constant due to closeness of values to saturation conditions.

TABLE D-15

Oxygen and Chloroform Gas Transfer Kinetics
Data: Run 15, June 29, 1978

Sample Number	Elapsed Time (Minutes)	(O_2) mg/ℓ	($CHCl_3$) µg/ℓ	Temperature °C
278	0	1.20	68	24.5
279	4	1.95	71	24.5
280	8	3.15	65	24.5
281	12	4.25	53	24.5
282	19	4.78	51	24.5
283	25	5.05	47	24.5
--	30	5.30	--	24.6
284	35	5.57	38	24.8
--	40	5.75	--	24.8
285	45	5.95	39	24.8
--	50	6.10	--	24.8
286	55	6.25	37	24.8
--	61	6.41	--	24.8
287	65	6.55	33	24.8
--	75	6.80	--	24.8
288	85	7.00	24.2	24.8
--	95	7.20	--	24.8
289	103	7.30	17.4	24.8
290	144	*7.80	11.6	24.8

Experimental Conditions

Initial O_2 Concentration = 1.10 mg/ℓ
Initial Temperature = 24.5°C
Saturation O_2 Concentration = 7.8 mg/ℓ
Turbulence Applied = 560 r.p.m. on Tri-R-Stir

Oxygen/Haloform Ratio Data

Oxygen	Chloroform
b = -0.23	b = -0.05
m = -0.0226	m = -0.0123
r^2 = 0.98	r^2 = 0.98

$$\frac{k\ O_2}{k\ ChCl_3} = 1.84$$

*Value not used in calculation of rate constant due to closeness of value to saturation conditions.

TABLE D-16

Oxygen and Chloroform Gas Transfer Kinetics
Data: Run 16, July 11, 1978

Sample Number	Elapsed Time (Min.)	Temp. °C	(O_2) mg/ℓ	($CHCl_3$) µg/ℓ	($CHCl\ Br_2$) µg/ℓ	($CHCl_2Br$) µg/ℓ	($CH\ Br_3$) µg/ℓ
291	0	24.3	1.85	248	60.4	39	48.8
292	2	24.3	2.51	246	65.1	41	51.3
293	5	24.3	3.40	233	59.7	38.5	47.0
294	8	24.3	4.10	216	54.2	37.4	45.7
295	11	24.2	4.50	192	49.4	30.7	43.7
296	16	24.2	5.40	123	41.2	25.5	41.7
297	23	24.2	6.10	88	34.6	21.2	34.3
--	29	24.2	6.50	--	--	--	--
298	35	24.3	6.78	67	27.4	13.3	30.2
--	41	24.2	6.93	--	--	--	--
299	46	24.1	7.0	49	21.3	10.1	24.0
300	60	24.1	7.20	30	15.8	6.1	21.6
301	75	24.1	7.20	16	9.3	3.3	13.1
302	--	24.3	7.20	--	--	--	--

Experimental Conditions

Initail O_2 Concentration = 1.20 mg/ℓ
Initial Temperature = 24.3°C
Saturation Applied = 7.20 mg/ℓ
Turbulence Applied = 510 r.p.m. on Tri-R-Stir
Lake Water Used
Mixture of Haloform Standards Injected

Table D-16 (cont.).

Oxygen/Haloform Ratio Data

Oxygen	Chloroform	Dichlorobromo-methane	Chlorodibromo-methane	Bromoform
b = 0.0422	b = -0.0171	b = 0.041	b = 0.0385	b = -1.66×10^{-3}
m = -0.0726	m = -0.0373	m = -0.0342	m = -0.0253	m = -0.0171
r^2 = 1.0	r^2 = 0.99	r^2 = 1.00	r^2 = 0.99	r^2 = 0.98

$\frac{k\ O_2}{k\ CHCl_3} = 1.95$ $\frac{k\ O_2}{k\ CHCl_2Br} = 2.12$ $\frac{k\ O_2}{k\ CHCl\ Br_2} = 2.87$ $\frac{k\ O_2}{K\ CHBr_3} = 4.25$

$\frac{K\ CHCl_3}{K\ CHCl_3} = 1.00$ $\frac{K\ CHCl_3}{K\ CHCl_2Br} = 1.09$ $\frac{k\ CHCl_3}{k\ CHCl\ Br_2} = 1.47$ $\frac{k\ CHCl_3}{k\ CHBr_3} = 2.18$

TABLE D-17

Oxygen and Chloroform Gas Transfer Kinetics
Data: Run 17, July 12, 1978

Sample Number	Elapsed Time (Min.)	Temp. °C	(O_2) mg/ℓ	($CHCl_3$) µg/ℓ	($CHCl\ Br_2$) µg/ℓ	($CHCl_2Br$) µg/ℓ	($CH\ Br_3$) µg/ℓ
303	0	24.1	2.1	216.3	39.6	54.2	49.7
--	1.5	24.1	2.25	--	--	--	--
--	2.5	24.1	2.45	--	--	--	--
--	3	24.1	2.53	--	--	--	--
304	5	24.1	3.65	194.4	39.5	53.5	49.0
--	8	24.1	4.32	--	--	--	--
305	10	24.1	4.70	174.0	34.0	49.0	44.4
--	13	24.1	5.25	--	--	--	--
306	21.5	24.1	6.20	104.0	22.2	34.3	32.5
--	25	24.1	6.42	--	--	--	--
307	32	24.1	6.80	74.0	16.7	28.5	29.6
--	37	24.1	7.00	--	--	--	--
308	45	24.1	7.20	45.2	10.5	19.2	22.4
--	53	24.1	7.30	--	--	--	--
309	60	24.1	7.40	22.4	6.2	12.3	15.5
--	70	24.1	7.44	--	--	--	--
310	80	24.1	7.50	9.9	2.6	6.9	11.1
311	180	24.2	7.70	2.7	<1.0	<1.0	1.71
312	211	24.2	7.70	<1.0	<1.0	<1.0	<1.0
313	245	24.2	7.70	<1.0	<1.0	<1.0	<1.0
314	300	24.2	7.70	<1.0	<1.0	<1.0	<1.0

Experimental Conditions

Initial O_2 Concentration = 1.50 mg/ℓ
Initial Temperature = 24.0°C
Saturation O_2 Concentration = 7.70 mg/ℓ
Turbulence Applied = 460 r.p.m. on Tri-R-Stir

Table D-17 (cont.).

Oxygen/Haloform Ratio Data

Oxygen	Chloroform	Dichlorobromo-methane	Chlorodibromo-methane	Bromoform
b = -0.07	b = 0.098	b = 0.143	b = 0.11	b = 0.04
m = -0.051	m = -0.0385	m = -0.034	m = -0.0261	m = -0.019
r^2 = 0.99	r^2 = 1.00	r^2 = 0.99	r^2 = 0.99	r^2 = 0.99

$$\frac{K\ O_2}{K\ CHCl_3} = 1.32 \qquad \frac{K\ O_2}{K\ CHCl_2B_2} = 1.50 \qquad \frac{K\ O_2}{K\ CHCl\ B_2} = 1.95 \qquad \frac{K\ O_2}{K\ CHBr_3} = 2.68$$

$$\frac{K\ CHCl_3}{K\ CHCl_3} = 1.00 \qquad \frac{K\ CHCl_3}{K\ CHCl_2B_2} = 1.14 \qquad \frac{K\ CKCl_3}{K\ CHCl\ Br_2} = 1.48 \qquad \frac{K\ CHCl_3}{K\ CHBr_3} = 2.03$$