# AN INVESTIGATION OF BIOSORPTION AND THE PURGE-AND-TRAP ANALYTICAL TECHNIQUE FOR SELECTED HALOGENATED HYDROCARBONS IN ACTIVATED SLUDGE SYSTEMS

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# CHAPTER I

## INTRODUCTION

The studies and development of analytical techniques for identifying and determining the concentrations of volatile organic compounds in water samples have burgeoned in recent years, stimulated in part by an increasing number and variety of potentially carcinogenic compounds being discharged into the environment, and partly due to the rising public concern over the effect of these man-made chemicals in our lives.

Stemming from the 1978 court settlement that came to be known as the "Environmental Protection Agency (EPA) Consent Decree," the EPA published a list of 129 "Priority Pollutants," of which 114 were organic compounds and 15 others were either heavy metals, asbestos or cyanide (1). Of particular interest to us were the 31 purgeable organic compounds in the list of 114, since these compounds suggest that volatilization may contribute significantly to the organic pollutants being discharged into the environment.

In order to regulate priority pollutants, establish effluent standards, enforce effluent guidelines, evaluate treatment effectiveness, and determine the source of pollution, highly sensitive analytical methodology is needed for correct identification and quantitative determination of the organic pollutants in water. Currently, one of the best available technologies (BAT) for analyzing purgeable organic compound quantities in solution is the "purge and trap/gas chromatography (PAT/

GC)" method. In essence, this method involves removal of volatile organics from water by purging with an inert gas and trapping (adsorbing) the organic compounds on a sorbent medium, followed by thermal desorption and GC analysis.

Within the confines of the laboratory environment, the PAT/GC technique offers a highly efficient, reliable, and relatively fast means for pollutant identification and determination. This technique has been extensively studied from an analytical development point of view. However, only limited data and work has been reported on pretreatment of the sample as a method of improving results.

By utilizing the PAT/GC analytical methodology, the objectives of this study were to:

1. Determine if biosorption was a removal mechanism of halogenated hydrocarbon compounds in a biological reactor.

2. Determine if the pretreatment of activated sludge samples containing halogenated hydrocarbons would significantly impact the GC results (positively or negatively). The pretreatment methods examined were pH alteration and sonification. Also examined were purge chamber configurations and variable stripping times. The effectiveness of these methods was compared with the control samples.

# CHAPTER II

## LITERATURE REVIEW

### Chemical Structures and Physical Properties of the Selected Organic Priority Pollutants

The chemical structures of the selected priority pollutants used in this study are shown in Table I. It is seen that all the compounds are halogenated hydrocarbons. The physical properties of these compounds are shown in Table II.

TABLE I

CHEMICAL STRUCTURES OF SELECTED ORGANIC PRIORITY POLLUTANTS

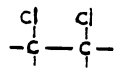
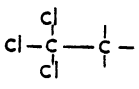
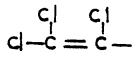
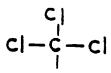
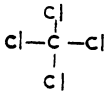
| | |
|---|---|
| 1, 2-Dichloroethane |  |
| 1,1,1-Trichloroethane |  |
| Trichloroethylene |  |
| Chloroform |  |
| Carbon Tetrachloride |  |

TABLE II

PHYSICAL PROPERTIES OF SELECTED PRIORITY POLLUTANTS

| Compound | Molecular Weight | Specific Gravity | Melting Point (°C) | Boiling Point (°C) | Vapor Pressure (mm Hg) | Solubility in Water (mg/l) | Henry's* Constant, H ($atm \cdot m^3/mole$) |
|---|---|---|---|---|---|---|---|
| 1,2-Dichloroethane | 98.97 | $1.256^{20/20}$ | -35.3 | 83.7 | 760 (83.7°C) | 9000 (0°C) | $1.1 \times 10^{-3}$ |
| 1,1,1-Trichloroethane | 133.42 | $1.325^{26/4}$ | -30.6 | 74.1 | 100 (20°C) | 950 | $4.9 \times 10^{-3}$ |
| Trichloroethylene | 131.40 | $1.466^{20/20}$ | -73.0 | 87.2 | 60 (20°C) | 1000 (25°C) | $1.2 \times 10^{-3}$ |
| Chloroform | 119.39 | $1.489^{20}$ | -63.5 | 61.2 | 200 (25.9°C) | 8200 (20°C) | $3.4 \times 10^{-3}$ |
| Carbon Tetrachloride | 153.84 | $1.595^{20/4}$ | -22.6 | 76.8 | 100 (23°C) | 800 (20°C) | $3.0 \times 10^{-2}$ |

*From reference 5

## Fate of Halogenated Hydrocarbons in the Activated Sludge Process

Although there is an abundance of literature published concerning analytical methodology developments for identifying the presence and magnitude of priority pollutants in the environment, a review of the technical literature indicates that only a limited data base is available concerning the fate of organic priority pollutants in the activated sludge process.

The importance of knowing the fate of the priority pollutants becomes apparent when one realizes that the treatability of an individual compound is intrinsically dependent on it. Research work conducted by Kincannon and Stover at Oklahoma State University has shown that the removal of priority pollutants during biological treatment can be the result of several interacting mechanisms. These removal mechanisms may include biodegradation, stripping, sorption, or a combination of these (2, 3, 4). Using the completely-mixed, continuous flow type of reactors with internal recycle (as outlined in the materials and methods section of this study), Kincannon and Stover (5) conducted studies of 24 organic compounds encompassing the various groups of the 114 priority pollutants. Synthetic wastewater containing the selected priority pollutants was employed to study the possibility of predicting the fate and effluent concentrations of the various priority pollutants in the activated sludge reactors. With regards to the halogenated hydrocarbons, they found that some were removed by stripping whereas others were removed by combined stripping and biodegradation. The results of the selected compounds in their work is shown in Table III.

TABLE III

FATE OF SELECTED HALOGENATED HYDROCARBONS IN ACTIVATED SLUDGE REACTORS

| Compound | Influent Concentration (mg/l) | % Removal | | | |
|---|---|---|---|---|---|
| | | Overall | Air Stripping | Biosorption | Biodegradation |
| Methylene Chloride | 180 | 99.7 | 8.0 | | 91.7 |
| 1,2-Dichloroethane | 258 | 100.0 | 99.5 | 0.5 | |
| 1,1,1-Trichloroethane | 118 | 100.0 | 100.0 | | |
| 1,1,2,2-Tetrachloroethane | 201 | 93.5 | 93.5 | | |
| 1,2-Dichloroplopane | 182 | 99.9 | 99.9 | | |
| Trichloroethylene | 95 | 99.7 | 65.1 | 0.83 | 33.8 |
| Chloroform | 35 | 98.9 | 19.0 | 1.19 | 78.7 |
| Carbon Tetrachloride | 19 | 99.3 | 33.0 | 1.38 | 64.9 |

Tabak et al. (6) used the static-culture flask-screening procedure to determine the biodegradability of 96 priority pollutants at two concentrations (5 and 10 mg/l) by wastewater microbiota. They found that carbon tetrachloride (carbon tet) exhibited rapid degradation, whereas chloroform and trichloroethylene (TCE) showed significant dissimilation with gradual adaptation, and 1,2-dichloroethane (1,2-DCE), 1,1,1-trichloroethane (1,1,1-TCE) showed only moderate biodegradation. A breif summary of the results on the five tested compounds is shown in Table IV.

Lurker, Clark, and Elia (7) conducted a study at a contact stabilization wastewater treatment plant receiving domestic and industrial waste to evaluate the wastewater and airborne concentrations of several chlorinated organic compounds at various locations of the plant. They found that compounds such as carbon tetrachloride and chloroform underwent aerial release from the grit-chamber weir, thus causing a marked reduction in the wastewater concentration of these compunds in the aeration basin. The conclusion was drawn that these compunds were predominantly released to the atmosphere and did not adsorb and concentrate onto the suspended solids.

It is apparent from these studies that stripping is a major removal mechanism of volatile organics in water, and that volatile priority pollutants are often discharged into the atmosphere from an activated sludge plant due to aeration/agitation. A review of the physical properties of the halogenated hydrocarbons from Table II shows that volatile organics are generally in liquid form at room temperature and have significant vapor pressure, indicating that they evaporate easily. Mackay (8) has shown that compounds with Henry's Law constants larger than about 0.001

TABLE IV

BIODEGRADABILITY OF HALOGENATED HYDROCARBONS BY THE STATIC-SCREENING-FLASK TEST METHOD

| Compound | Concentration (mg/l) | Performance Summary | Avg. Total Loss of Test Compound in 7 Days Incubation Time (%) | | | | Volatilization Loss (%) 25°C |
|---|---|---|---|---|---|---|---|
| | | | Original | First | Second | Third | |
| 1,2-Dichloroethane | 5 | B[1] | 26 | 41 | 54 | 63 | 27 |
| | 10 | B | 20 | 35 | 51 | 53 | 5 |
| 1,1,1-Trichloroethane | 5 | B | 29 | 64 | 76 | 83 | 27 |
| | 10 | B | 23 | 53 | 68 | 75 | 7 |
| Trichloroethylene | 5 | A[2] | 64 | 73 | 82 | 87 | 29 |
| | 10 | A | 38 | 56 | 76 | 84 | 22 |
| Chloroform | 5 | A | 49 | 85 | 92 | 100 | 24 |
| | 10 | A | 46 | 70 | 80 | 100 | 6 |
| Carbon Tet | 5 | D[3] | 87 | 100 | 100 | 100 | 23 |
| | 10 | D | 80 | 100 | 100 | 100 | 5 |

[1]Slow to moderate biodegradative activity.

[2]Significant degradation with gradual adaptation.

[3]Significant degradation with rapid adaptation.

atm $m^3$/mol tend to partition predominantly into the atmosphere (i.e. they are sparingly soluble), and the rate at which these compounds evaporate from water is usually controlled by the liquid phase mass-transport resistance. In other words, the volatile organics with the characteristics of low solubility (hydrophobic) and an affinity for the vapor phase make stripping a dominant factor in the removal mechanism. Stripping, therefore, is an effective process to remove the volatile organics from water in treatment plants or in laboratory experiments.

## Analytical Methodologies for Volatile Organics

### General

A variety of trace organic compounds have been found in water. Coleman et al. (9) identified 72 volatile organics in the finished water of five U.S. cities. Chloroform and other volatile halogenated hydrocarbon compounds have also been found in the drinking water of New Orleans, Louisiana and other U.S. cities (10). Investigations by Rook (11) and Dowty, Carlisle, and Laseter (12) have indicated that the formation of trihalomethanes (THMs) is the result of the chlorination of raw and waste waters. Due to the potential toxic and carcinogenic effects posed by THMs, the U.S. government organized the National Organics Reconnaissance Survey (NORS) to conduct a survey of 80 U.S. cities for THMs in drinking water (13). The NORS study found that four THMs-chloroform, bromodichloromethane, dibromochloromethane, and bromoform, were widespread in drinking water and were indeed the result of chlorination. The detection of these contaminants and the resultant task of removing them from the water have in effect created an urgent need for the development of a fast, convenient and accurate analytical technique

suitable for routine monitoring of any water body. Highly sensitive analytical techniques are needed for precise identification and quantitative determination of organics to the one microgram per liter (1ppb) concentration.

In the past, a significant amount of research and time was required to identify the few trace organics in water, with the results being sometimes suspect and occasionally erroneous. The development of computerized gas chromatography/mass spectrometry (GC/MS) has revolutionized the analytical techniques for determining organic pollutants. Currently, there are several available techniques for analysis of volatile organic compounds; all the analytical methods are used with GC/MS. These methods are subdivided and discussed under the following headings.

Purge-and-Trap (PAT) Methods

The PAT method is also known as the stripping or dynamic head space method. In this analytical technique, a water sample containing organic compounds is purged with an inert gas, usually nitrogen or helium, for a finite period of time, and the organic compounds are concentrated in a cold trap containing an appropriate adsorbent that has a high affinity for the organic compounds and virtually no tendency to adsorb water. The organic compounds concentrated in the trap are subsequently desorbed thermally by raising the trap temperature. The organics are then swept into the GC column by a stream of inert carrier gas, and subsequent identification and concentration of compounds are done by GC/MS.

Employment of the PAT concept for trace organic analysis is not new. It was reported by Swinnerton and Linnenbom (14) as an effective means of determining small amounts of gaseous hydrocarbon compounds in

sea water. In their experiment, the stripping chamber was capable of holding up to 1.2 liters of sea water, helium was used as the stripping gas, two traps immersed in an acetone dry-ice bath at -80°C were used to concentrate the gaseous hydrocarbons, and methane was adsorbed on the activated charcoal trap while ethane, propane, and butane were adsorbed on a column filled with activated alumina. After stripping was completed, the traps were immersed in 90°C water for one minute for the purpose of desorption. Helium from a secondary supply carried the sample into the GC. Swinnerton and Linnenbom claimed the technique was capable of determining gaseous hydrocarbons in water to concentrations as low as one part in $10^{13}$ by weight ($10^{-4}$ ppb). There is no doubt that such a low detection limit was in part due to the large sample volume used (1.2 L). Novak et al. (15) employed a similar procedure for identifying organic compounds in polluted drinking water. The volatile compounds were concentrated into a capillary sample loop cooled to the temperature of liquid nitrogen, and an oil-bath was used to rapidly heat the freezing loop to 150°C for desorption. A combined GC/MS with a packed glass column containing 10 percent Carbowax 20M on Chromosorb WAW carried out the analysis. Fourteen organic compounds, ranging from methane to xylene, were found in that particular water sample and the detection limit was found to be $10^{-3}$ ppm to $10^{-4}$ ppm. Zlatkis, Lichtenstein, and Tishbee (16), for their study of volatile organics in Houston, Texas air, compared and evaluated three adsorbant materials for sampling. Tenax GC fullfilled the requirements of efficient adsorptivity and desorptivity and proved to be superior as a general adsorbent when compared to Porapak P and Carbosieve.

Utilizing the ideas from the above mentioned methods, Bellar and

Lichtenberg (17) of EPA developed another technique for isolating volatile organics from water. This technique had proven its validity for the analysis of organics in drinking water, as demonstrated in references 10 and 13. Thus, it had become the most widely used technique and the unofficial standard that all other techniques were compared to. In this procedure, 5 ml of sample were injected into the purging device and purged by nitrogen gas for 11 minutes. The stripped volatile organics were concentrated on a Tenax GC trap which was then inserted into the desorber and backflushed with nitrogen for three minutes at temperatures between 125 and 130$^{o}$C. The heat source for desorption was supplied by the heater wire surrounding the desorber housing, and the desorbed organic compounds from the trap were then sent into a GC column for separation and quantification. For a detailed description of the Bellar and Lichtenberg method, the reader is referred to reference 17.

Since the PAT technique involves stripping and GC quantification, it is understandably, very time consuming. To make improvements on the process, research efforts have been concentrated on improving the sensitivity and simplification of operation. Bertsch and Anderson (18) proposed a technique where a high-resolution glass capillary column was used in the GC to increase separation power and sensitivity. However, no comparisons of analytical results between that of glass capillary columns and packed columns were given in their report. The development of microcomputer controlled GC/MS systems for simplifying operation has also become popular. Dowty, Green, and Laseter (19) developed a computer based automatic water pollution anaysis technqiue wherein the collection, trapping, injection, analysis and printout procedures were automated. Beggs (20) recommended a semi-automatic GC/MS system for

the analysis of organic pollutants in water. The computer controlled GC/MS was programmed to automatically set proper GC and MS conditions. An operator only needed to insert the water sample; subsequent sampling, analysis and data reduction were carried out automatically. Lingg et al. (21) also incorporated the service of computers in their study of nine organic compounds identified in the NORS. Quantitative analysis of the volatile organic compounds was done with GC/MS, and the computer stored the information so that it could be recalled later for comparison and quantitative analysis.

## Solvent Extraction Methods

Solvent extraction is another popular method employed extensively in laboratory determination of THMs in water. To put forth its principle simply, the technique involves the separation of two or more miscible liquids by the use of a solvent which preferentially dissolves one of the miscible liquids. Thus, separation is based on solubility differences, whereas the stripping technique utilizes the volatility differences.

Bevenue et al. (22) used this technique to successfully extract 3500 ml of sample using 100 ml of hexane solvent. The hexane layer was then concentrated by a steam bath to the final 0.5 ml volume, after which a small quantity (10 µl) was applied to the GC. Henderson, Peyton, and Glaze (23) used 3 - 5 ml of pentane as solvent to extract THMs contained in 120 ml of water sample. A 5 µl sample of the pentane layer was removed for GC analysis, and the detection limit was 1 µg/l (1 ppb). Richard and Junk (24) carried out an experiment similar and complimentary to that of Henderson et al. The volumes of pentane solvent and

water sample used were 1 ml and 10 ml, respectively. The detection limit of halomethanes was found to be 0.1 µg/l (0.1 ppb). The increase in detection limit was in part due to the higher solvent to sample ratio of 1 to 10 as compared to the previous study conducted by Henderson et al. in which it was 1 to 24. They also found pentane to be a more desirable solvent than iso-octane. Mieure (25) used 1 ml of methylcyclohexane as the solvent to extract water samples containing chloroform at the various solvent to sample ratios of 1 to 1, 1 to 5, and 1 to 25. He found the recovery decreased as the solvent-to-water ratio decreased. Varma et al. (26) conducted a laboratory study where the extraction of chloroform was performed with three different solvents, pentane, methylcyclohexane, and iso-octane, and their efficiencies compared. Their finding confirmed the previous study (24) that pentane is a better solvent than iso-octane. They also found that methylcyclohexane was capable of extracting more chloroform than pentane.

The popularity of the solvent extraction technique could be attributed to the advantages claimed in the various papers. Some of the advantages are: low cost and speed of analysis, no need for special apparatus (24, 25), an error potential believed to be less than with gas stripping (24), and simplicity and reliability (26).

## Headspace Methods

The head space method is also known as the static headspace method. To conduct the experiment, a vapor sample is taken from the head space of a container containing the water sample and injected into the GC column for analysis. The principle of the procedure is based on the fact that, for volatile organic compounds in water at constant temperature

and pressure, there is an equilibrium partitioning of the compounds in both the gaseous and aqueous phases, that is, the ratio of concentration in the gaseous phase to aqueous phase is constant. This partition constant is unique for each organic compound. Therefore, by knowing the gaseous phase concentration and applying the appropriate partition constant, the concentration of the organic compounds in liquid can be calculated.

Morris and Johnson (27) utilized this technique for detecting halomethanes in drinking water. Cowen, Cooper, and Highfill (28), in an effort to eliminate the problem of septum failure encountered during syringe injection, described an alternate method wherein the samples were delivered to the column by controlling a gas sampling valve, thereby eliminating the need for septums. Analyses of acetone, 1-propanol, and chloroform by the syringe injection and septumless injection methods were compared, with the latter technique giving better precision than the former. Kaiser and Oliver (29) also made some modifications of the headspace technique in which the water sample and headspace gas were equilibrated under reduced pressure at elevated temperature. 5 µl of headspace sample was injected into the GC, and the resultant highest sensitivity was found to be associated with elevated temperatures. For chloroform, the headspace concentration at 30°C was approximately one-tenth that at 90°C. Chian et al. (30) combined distillation with headspace methods in their study of volatile polar organics (VPO) such as the low molecular-weight alcohols, ketones, and aldehydes. The distillation step was used to concentrate the VPOs, and headspace GC analysis was performed later. VPO concentrations as low as 8 µg/l (8 ppb) were attainable using the distillation/headspace/GC methods.

Again, like the solvent extraction technique, the attractiveness of the headspace method lies in its simplicity, accuracy, and convenience for the routine analysis of water samples.

## Direct Injection Methods

This is a simple and direct technique which grew out of the need for a method where the sometimes laborious and cumbersome concentration steps prevalent among stripping, solvent extraction, and headspace techniques could be eliminated. A small amount of aqueous sample is directly injected onto the GC column and no concentration, stripping, or extraction is required.

In 1974, Harris, Budde, and Eichelberger (31), in their study of 32 organic compounds, found the detection limits attained were 1-50 ppm. They also found that relatively large pressures of water vapor had no significant effect on the performance of the GC/MS system. They concluded that this technique is only applicable to the analysis of relatively clean surface or drinking water. Nicholson and Meresz (32) found that the detection limit for 8 of the 13 compounds in their study was below 10 µg/l (10 ppb). However, their analytical technique was unsuitable for detecting trace levels of the dichlorinated hydrocarbons in water, as the detection limit varied from 60 to 500 µg/l for 1,2-dichloropropane and dichlorobenzene, respectively. One positive note was that very little deterioration of the detector was observed. Fujii (33) injected 100 µl samples and was able to obtain very high sensitivity (<1 ppb) results. He concluded that direct aqueous injection is an effective and practical method for the measurement of organohalides in water samples.

Direct Adsorption

In the direct adsorption method, a water sample is passed through a resin adsorbent which removes the soluble organics. The adsorbent is then eluted with a solvent and a portion of the solvent extract containing the organics is injected into the GC for compound analysis.

Kissinger and Fritz (34), to determine haloform concentrations in drinking water, used acetylated XAD-2 resin as the adsorbent and pyridine as the solvent. For a 200 ml sample, haloforms could be determined to a low concentration of 0.1 µg/l (.1 ppb), and the detection limit could be improved by using a larger sample. Suffet, Brenner, and Silver (35) also used XAD-2 resin and eluted the resin bed with 200 ml of ether in study of 1, 1,1-trichloroacetone presence in drinking water. Junk et al. (36) gave an excellent review of the direct adsorption technique in which they pointed out several critical steps where proper technique and conditions were essential to ensure that accurate result was obtained. The results of their study of 85 organic compounds indicated that the procedure is reliable, accurate and could be used with confidence for analysis of water of unknown composition, provided all proper procedures were followed.

## Evaluation of Methodologies

The evaluation of the various methodologies is a complex task and the selection of a particular technique suitable for a unique purpose is very difficult. When comparing the various analytical techniques, there are specific characteristics inherent to the particular techniques that must be considered in the overall evaluation plan. Some of these characteristics are the detection limit, economics, speed of analysis,

reproducibility, and interferences. There is not an all-perfect analytical technique currently available, thus one must evaluate these different characteristics and choose the one method that satisfactorily meets the requirements for most analytical problems.

For the determination of halogenated hydrocarbons in water, the techniques of direct adsorption, direct injection, and headspace were rejected immediately due to their inherent limitations. In the direct adsorption method, the elution of organics sorbed on the resin could be a time consuming step. Also, the solvent may interfere with the resultant peaks and, where the eluant required concentration, massive loss (about 80%) of volatile materials could be encountered (36). The direct injection method is fast and convenient but the result is limited in sensitivity since only a small quantity of sample water can be injected; large quantities of water could have a deteriorating effect on the GC detector. In addition, non-organic compounds in water may interfere with the measurement. The headspace method is direct and simple, but its detection limits are restricted by the compound's vapor phase partial pressure as well as the limited amount of headspace gas which can be sampled and analyzed. For compounds of low partial pressure, this technique would not be very effective. It has also been shown that the headspace method yields lower results when compared to the solvent extraction method (26).

Solvent extraction has its share of limitations, the most serious being loss of very volatile compounds by vaporization during the extraction concentration step. Other drawbacks include the extraction of nonhydrocarbon organic compounds (37) and the failure to extract efficiently a variety of volatile but water soluble organic compounds (31).

These organic compounds referred to as the volatile polar organics (VPO), include the low molecular weight alcohols, ketones, aldehydes, and ethers. In certain cases, the extraction solvent may also interfere with measurement. As for the PAT method, the major complaint has been that this method requires special equipment for stripping, adsorption, and desorption procedures, and, therefore, incurs more cost, more equipment, and operator experience. Furthermore, this technique demands a considerable amount of time and has been suspected of inadequacies in purging all organics. Dressman et al. (38) compared the solvent extraction and the PAT methods with regard to both quantitative and qualitative accuracy in THM determination. They found that both methods were comparable to one another in quantitative analysis. However, the work conducted by Varma, Siddique, and Doty (39) concluded otherwise. They found that the recovery of THMs via the PAT method was much higher than the solvent extraction method. Such contradicting reports further add to the confusion as to which method is superior.

For this study, PAT was chosen as the technique for compound analysis because it was determined to be the most attractive alternative and seems to be the most promising for analyzing all the probable volatile organics contained in water samples. This technique has gained wide attention within the past decade and received widespread acceptance because of frequent use by government sponsored investigations (such as the NORS). It is a highly sensitive method, capable of determining VPOs to the ppb level (40), which the solvent extraction method can not do as efficiently. It is also more suitable for the analysis of the more volatile compounds which would otherwise be lost in the extraction procedure. It should be pointed out that the added apparatus needed to

conduct the stripping step of the PAT analysis should not be held as a liability against its use. In view of the possibly more stringent government regulations governing the effluent standards in the future, such additional apparatus may become a mandatory requirement. Thus, using excuses such as cost saving to rationalize the selection of other techniques seems to be inappropriate.

## Air Stripping: Applications and Theory

Since stripping is an important aspect of the overall PAT technique, a brief discussion of its applications and theory is warranted.

Stripping, the reverse of gas absorption, is also known as desorption. In this process, a volatile solute is removed by contacting the solvent with a gas, causing the volatile components to be transferred from the liquid to the gaseous phase (41). Air stripping is often employed in the petro-chemical industry as a purification step for chemical products. In addition, it has found wide applications in the waste treatment field. Aeration, the transfer of air into liquid, is in essence an air stripping process. Aeration is commonly applied in activated sludge systems to provide the oxygen needed by the microorganisms for aerobic decomposition of organic matter. In the aeration process, some gases and other volatile substrates are removed from the wastewater. A study conducted by Singley, Ervin, and Williamson (42) has shown aeration to be an effective tool for removing high concentrations of total organic carbon from water supplies. The water treatment process also utilizes air stripping for removal of ammonia, carbon dioxide, and hydrogen sulfide. Another area that has received increased attention is the removal of trace volatile organics by the air stripping technique.

Laboratory studies have demonstrated that air stripping is a very effective tool in that respect (2, 43, 44) and undoubtably will play an even more important role in the field of pollution abatement in the future.

An enormous amount of literature has documented the theory of stripping, and it is not this study's intention to give a detailed review of the literature available. Therefore, a brief review of this topic should suffice.

The traditional approach to calculating the mass transfer rate of sparingly soluble solutes from the gas to the liquid phase (absorption), or from the liquid to the gas phase (stripping), is to use the two-film concept, developed by Lewis and Whitman (45), which assumes that the concentrations on either side of the interface are in equilibrium. A mathematical equation that describes the mass transfer rate across the interface boundary can be expressed in terms of the overall liquid mass transfer coefficient and the concentration driving force.

$$\frac{-dC}{dt} = K_L \cdot a \cdot (C - C^*) \qquad (1)$$

where:

$C$ = the molar concentration of a component in the bulk liquid stream (mole/$L^3$);

$t$ = time (T);

$K_L$ = the overall mass transfer coefficient (L/T);

$a$ = the interfacial area, the contacting area between the gas and liquid solution per unit volume of liquid solution ($L^2/L^3$); and

$C^*$ = the concentration of a component in liquid that is in equilibrium with the bulk concentration of gas phase (mole/$L^3$).

At the gas-liquid interface, where equilibrium is assumed to exist, C* may be related to the partial pressure of a component in the bulk gas stream, $P_p$ (atm), by the expression

$$C^* = \frac{P_p}{H} \tag{2}$$

where:

H = Henry's constant (atm · $L^3$/mole)

Henry's constant, in essence, is a coefficient representing the equilibrium distribution of a substance between the gas and the liquid phases.

The overall mass transfer coefficient, $K_L$, of Equation (1) can also be expressed as a function of the two individual phase mass transfer coefficients, $K_l$ for the liquid and $K_g$ for the vapor. The relationship is

$$\frac{1}{K_L} = \frac{1}{K_l} + \frac{R \cdot T}{K_g \cdot H} \tag{3}$$

where $K_l$ is a measure of the rate of substance transport to the interface in the water, and $K_g$ is a measure of the rate of substance transport away from the interface and into the air. R is the gas constant ($8.2 \times 10^{-5}$ $m^3$ · atm/mol · K) and T is the absolute temperature ($^oK$). Equation (3) is essentially the addition of two phase resistances in series to yield an overall resistance

$$\frac{1}{K_L} = \frac{1}{K_l} + \frac{1}{K_g \cdot H} \tag{4}$$

From Equation (4), it is possible to calculate the relative contribution of each resistance. The volatile organic compound's mass transfer rate

could be controlled by the liquid phase mass transfer resistance ($K_l$), the gas phase resistance ($K_g$), or a combination of both, depending on the value of H. If H were very large, then $1/K_l >> 1/(K_g \cdot H)$ and the overall rate of mass transfer would be controlled by the liquid film resistance. Conversely, if H were very small (resulting in $1/K_l << 1/(K_g \cdot H)$, then the overall transfer rate would be controlled by the gas film resistance.

Studies have shown that compounds having low H values tend to partition predominantly into the water, the transfer rate being controlled by Kg. Conversely, compounds of high H values tend to partition predominantly into the air, the transfer being liquid phase controlled (46). Most hydrocarbons and chlorinated hydrocarbons are only sparingly water soluble (hydrophobic) and have high H values. Therefore, the resistance of mass transfer lies in the liquid phase (47). The characteristics of low solubility and an affinity for the gas phase make air stripping an effective means of removing those compounds having high H values. In essence, during the stripping process, the sparging of the inert gas overcomes the liquid phase resistance, thus facilitating the liberation of the pollutants into the gas phase.

The significance of $K_l$, $K_g$, and H lies the role they play in the estimation of the volatilization rate. A considerable amount of information has been accumulated on values of $K_l$, $K_g$, and H. For a brief review on the volatilization rate prediction of high volatility chemicals from water, references 48, 49, 50, 51, and 52 are recommended.

It should be noted that the volatilization rate between an activated sludge reactor and a biomass-free reactor could be significantly different. Kincannon and Stover (2, 4) have reported that for some

volatile organics, the percent of compound stripped in the nonbiological reactor was far greater than that in the biological reactor. Lawson and Siegrist (53) have also reported that the rate of removal by stripping in nonbiological reactors was greater than the removal measured in biological reactors. Therefore, one should distinguish the stripping-rate constants of a biological reactor from that of nonbiological reactor; the constants of a biological reactor should not be predicted from theoretical considerations or from measurements based on clean-water (nonbiological) tests and vice versa.

# CHAPTER III

# MATERIALS AND METHODS

## Activated Sludge System

### Biological Reactor System

The reactors employed in this study were the bench-scale, once-through, continuous-flow, stirred-tank type (CSTR). The complete system, shown in Figure 1, was composed of a feed tank, the CSTR, the effluent bottle, and the optional off-air sampling apparatus.

The synthetic wastewater feed was kept in a scaled 55 liter tank and coveyed to the reactor by a stainless steel Milroyal D controlled-volume pump. The CSTR was of the internal recycle type consisting of an activated sludge reactor and a settling compartment separated by a steel baffle which also served to adjust the recycle rate of the biological solids. The aeration and settling compartment volumes were 3.0 and 3.2 liters, respectively. Complete mixing and oxygen to the microbial population in the reactor were obtained by vigrous aeration provided by compressed air dispersed through two porous carborundum diffusers. The air flow rate was measured and adjusted by a Bendix flow meter. The influent wastewater flow rate was regulated at 6.25 ml/min to provide a hydraulic detention time of eight hours in the aeration reactor. The effluent from the settling compartment flowed by gravity to the effluent bottle.

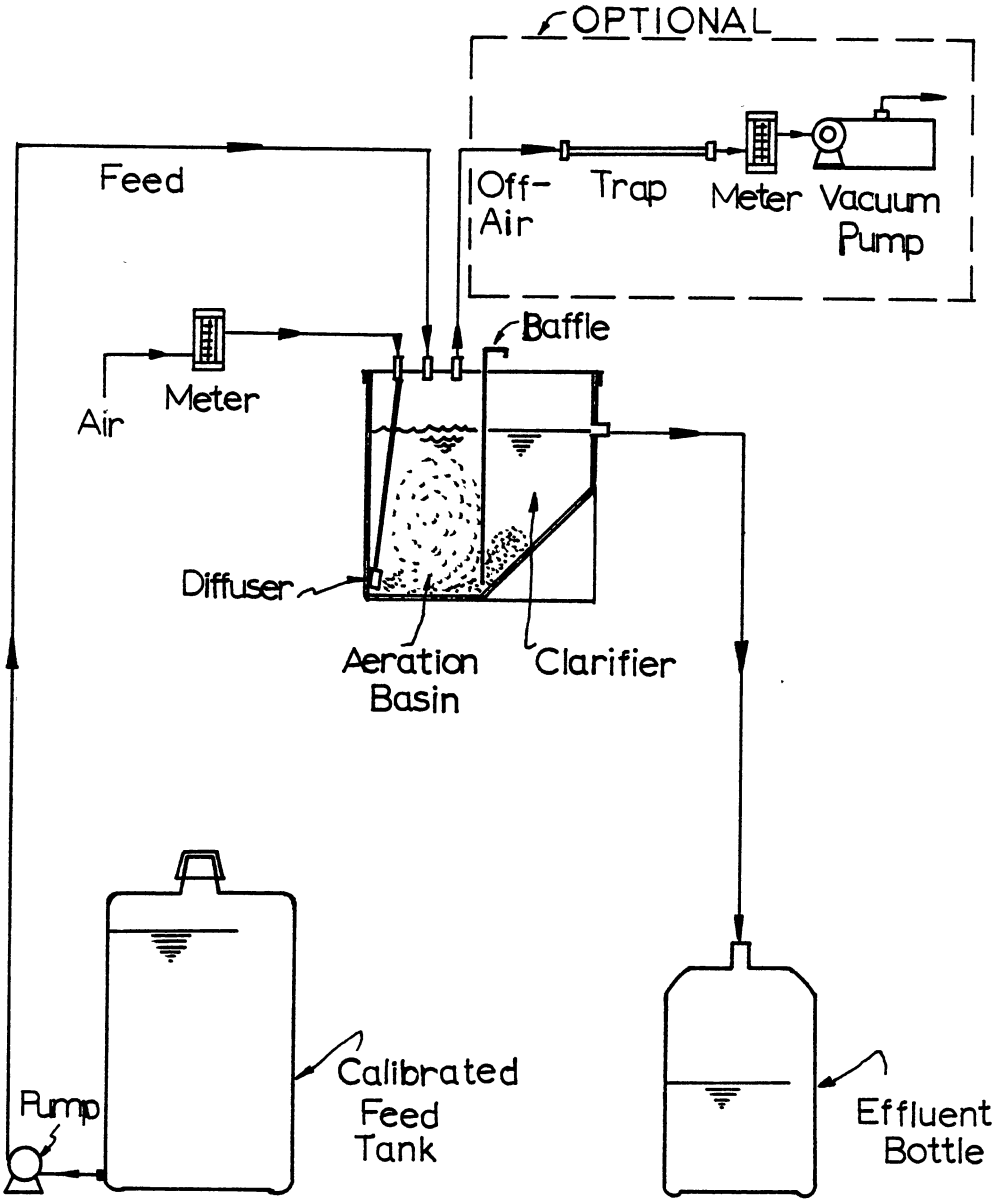



Figure 1. Bench Scale Internal Recycle Activated Sludge System

To minimize any possible contamination, all parts in contact with the wastewater were made of metal, stainless steel for the reactor and aluminum for tubing. The feed line was flushed daily with Chlorox solution and tap water to prevent slime growth. In addition, the feed tank was cleaned with acid solution everytime new feed was made. The system temperature was not regulated but was kept in the range of 25 ± 5°C (room temperature).

## Synthetic Wastewater Feed

The feed was prepared by mixing the specific compounds (priority pollutants) with the readily biodegradable substrate, the base mix, and filled with tap water to the 55 liter mark of the feed tank. The base mix and specific compounds were mixed by proportion such that the 5-day biochemical oxygen demand ($BOD_5$) was approximately 250 mg/l. Each freshly prepared feed batch was used for two days. The base mix composition is listed in Table V.

## Start-Up and Operation Procedures

The activated sludge for initial seeding was taken from the Ponca City, Oklahoma domestic sewage treatment plant. The biological solids were acclimated to the full strength base mix for one week, then a specific compound was gradually added to the system such that the desired concentration was reached in two weeks.

The exact amount of specific compound added depended on three factors: compound solubility, GC detection limit, and mixed-liquor-suspended-solids (MLSS) concentration. For some compounds, where low solubility prohibited dissolution to the desired concentration, the

TABLE V

COMPOSITION OF BASE MIX

| Compound | Concentration (mg/l) |
|---|---|
| Ethylene Glycol | 113.0 |
| Ethyl Alcohol | 113.0 |
| Glucose | 113.0 |
| Glutamic Acid | 113.0 |
| Acetic Acid | 113.0 |
| Phenol | 22.6 |
| Ammonium Sulfate | 100.0 |
| Phosphoric Acid | 15.74 |
| Salts | |
| $CaCl_2$ | 8.0 |
| $MnSO_4$ | 8.0 |
| $FeCl_3 \cdot 6 H_2O$ | 0.4 |
| $MgSO_4 \cdot 7 H_2O$ | 80.0 |

maximum solubility was applied. Care was also taken so that the minimum detection limit of the GC instrument would be met. With regard to MLSS, sometimes, a decrease of base mix would result in a drop of biological solids in the reactor. To counter such conditions, the specific compound's concentration would be cut back with a corresponding increase in base mix to maintain a steady MLSS concentration.

In an activated sludge system, the mean cell residence time (MCRT or $\theta_c$) is a design and operation parameter which influences the degree of biodegradation. For a once-through CSTR without recycle, $\theta_c$ is constant and equal to the hydraulic retention time. Thus, precise and reliable control of $\theta_c$ can be obtained by precise adjustment and control of the feed flow rate. But for reactors with recycle, the control of $\theta_c$ is more time consuming and complex.

A CSTR with recycle was employed in this study because it has the advantage of higher MLSS concentrations along with a shorter hydraulic detention time. It is also physically operated more closely to the actual activated sludge process. Three MCRTs of two, four, and six days were initially operated for this study. Later only the two and six days reactors were maintained. The sludge age was maintained by wasting MLSS daily from the reactors. The amount of MLSS wasted was determined by using Lawrence and McCarty's mean cell residence time model

$$F_w = \frac{\frac{VX}{\theta_c} - FX_e}{X - X_e} \qquad (5)$$

Where:

$F_w$ = sludge wasted (l/day);

$\theta_c$ = sludge age (days);

V = reactor volume (l);

F = influent flow rate (l/day);

X = mixed liquor volatile suspended solids, MLVSS (mg/l); and

$X_e$ = effluent volatile suspended solids.

When the biological system reached steady-state, as confirmed by the reactor and effluent MLVSS and the chemical oxygen demand (COD) data, samples for specific compound analysis were taken as part of the data collection procedure. The treatment performance of the system was monitored with respect to $BOD_5$, COD, and total organic carbon (TOC). Other system operating characteristics monitored were pH, temperature, dissolved oxygen, and oxygen uptake rate.

## Gas Chromatograph (GC) Analysis

### Instrumentation

The purge-and-trap (PAT) technique was chosen as the analytical method for this study. PAT consisted of three steps: 1) purge and trap, 2) desorb, and 3) chromatograph and detect. For steps 1 and 2, a Tekmar Liquid Sample Concentrator (Model LSC-1) purge and trap device was used. The stripped compounds were concentrated onto a 12 in x 1/8 in metal tubing (trap) containing 6 in Tenax and 4 in silica gel. The quantitative analysis was carried out on an F&M Scientific Corporation Model 810 GC equipped with flame ionization detector. The column in the GC oven, containing 0.2 percent Carbowax 1500 on 80/100 mesh Carbopack C, carried out the job of separating the different compounds. The GC column was made of thin wall stainless steel tubing and preconditioned before

placed into service. A Hewlett-Packard (HP) Model 3380 Integrator/ Recorder was used to integrate peak areas and print out the retention time and area of the specific compounds.

Standard Solutions Preparation

Separate standard solutions were prepared for each specific compound. The general procedure of standard solution preparation is given here.

A stock solution for each specific compound was prepared first. A syringe was used to measure out the necessary amount of specific compound, which was then injected into a volumetric flask below the waterline. The flask was filled to volume with distilled water and shaken vigorously to ensure complete mixing of the compound. A 1:1 dilution of the stock solution produced a standard solution with a 50 percent reduction in concentration. By this serial dilution technique, several standards covering the expected concentration range of each specific compound were prepared. The standard solutions were stored in a refrigerator when not being used.

Each set of standard solutions were purged using the Tekmar LSC, and the corresponding peak area and retention time were recorded on the HP-3380 Integrator. The standards were run in order of ascending concentrations and, when this was done, a graph of peak area versus concentration could be constructed. The standard curves showed a linear relationship between peak areas and concentrations for the specific compounds tested in this study.

Procedures for Specific Compound Analysis

To initiate the specific compound analysis step, a sample was taken and placed in the Tekmar LSC. The purge chamber used to hold the sample was a glass cylinder 9-1/2 in long, approximately 9/16 in inside diameter and contained a porcelain sieve in the lower end. The purge chamber's actual working volume was approximately 30 ml. Figure 2 is a schematic diagram of the Tekmar LSC and the trap in the purging mode.

After the sample had been introduced into the purge chamber, the inlet and discharge lines were tightly connected to prevent leakage, and purging by nitrogen ($N_2$) carrier gas was started. The sieve at the chamber's bottom broke up the $N_2$ into fine bubbles to increase the gas-liquid interfacial area, which in turn increased the mass transfer of volatile organics from the liquid phase to the gaseous phase. The purged gases were passed through a 6-way sampling valve (loop), with the cold trap inserted between the loop. The volatile specific compounds were trapped onto this trap and the organic-free $N_2$ was vented to the atmosphere. The stripping time was 12 minutes with a $N_2$ flow rate of 60 ml/min. The entire system is shown in Figure 2.

As soon as the stripping was completed, the Tekmar LSC system was manually switched into the desorb mode, and the HP-3380 Integrator/Recorder was also activated manually. Several things happened simultaneously during the desorb mode. The 6-way valve was automatically turned such that the trap was closed to the discharge end of the purge chamber, but opened up to the $N_2$ carrier gas flowing from a second supply which carried the sample into the GC. At the same time, the housing surrounding the trap was heated to a temperature higher than the boiling point of the compound, the heat source being supplied by

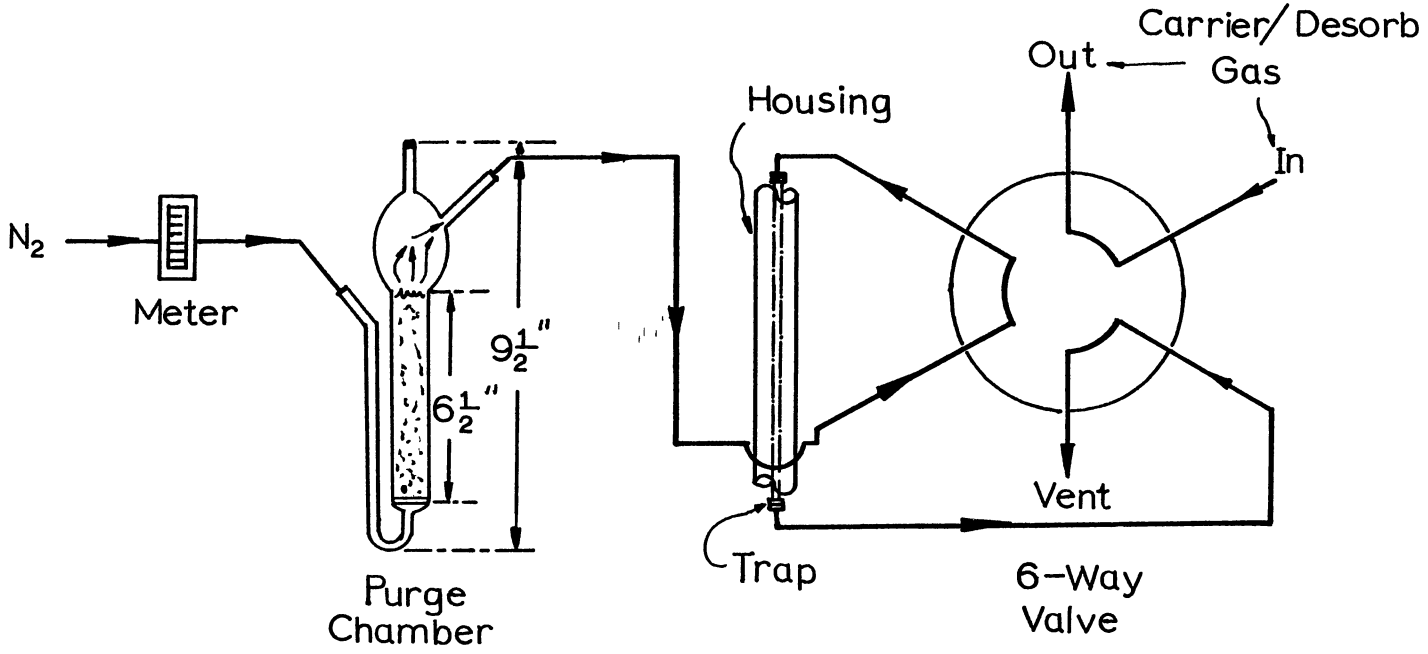



Figure 2. Liquid Sample Concentrator Purge-and-Trap System; In Purging Mode

the electrical wiring surrounding the desorber housing. While the $N_2$ transported the desorbed sample from the trap to the GC column in the oven, the oven temperature was increasing at a preprogrammed rate. The HP-3380, in the mean time, was printing out the various peak areas on paper. The entire process is schematically illustrated in Figure 3.

Qualitative and quantitative determination of the specific compound was done by comparing the output with that of a standard curve. When the desorb mode was completed, the trap and GC column were cooled down to room temperature by separate built-in fans. Then, another sample was placed in the purge chamber and the whole process repeated again. The operating parameters for GC analysis of each specific compound are listed in Table VI.

## pH Alteration of Samples

With regard to samples that were to be purged at extreme pH values, the procedure for preparation is described here.

After the sample was placed in the purge chamber, an appropriate amount of technical grade $66^{o}$ Baume sulfuric acid ($H_2SO_4$) was added by a pipet to the chamber. When the sample pH reached 2 or less, it was immediately put on the Tekmar LSC device for purging. The remaining procedure followed that outlined previously. The identical procedure was carried out for samples that were made basic, but, an appropriate amount of caustic solution (NaOH) was added to raise the sample pH to 12 or greater. Since purging of the caustic solution caused foaming, a filter was placed in the discharge end of the purge chamber to prevent the caustic foam from entering the trap. There were no foaming problems encountered for the acidic solution.

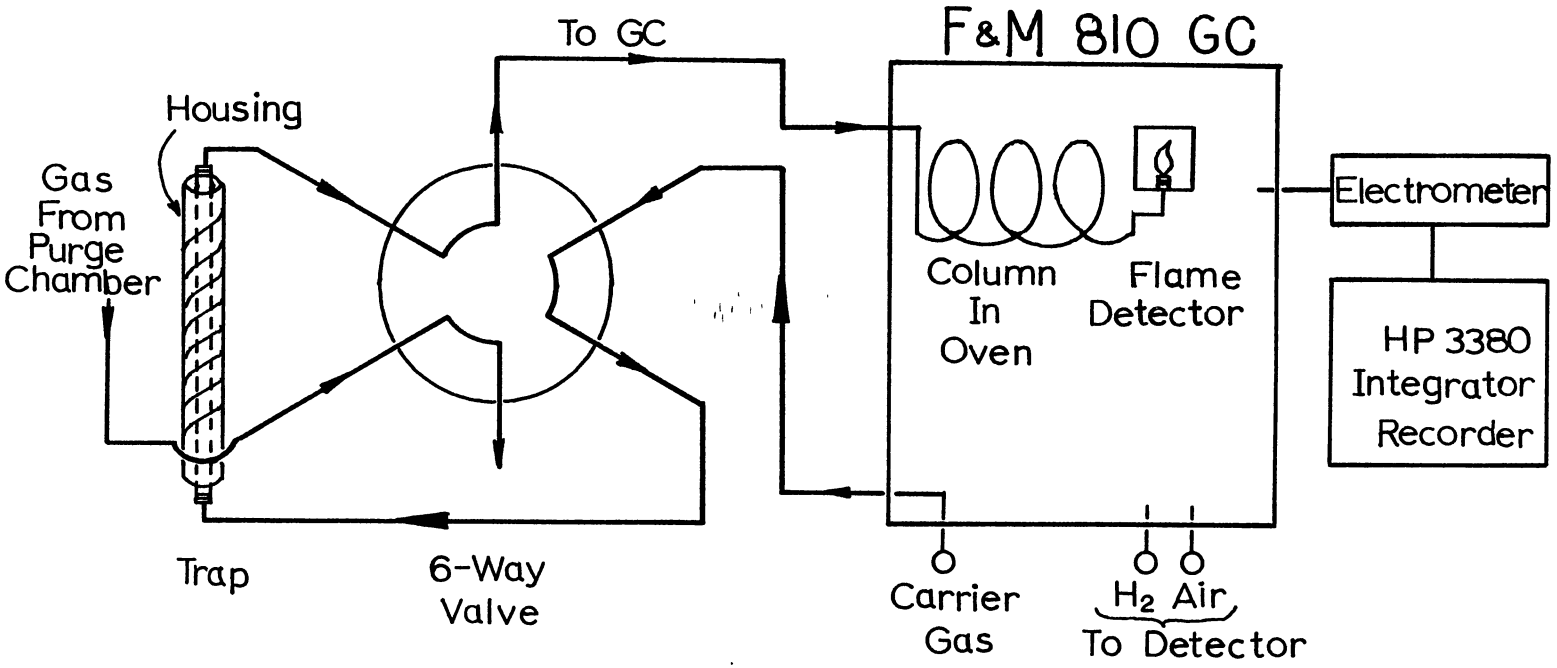



Figure 3. Liquid Sample Concentrator Purge-and-Trap System; In Desorbing Mode

TABLE VI

SPECIFIC CONDITIONS OF GC ANALYSIS FOR EACH COMPOUND

| Compound | Purge-and-Trap | | | GC | | | | |
|---|---|---|---|---|---|---|---|---|
| | Desorb Temp. (°C) | Carrier Gas (ml/min) | Purge Time (min) | Initial Oven Temp. (°C) | Oven Temp Program (°C/min) | Final Oven Temp. (°C) | Detector Temp. (°C) | Injector Temp. (°C) |
| 1,2-DCE | 150 | 60 | 12 | 105 | - | 105 | 270 | 220 |
| 1,1,1-TCE | 200 | 60 | 12 | 100 | 8 | 180 | 200 | 200 |
| TCE | 200 | 60 | 12 | 100 | 8 | 180 | 310 | 290 |
| Chloroform | 200 | 60 | 12 | 60 | 8 | 140 | 260 | 210 |
| Carbon Tet | 200 | 60 | 12 | 70 | 8 | 160 | 260 | 210 |

## Sonification of Samples

### Apparatus

The apparatus employed in this investigation is schematically illustrated in Figure 4. The complete sonifier system consists of a transistorized power supply, and a sonic converter with step horn, all made by Branson Power (Model S-75). The power supply converts 50/60 cycle ac at 115 volts to radio-frequency power at 20,000 cycles per second, with the electrical output being equivalent to 75 watts. The sonic converter transforms the radio-frequency power to mechanical energy at the same frequency of 20,000 cycles per second. The step horn then concentrates and intensifys this energy at the tip. The resulting energy radiates from the tip into the sample being treated.

### Procedure

A 50 ml sample was placed in a beaker and, since sonification generates heat, the beaker was in turn placed in an ice water bath to provide for heat exchange. The sonic converter was lowered into the sample beaker until the tip was 1/2 in from the beaker bottom to ensure good mixing. The power was turned on and the sample sonified for a time duration before turning it off. The sonified sample was then placed in the purge chamber for purging and GC quantification. The sonification step was repeated using another batch of fresh sample.

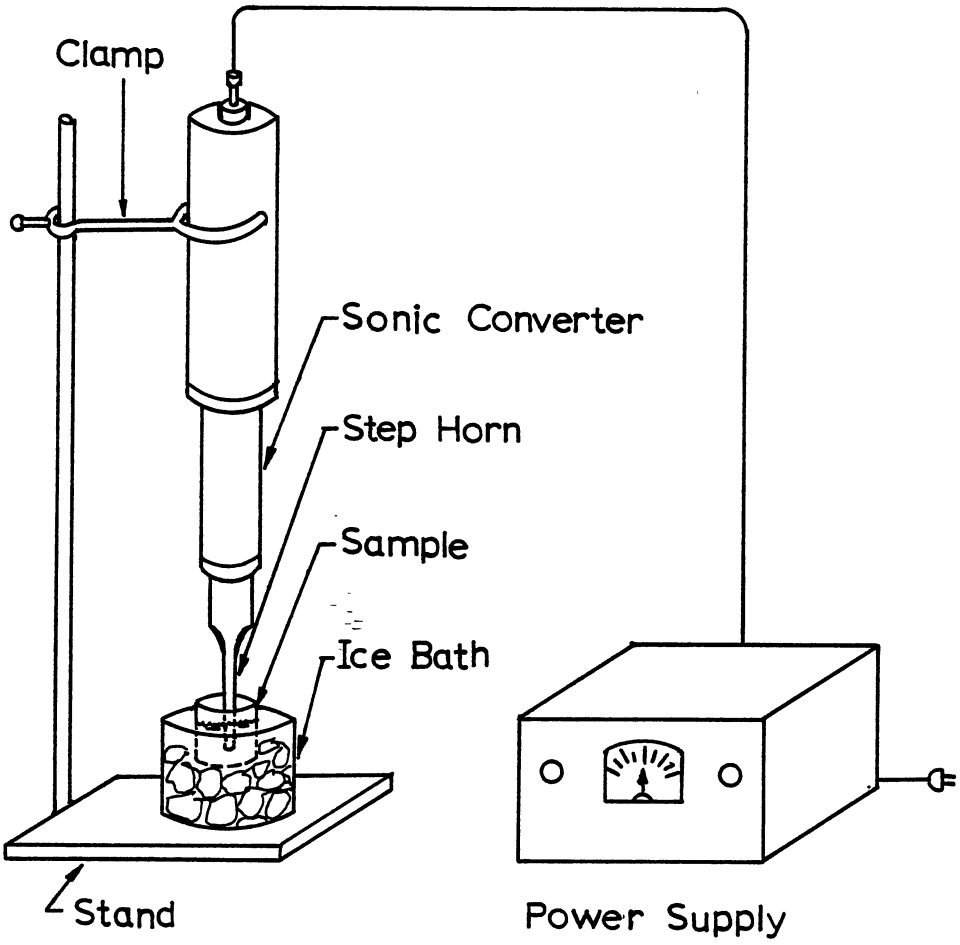



Figure 4. Schematic Diagram of the Branson Sonifier System

# CHAPTER IV

## RESULTS AND DISCUSSION

A review of the literature indicated that only limited data exist describing biosorption and stripping in biological reactor systems. The lack of information had, in effect, eliminated the source of proven testing methods. Without such guidelines and references, the testing methods conceived for this study were put through a trial period and, therefore, the five selected halogenated hydrocarbons were not subjected to the same tests. As during the testing period, those methods shown to have no impact were dropped and new methods added to the list.

In chronological order, the compounds first tested were 1,2-dichloroethane (1,2-DEC), 1,1,1-trichloroethane (1,1,1-TCE), and trichloroethylene (TCE). Chloroform and carbon tet were tested at a later time. All testing was conducted while the biological reactors were in the steady-state condition, as verified by the MLVSS and COD data.

### Biosorption Determination

In their study of the EPA priority pollutant biokinetic constants, Kincannon and Stover (5), concluded that sorption was one of the many removal mechanisms taking place in a biological reactor. The sorption quantities, listed in Table III, were 0.5, 0.83, 1.19, and 1.38 percent for 1,2-DCE, TCE, chloroform, and carbon tet, respectively. No sorption was detected for the compound 1,1,1-TCE.

The sorption values reported by Kincannon and Stover were derived through a complex material balance scheme involving numerous experimental procedures. Since these sorption values were so minute, it could be argued that they were the result of sampling and experimental errors rather than being the actual measurement of sorption. Thus, the incentive here was to undertake some simple testings to determine if biosorption indeed existed, and at the same time eliminate as much error as possible. The testing methods are discussed under separate headings after a brief discussion about analytical reproducibility.

## Analytical Reproducibility

Most results in this study consisted of pairwise data comparison. In such cases, the variability factor is not applicable as a measure of data variance. Instead, the reproducibility factor becomes a more important consideration.

To test reproducibility, carbon tet standards were prepared from 50 to 250 µg in increments of 50 µg. Carbon tet was chosen over the other four compounds due to its higher Henry's constant. In other words, since carbon tet is more volatile than the others, the reproducibility data would represent the "best possible case." Each standard was run four times in the order listed in Table VII. The data shows that four of the five average deviations were 4 percent or less, the only exception being the 50 µg standard.

As a further check on reproducibility, 54 pairwise samples encompassing the compounds 1,1,1-TCE, TCE, chloroform, and carbon tet were taken during the study. The procedure involved taking two samples from the same source (feed, ML, or effluent), and calculating the percent

TABLE VII

REPRODUCIBILITY OF CARBON TETRACHLORIDE STANDARDS

| Standard (µg) | Concentration of Each Analysis (µg) (% Deviation from Standard) | | | | Avg. % Deviation |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | |
| 50 | 46.1 (7.8) | 50.0 (0) | 42.5 (15.0) | 57.2 (14.4) | 9.3 |
| 100 | 96.9 (3.1) | 105.4 (5.4) | 97.4 (2.6) | 101.8 (1.8) | 3.2 |
| 150 | 153.1 (2.1) | 154.8 (3.2) | 147.3 (1.8) | 162.9 (8.6) | 3.9 |
| 200 | 199.0 (0.5) | 199.1 (0.5) | 197.1 (1.5) | 206.5 (3.3) | 1.5 |
| 250 | 269.9 (8.0) | 244.3 (2.3) | 245.9 (1.6) | 246.9 (1.2) | 3.3 |

deviation from the average value. A histogram is used to present the data in Figure 5. The majority of the data (46/54 = 85%) deviated from the average value by 5 percent or less. This compares fairly well with the 4 percent deviation derived in the carbon tet standard testing. Therefore, the figure of ±5 percent is used to represent reproducibility and errors for this study.

Filtered vs. Nonfiltered Samples

A well-mixed mixed-liquor (ML) sample from a biological reactor was taken and divided into two, one sample filtered free of biological solids and the second one left unfiltered. The samples were purged and the specific compound concentration determined. It was believed that any concentration difference between the two samples would be attributed to biosorption, provided, of cource, that biosorption existed and stripping was complete.

The results of 1,2-DCE are shown in Table VIII. To make the data easily recognizable for comparison purpose, the concentration values are also expressed on a ratio basis. This procedure is done hereafter for all data presented in table form.

It appears that the large discrepancy between the filtered and nonfiltered samples are due to biosorption, when in fact the discrepancy is more likely caused by the vacuum pump. The force exerted by the pump during the separation process could have very easily stripped off the 1,2-DCE, leading to erroneous results.

It might be argued that three pairwise samples are too few in number to be a good representation of the whole picture. However, the basic goal was to eliminate errors in order to obtain more accurate

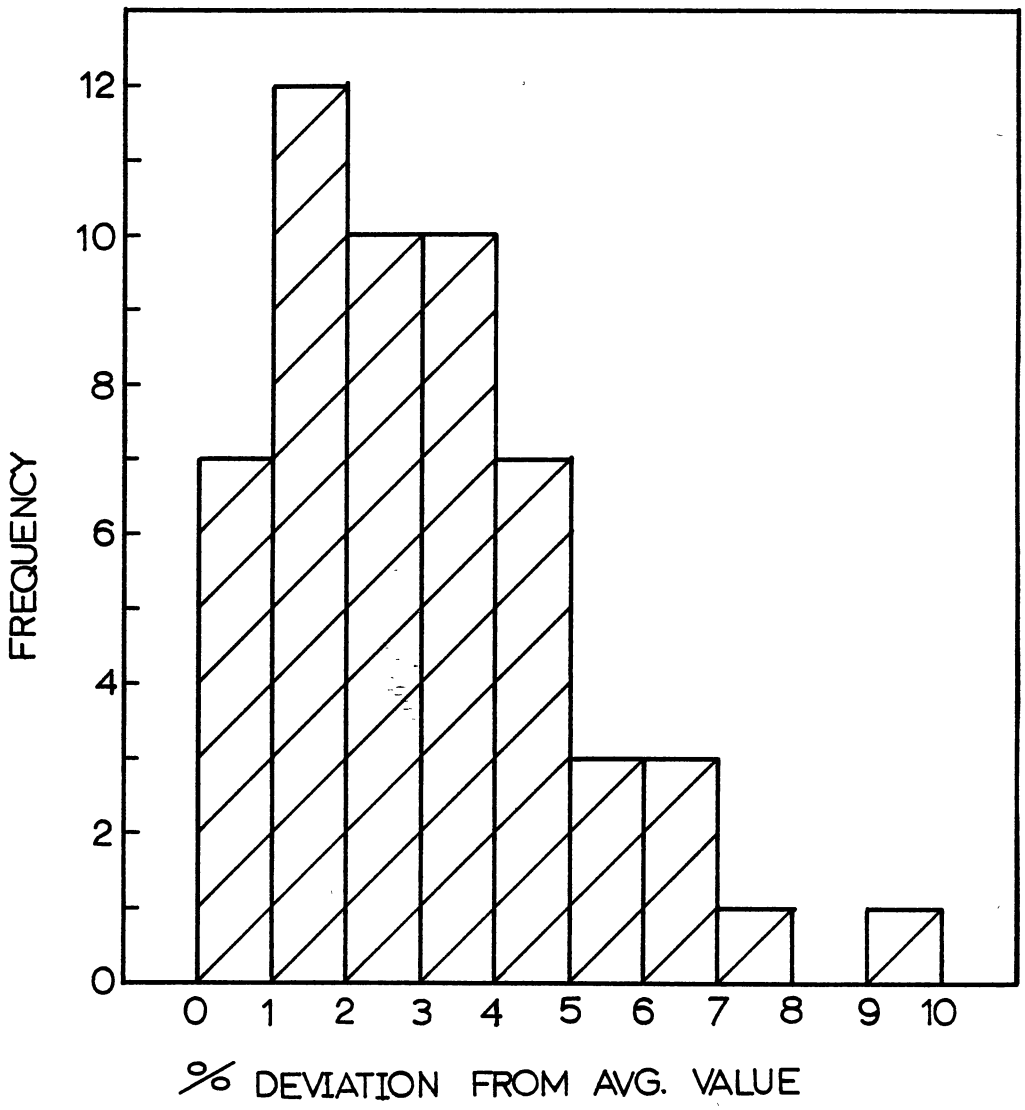



Figure 5. Distribution of % Deviation from Average Value for 54 Pairwise Samples

TABLE VIII

1,2-DICHLOROETHANE CONCENTRATIONS IN FILTERED AND NONFILTERED SAMPLES

| Sample No | Conc. (mg/l) | | Ratio |
|---|---|---|---|
| | Filtered | Nonfiltered | Filtered : Nonfiltered |
| 1 | 2.38 | 4.30 | .55 |
| 2 | 3.55 | 4.35 | .82 |
| 3 | 1.25 | 1.43 | .87 |

TABLE IX

SPECIFIC COMPOUND CONCENTRATIONS IN SUPERNATANT AND MIXED-LIQUOR

| Compound | Sample No | Conc. (mg/l) | | Ratio |
|---|---|---|---|---|
| | | Supernatant | ML | Supernatant : ML |
| 1,1,1-TCE | 1 | .450 | .500 | .90 |
| | 2 | .255 | .275 | .93 |
| | 3 | 2.220 | 2.350 | .94 |
| | 4 | .400 | .410 | .98 |
| TCE | 1 | .155 | .170 | .91 |
| | 2 | .130 | .135 | .96 |
| | 3 | .295 | .280 | 1.05 |
| | 4 | .215 | .195 | 1.10 |

results. The vacuum pump defeats that purpose by adding another factor into the whole spectrum of errors. In addition, 1,2-DCE is such a volatile compound that during the separation process, the reduction in pressure above the filtrate would no doubt affect the stripping of 1,2-DCE. Consequently, it was decided not to extend this testing method to other compounds.

Supernatant vs. ML

A well-mixed ML sample from the aeration basin was taken and placed in a container to let settle. Both supernatant and settled sludge samples (ML) were then taken from the container, purged, and quantified. If no biosorption occurred, the supernatant and ML concentrations should be fairly close to one another.

Table IX (page 44) gives the results of this test. It is seen that six of the eight supernatant concentrations were less than the ML, which seem to suggest that biosorption took place. However, eight data sets are not a sufficient quantity to constitute the entire situation. In other words, more data are needed to identify a positive trend and to establish a relationship.

There is still another way of looking at the issue, however. It is seen that the supernatant concentrations range from 10 percent lower to 10 percent higher (±10%) than the ML concentrations. Subtracting the ±5 percent reproducibility/errors factor from the ±10 percent figure leaves the supernatant within ±5 percent of the ML concentrations. This means that the supernatant and ML concentrations are very close to one another, and perhaps an indication of nonbiosorption. Furthermore, the figure of +5 percent is unacceptable as a proof of biosorption, since

the supernatant concentrations should be less than that of the ML if biosorption occurred. Therefore, based on the data in Table IX alone, it is difficult to determine if biosorption had taken place in this particular investigation.

Effect of Biomass on Concentration

A series of experiments were conducted in which varying biomass (MLVSS) concentrations were purged and the corresponding specific compound concentrations determined. Had biosorption taken place, a direct relationship would exist between the biomass level and the specific compound concentration. In other words, as the MLVSS increased, the specific compound concentration would do likewise due to the higher biosorption saturation capacity of the biomass.

Figures 6 and 7 give the results of the 1,1,1-TCE and TCE investigations, respectively. The graphs show a positive relationship between compound concentration and MLVSS, thus giving the firmest evidence yet that biosorption did take place in the reactors.

To express the extent of biosorption in numerical terms, the increase in specific compound concentration per 1000 mg of MLVSS was calculated for each data line of 1,1,1-TCE and TCE. The results are listed in Table X.

Judging by the values in the last column of Table X, the biosorption figures might be considered to be fairly significant. However, taking into consideration the 5 percent reproducibility/errors factor, these biosorption values seem to be insignificant. Nevertheless, this does not lessen the major significance of this investigation's finding, which is that biosorption indeed took place in the biological reactor.

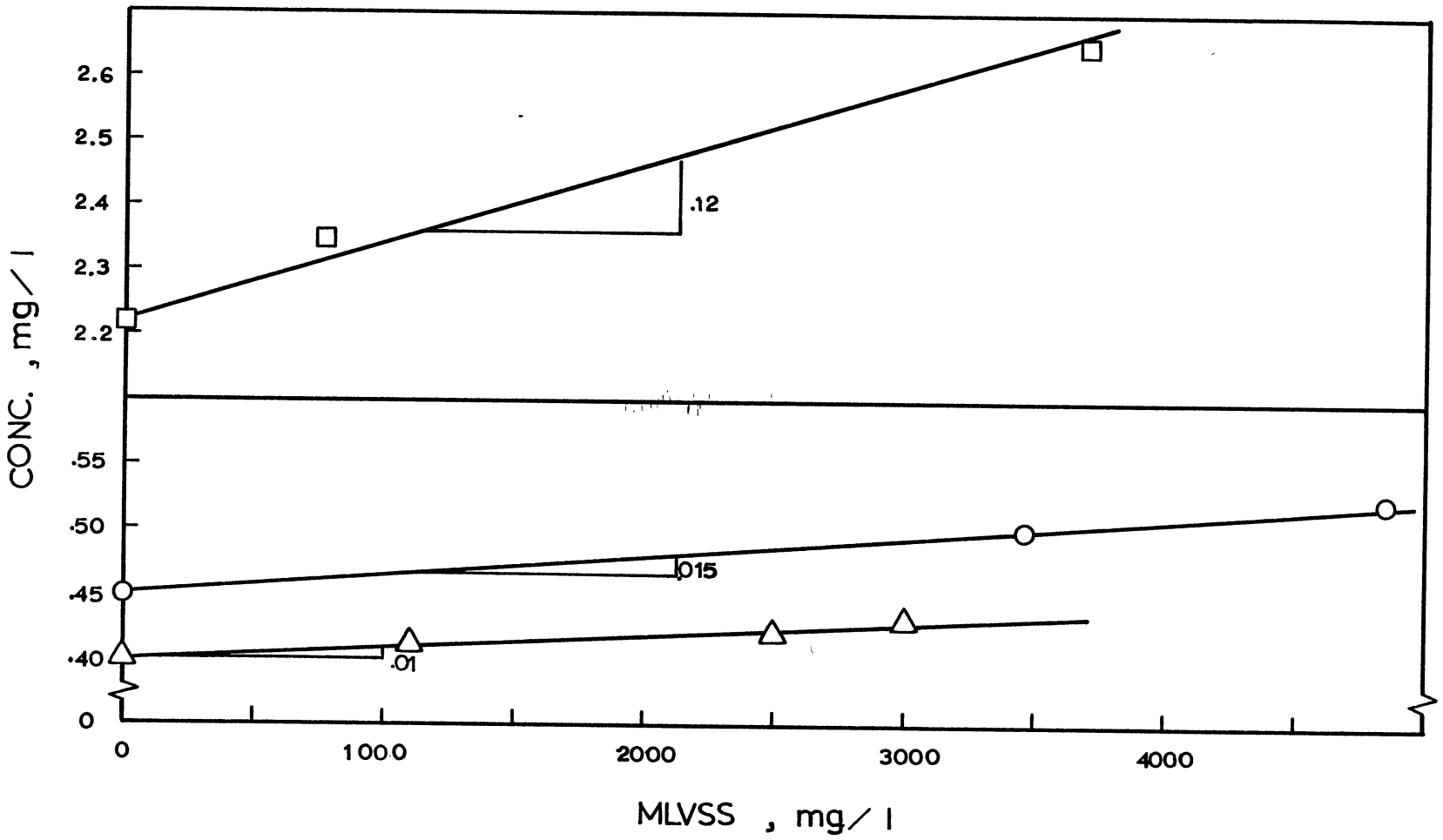



Figure 6. 1,1,1-Trichloroethane Concentration in Mixed-Liquor, Samples Taken from One Reactor on Same Date

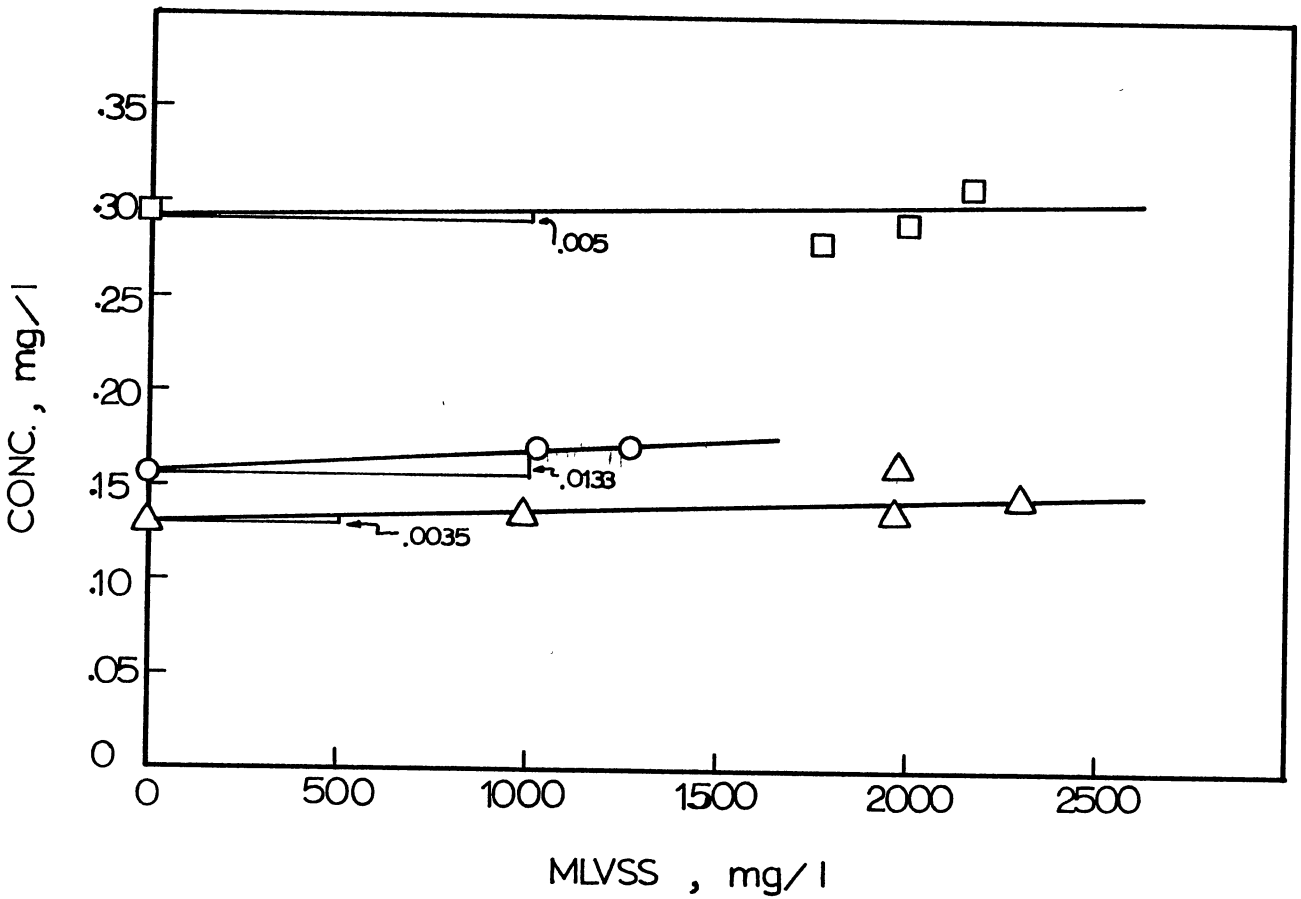



Figure 7. Trichloroethylene Concentration in Mixed-Liquor, Samples Taken from One Reactor on Same Date

TABLE X

SPECIFIC COMPOUND CONCENTRATION INCREMENT
PER 1000 MG MLVSS

| Compound | Initial Conc. MLVSS = 0 mg (mg) | Conc. Increased Per 1000 mg MLVSS (mg) | % Conc. Increased Per 1000 mg MLVSS Per Initial Conc. |
|---|---|---|---|
| 1,1,1-TCE | .400 | .010 | 2.5 |
| | .450 | .015 | 3.3 |
| | 2.220 | .120 | 5.4 |
| TCE | .130 | .007 | 5.4 |
| | .155 | .013 | 8.4 |
| | .290 | .005 | 1.7 |

As a matter of interest, it should be pointed out that each data set, which made up a graph line in Figures 6 and 7, represents samples taken from the same reactor within a few hours of one another. This was done to eliminate the variability factors so prevalent in biological reactors. As an example, data for 1,1,1-TCE gathered from different MCRT reactors on different dates were put together and presented in Figure 8. The scattered data points suggest that no correlation exists between compound concentration and MLVSS. When the data were separated by MCRT and analyzed, still no correlations were seen. The same results were observed for TCE, chloroform, and carbon tet.

The scattering of data points should not be taken as a sign of non-biosorption, but merely a suggestion that as a means of data analysis, graphs such as that of Figure 8 are not suitable for this particular investigation. Variability factors, such as daily variations in MLVSS level and specific compound concentrations, probably caused the scattering of data in Figure 8. The variation of MLVSS, in a supposedly steady-state reactor, might be due to the existance of the natural cycling of microorganisms and biomass. The variation in specific compound concentrations is more complex. First of all, it should be made clear that the compound concentration in the feed tank does not remain constant through time, but decreases daily according to the vapor space available in the feed tank. This condition was later demonstrated in the chloroform and carbon tet feed systems. Second, COD and BOD measure the substrate concentration but, since the specific compound constitute only a minor percentage of the total substrate, the COD and BOD tests might not be an accurate assesement of specific compounds in the substrate. Therefore, just because a biolgocial reactor is in

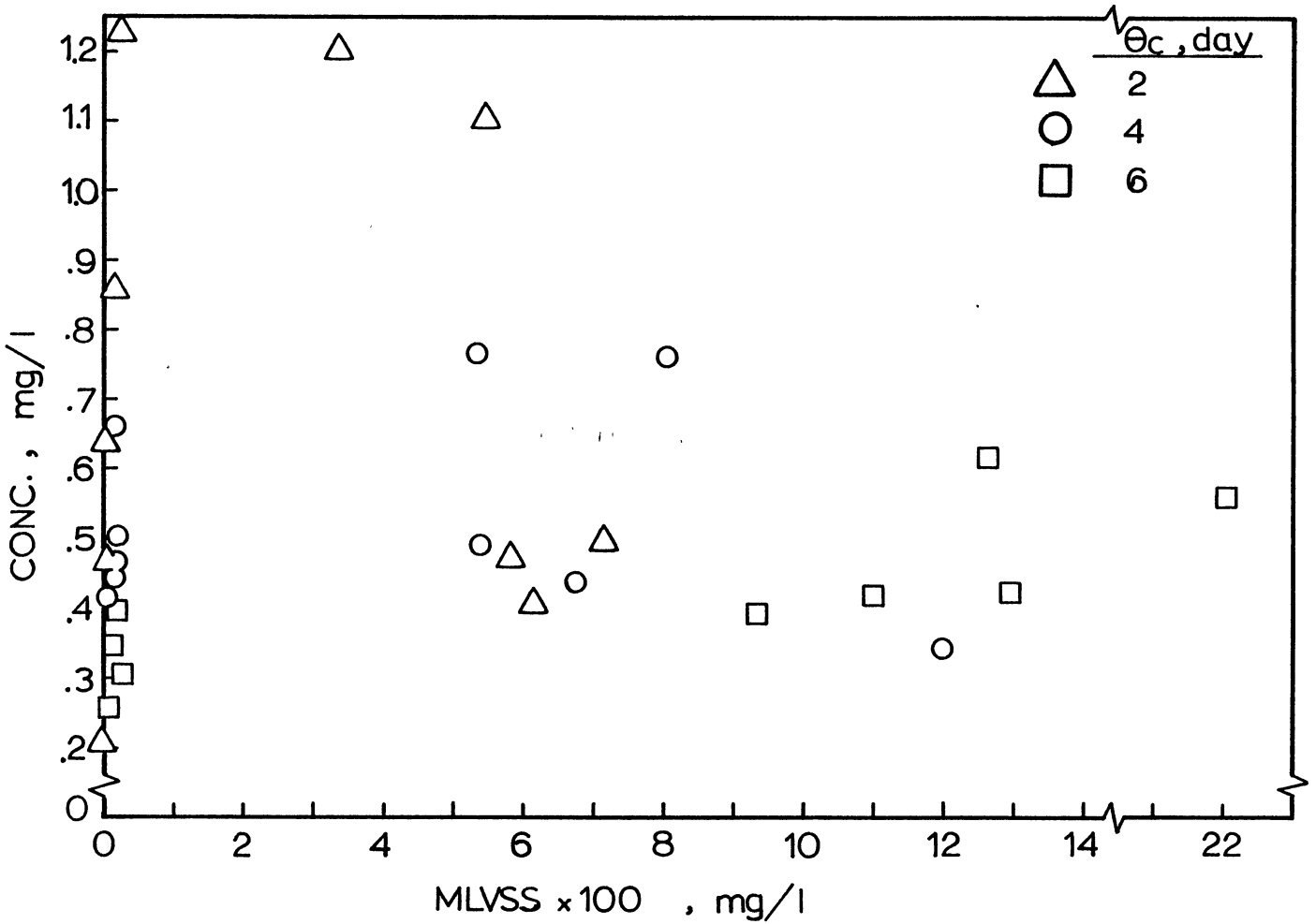



Figure 8. 1,1,1-Trichloroethane Concentration in Mixed-Liquor, Samples Taken from Three Reactors on Different Dates

steady-state with respect to COD, BOD, and TOC does not necessarily mean that the specific compound concentration is also in steady-state. The compound concentration could be fluctuating while the COD and BOD are in steady-state.

It might be possible to put together COD, BOD, and TOC data from different MCRT reactors or dates, and conduct data analyses to gain some insights and information. However, this procedure is not applicable to the specific compounds. Therefore, to be able to detect any correlation between the compound concentration and MLVSS, the data of this investigation had to be analyzed according to each individual reactor and taken during a time span not exceeding 24 hours. Such was the case with Figures 6 and 7.

ML vs. Effluent

Samples from the aeration basin and settling compartment (clarifier) were collected, purged, and quantified. In a completely-mixed, internal-recycle CSTR, the incoming feed is instantaneously mixed such that the substrate and biomass are evenly distributed in all parts of the reactor. Consequently, the specific compound concentration in the effluent (taken from the clarifier) should be identical to that in the aeration reactor. Therefore, any discrepancy in concentrations between the two samples would be attributed to either biosorption, errors, or a combination of both.

Table XI gives the results of the 1,1,1-TCE investigation. It is seen that the six day reactor's ML:Effluent (ML:EFF) ratios were higher than either the two or four day ratios. Since the six day reactor had the highest biomass (MLVSS) of the three reactors, it seems to indicate that the quantity of biosorption was a function of the biomass

TABLE XI

1,1,1-TRICHLOROETHANE CONCENTRATION IN ML AND EFFLUENT

| Sample No. | Two Day MLVSS = 560 mg/l | | | Four Day MLVSS = 750 mg/l | | | Six Day MLVSS = 1360 mg/l | | |
|---|---|---|---|---|---|---|---|---|---|
| | Conc. (mg/l) | | Ratio | Conc. (mg/l) | | Ratio | Conc. (mg/l) | | Ratio |
| | ML | Eff | ML:Eff | ML | Eff | ML:Eff | ML | Eff | ML:Eff |
| 1 | .405 | .205 | 1.98 | .760 | .465 | 1.63 | .615 | .405 | 1.52 |
| 2 | 1.100 | .860 | 1.28 | .765 | .660 | 1.16 | .390 | .260 | 1.50 |
| 3 | .470 | .465 | 1.01 | .435 | .417 | 1.04 | .415 | .305 | 1.36 |
| 4 | 1.200 | 1.230 | .98 | .490 | .500 | .98 | .560 | .415 | 1.35 |
| 5 | .495 | .640 | .77 | .340 | .450 | .76 | .422 | .345 | 1.22 |

concentration. Also note that the majority of the ML:EFF ratios were greater than one, indicating that the 1,1,1-TCE concentrations were greater in the ML than in the effluent, a clear indication of biosorption.

There were four ML:EFF ratios where the values were very close to one. Since the differences were within the ±5 percent reproducibility/errors range, these ratios, for all practical purposes, should be considered to be equal, indicating that the concentrations were the same in the ML and effluent.

There were two ratios where the values were less than one, indicating that the 1,1,1-TCE concentrations in the ML were less than that of the effluent. This is an improbable but not an impossible occurrence. It is speculated that this curious occurence was created by a combination of three factors: 1) the dead-zone space, 2) the feed concentration variance, and 3) the time-lag. The dead-zone phenomena is self-explanatory. There were spots in the reactor which were not uniformly mixed, thus generating different concentration gradients. The feed concentration variance was due to the volatile nature of 1,1,1-TCE. As the feed tank level decreased, the additional headspace available would promote the volatilization of 1,1,1-TCE, resulting in a decrease of feed concentration. With regard to time-lag, theoretically, it should not have happended in a completely-mixed reactor, as can be proven by the dilute-in/dilute-out test. However, whether by design or accident, the steel baffle separating the two compartments of the reactor (aeration and clarifier) was, at times, completely closed. The free-flowing fluid motion was thus impeded and instantaneous mixing hindered. As a result, time-lag occurred between the fluid flowing from the aerator to the

clarifier. Anyone of these factors occurring independently probably would have little effect on the ML:EFF ratio. However, the cumulative effect due to the simultaneous occurrence of the three factors could have resulted in the 1,1,1-TCE concentration being lower in the ML than in the effluent.

Table XII gives the results of the chloroform investigation. All ML:EFF ratios were greater than one, thus indicating biosorption. Note that the quantity of biosorption was not a function of biomass concentration, since the two day ML:EFF ratios were slightly greater than the six day ratios. This occurrence (without getting into the complex biodegredation mechanisms and, for the time being, ignoring the effect of biodegredation) could be explained in terms of the competing effects between the aeration air flow rate and the biomass concentration.

Stripping has been determined as a major removal mechanism of volatile compounds in a biological reactor (5). Chung (54), while conducting a study of the stripping characteristics of priority pollutants in non-biolgocial ractors, found that more ethyl acetate was stripped at an aeration rate of 2.0 l/min than 1.5 l/min, the same air flow rates supplied to the six and two day reactors, respectively, of this study. Since the six day reactor has the greater air flow, one would be inclined to conclude that more chloroform should be stripped. However, this was not the case here.

This study assumed that the quantity of specific compounds stripped were about the same in both two and six day reactors. The assumption is based on the role played by the biomass in air stripping. Since biomass has weight and takes up volume space, it acts as resistance to the stripping air to hinder stripping. Therefore, higher biomass levels in a

TABLE XII

CHLOROFORM CONCENTRATION IN ML AND EFFLUENT

| Sample No. | Two Day MLVSS = 860 mg/l Conc. (mg/l) ML | Eff | Ratio ML:EFF | Six Day MLVSS = 1810 mg/l Conc. (mg/l) ML | Eff | Ratio ML:Eff |
|---|---|---|---|---|---|---|
| 1 | .290 | .130 | 2.23 | .275 | .118 | 2.33 |
| 2 | .285 | .145 | 1.97 | .345 | .240 | 1.44 |
| 3 | .335 | .188 | 1.78 | .340 | .250 | 1.36 |
| 4 | .580 | .355 | 1.63 | .715 | .535 | 1.34 |
| 5 | .320 | .205 | 1.56 | .390 | .220 | 1.32 |
| 6 | .293 | .200 | 1.47 | .635 | .490 | 1.30 |
| 7 | .570 | .405 | 1.41 | .655 | .510 | 1.28 |
| 8 | .295 | .215 | 1.37 | .800 | .628 | 1.27 |
| 9 | .570 | .440 | 1.30 | .390 | .310 | 1.26 |
| 10 | .540 | .425 | 1.27 | .270 | .218 | 1.24 |
| 11 | .545 | .440 | 1.24 | .270 | .228 | 1.18 |
| 12 | .320 | .280 | 1.14 | .520 | .440 | 1.18 |
| 13 | .645 | .570 | 1.13 | .630 | .545 | 1.16 |
| 14 | .445 | .400 | 1.11 | .600 | .540 | 1.11 |
| 15 | .490 | .450 | 1.09 | .480 | .455 | 1.05 |

reactor would have greater resistance to stripping. In essence, the two variables, biomass level and aeration air, acted as opposite and competing effects during stripping in the biological reactors. In the six day reactor, the effect exerted by the higher air flow was countered by the greater resistance exerted by the higher biomass level. Similarly, the two day reactor received less air flow but also had smaller biomass resistance to overcome. The net effect was that a delicate balance was maintained between the two variables, and the quantity of specific compounds stripped from the individual reactor was about equal.

In the case of the two day reactor, the balance between the biomass level and air flow rate was apparently not maintained. An inquiry into the data revealed that two associated factors would be considered to be slightly out of norm. One was that the two day biomass level might be a little high (860 mg/l), and the other one was that the quantity of chloroform stripped in the two and six day reactors were not equal. It is seen from Table XIII that, though the chloroform stripped in both reactors could be interpreted as approximately equal, a slightly lesser amount was stripped from the two day reactor. This, perhaps, indicates that the higher biomass level in the two day reactor had increased the biosorption, and at the same time, decreased the amount of chloroform stripped.

It could always be argued that biosorption is compound specific among the halogenated hydrocarbons, or maybe even MCRT specific, and not dependent on biomass concentration or air flow rate. However, in the absence of concrete data, these arguments remain, at best, speculative. Therefore, it is concluded that for the chloroform investigation, the two day ML:EFF ratios were higher than the six day ratios due to a

TABLE XIII

CHLOROFORM QUANTITY STRIPPED FROM THE TWO AND SIX DAY REACTORS

| Sample No | Sampling Time (Hr) (Same for Both Reactors) | Conc. (µg/l) | |
|---|---|---|---|
| | | Two Day | Six Day |
| 1 | 1.0 | 9 | 14 |
| 2 | 1.5 | 14 | 15 |
| 3 | 1.5 | 14 | 16 |
| 4 | 1.0 | 18 | 20 |
| 5 | 1.5 | 20 | 17 |
| 6 | 1.5 | 21 | 20 |
| 7 | 1.5 | 23 | 30 |
| 8 | 2.0 | 30 | 38 |

slightly higher level of biomass in the two day reactor. The increased amount of biomass promoted biosorption and hindered stripping, leaving more than the normal quantity of chloroform in the reactor.

Table XIV gives the results of the carbon tet investigation. Since the great majority of the ML:EFF ratios were greater than one, it was interpreted as an indication of biosorption. For those ratios within ±5 percent of one, the ML and effluent concentrations were considered to be equal to one another.

It is seen that the six day ratios were far greater than the two day ratios, an indication that the six day reactor had greater biosorption capacity than the two day reactor due to its higher biomass concentrations. In other words, in the carbon tet case, the biosorption quantity was a function of the biomass concentrations. Note that in the two day reactor, the carbon tet concentration in the ML was never more than 10 percent greater than in the effluent whereas, for the six day reactor, a greater difference was observed. A simple explanation of this occurrence is that biosorption simply did not occur to a great extent in the two day carbon tet reactor. The same explanation used for the two day chloroform reactor also applys here, but with the opposite effect taking place. It seems that the biomass level was not high enough to resist stripping, and the air flow might also be a bit high, resulting in greater stripping of carbon tet and lesser biosorption.

As a final note on this investigation, it could be taken for granted that biosorption and errors both contributed to the large concentration differences between ML and effluent samples. Since the ML and effluent concentration differences were consistantly far greater than the 5 percent reproducibility/errors factor, it could be safely stated that the

TABLE XIV

CARBON TETRACHLORIDE CONCENTRATION IN ML AND EFFLUENT

| Sample No. | Two Day MLVSS = 710 mg/l Conc. (mg/l) ML | Eff | Ratio ML:Eff | Six Day MLVSS = 1450 mg/l Conc, (mg/l) ML | Eff | Ratio ML:Eff |
|---|---|---|---|---|---|---|
| 1 | .218 | .193 | 1.13 | .275 | .027 | 10.20 |
| 2 | .263 | .238 | 1.11 | .345 | .050 | 6.90 |
| 3 | .313 | .283 | 1.11 | .313 | .113 | 2.77 |
| 4 | .193 | .175 | 1.10 | .163 | .063 | 2.59 |
| 5 | .290 | .263 | 1.10 | .193 | .090 | 2.14 |
| 6 | .148 | .138 | 1.07 | .283 | .145 | 1.95 |
| 7 | .268 | .253 | 1.06 | .308 | .165 | 1.87 |
| 8 | .333 | .313 | 1.06 | .325 | .175 | 1.86 |
| 9 | .203 | .195 | 1.04 | .230 | .133 | 1.73 |
| 10 | .240 | .233 | 1.03 | .295 | .203 | 1.45 |
| 11 | .200 | .203 | .99 | .313 | .218 | 1.44 |
| 12 | .185 | .188 | .98 | .175 | .145 | 1.21 |
| 13 | .233 | .238 | .98 | .263 | .220 | 1.20 |
| 14 | .238 | .245 | .97 | | | |

reproducibility/error factor played a minor role in concentration differences and biosorption indeed took place with the compounds 1,1,1-TCE, chloroform, and carbon tet.

A Final Note on Biosorption

It is concluded that biosorption did occur in the biological reactor systems. An estimate of the biosorption quantities indicated that they were insignificant when compared to the 5 percent reproducibility/errors factor. The exact quantity of biosorption was not determined due to technical considerations which prevented accurate prediction. In addition, the primary goal was to determine if biosorption had taken place, quantitative determination was considered secondary and not a particular concern of this study.

The primary goal had been accomplished and the results indicated that the testing methods employed were adequate for determining biosorption. What remained to be resolved was whether or not the PAT technique employed was adequate.

## Testing Methods to Improve Stripping Efficiency of the PAT Technique

Tests were conducted to determine if the PAT technique, as applied in the laboratory environment, was an effective tool for volatile compound analyses. Two of the tests investigated, pH alteration and sonification, involved pretreatment of the biomass sample. The other two tests examined the effect of purging chamber configuration and variable stripping time on stripping efficiency.

Effect of pH on Stripping

A well-mixed ML was taken from the aeration reactor and divided into three equal samples. The pH of the samples were changed such that one was at a pH of two or less, the other one at 12 or more, and the third sample was left unchanged at a neutral pH. The three samples were then purged and quantified.

The effect of pH on the stripping of halogenated compounds is not well known since very little information is available. However, the pH effect on ammonia stripping is well documented. At a pH of 11 or higher, ammonia in water exists as ammonia gas and can be removed by air stripping. Hence, high pH enhances the stripability of ammonia. Extraction application is another area where the benefit of pH variation is maximized. The drastic change in pH affects the solubility of the extractable compounds. The net result is an increase of specific compound concentrations in the extraction solvent.

Table XV gives the results of this investigation. It is seen that, contrary to ammonia stripping and extraction application, pH alteration had no effect on the stripping of the four halogenated hydrocarbon compounds. The quantities of specific compounds stripped did not increase under acidic conditions and, in fact, decreased under alkaline condition.

It might be argued that the effect of pH could be compound specific and that insufficient data were presented for 1,2-DCE and 1,1,1-TCE. However, the general trend indicated that the majority of the acidic sample concentrations were never more than 10 percent greater than the regular samples, and the alkaline samples were mostly 20 percent less than the regular sample concentrations. When taking the 5 percent reproducibility/errors factor into account, the increase in concentration

TABLE XV

SPECIFIC COMPOUNDS CONCENTRATIONS AT DIFFERENT pH

| Compound Sample No | Conc. (mg/l) | | | Ratio | |
|---|---|---|---|---|---|
| | Acidic | Regular | Alkaline | Acidic:Regular | Regular:Alkaline |
| 1,2-DCE | | | | | |
| 1 | 3.500 | 3.550 | 3.020 | .99 | .85 |
| 2 | 3.550 | 3.900 | 2.550 | .91 | .65 |
| 1,1,1-TCE | | | | | |
| 1 | .220 | .180 | .180 | 1.22 | 1.00 |
| 2 | 2.000 | 2.350 | 1.850 | .85 | .79 |
| 3 | .435 | .500 | — | .87 | — |
| 4 | .275 | .275 | — | 1.00 | — |
| Chloroform | | | | | |
| 1 | .715 | .655 | .610 | 1.09 | .93 |
| 2 | .610 | .570 | .520 | 1.07 | .91 |
| 3 | .303 | .290 | .305 | 1.04 | 1.05 |
| 4 | .285 | .275 | .265 | 1.04 | .96 |
| 5 | .605 | .580 | .530 | 1.04 | .91 |
| 6 | .730 | .715 | .600 | 1.02 | .84 |
| Carbon Tet | | | | | |
| 1 | .228 | .163 | .130 | 1.40 | .80 |
| 2 | .318 | .275 | .240 | 1.15 | .87 |
| 3 | .480 | .440 | .415 | 1.09 | .94 |
| 4 | .245 | .230 | .338 | 1.07 | 1.47 |
| 5 | .850 | .750 | .500 | 1.06 | .86 |
| 6 | .205 | .193 | .163 | 1.06 | .84 |
| 7 | .273 | .263 | .258 | 1.04 | .98 |
| 8 | .308 | .300 | .263 | 1.03 | .88 |
| 9 | .270 | .265 | .225 | 1.02 | .85 |
| 10 | .263 | .263 | .238 | 1.00 | .90 |
| 11 | .295 | .295 | .250 | 1.00 | .85 |
| 12 | .353 | .355 | .325 | .99 | .92 |
| 13 | .318 | .325 | .240 | .98 | .74 |
| 14 | .620 | .670 | .540 | .93 | .81 |
| 15 | .193 | .208 | .165 | .93 | .79 |
| 16 | .283 | .313 | .280 | .90 | .89 |

of the acidic samples then seemed negligible. It is speculated that the slight rise of temperature in the purge chamber might have contributed to the increase in stripping. The rise of temperature was caused by the exthothermic reaction of sulfuric acid reacting with water. For the alkaline samples, the explanation for the decrease in stripping efficiency might rest with fluid viscosity. Caustic added to the sample made the liquid slimy, thus making it more viscous, which in turn increased the liquid film resistance. Since the stripping air flow was kept at the same rate as in the other tests; no adjustment was made to offset the increased resistance, fewer specific compounds were stripped. In addition, foaming was a problem when the alkaline samples were being purged. Though precautions were taken, sometimes the foam would still make it into the trap and foul up the results.

As an after thought, caution must be exercised when drawing analogies between ammonia and specific compound stripping. Ammonia is far more soluble and less volatile than the specific compounds. Consequently, ammonia is more likely to be influenced by a greater number of factors, such as pH, temperature, and air-to-liquid ratios during the stripping process. The specific compounds of this investigation are so volatile and the purging sample volumes used so small (20 or 25 ml), it is likely that, as long as sufficient purging air was provided, stripping would occur regardless of the other factors. Furthermore, the aquatic chemistry of these two types of compounds could be vastly different. Ammonia is an inorganic compound and the specific compounds are organics. Aquatic chemistry will not be discussed here since it is beyond the scope of this study. Suffice to state that it is not appropriate to draw conclusions about the pH effect on specific compounds based on ammonia stripping.

Sonification

In this investigation, samples were sonified before being purged and quantified. It was believed that the application of sound waves (sonification) could liberate the specific compounds sorbed on the biomass and microorganisms, resulting in an increase of compounds stripped during purging.

The theory of sonification is best explained by the "gaseous cavitation" activity. If the sound wave applied to the liquid is strong enough, microscopic bubbles are formed and collapsed with explosive force, producing regions of intense pressure and local heating. In doing so, the biomass and microorganisms in the liquid are fragmentated.

This investigation's results are presented in graphic form as depicted in Figure 9. To gain a better understanding of the results, a brief explanation of the stripping kinetics is desirable. Using Haney's notation (52), the mathematical expression for stripping kinetics may be given as

$$-\frac{dC}{dt} = K' \cdot \left(\frac{A}{V}\right) \cdot (C_t - S) \qquad (6)$$

where $-\frac{dC}{dt}$ is the rate of change in concentration, K' the kinetic constant, A the area available for transfer, V the volume of fluid subjected to stripping, and $(C_t - S)$ the concentration of the removable volatile compound remaining at any time t. If the residual value S is neglibible or nonexistant and if $\frac{A}{V}$ is incorporated into the term K' to form an overall K constant, Equation (6) may be modified to become

$$-\frac{dC}{dt} = K \cdot C_t \qquad (7)$$

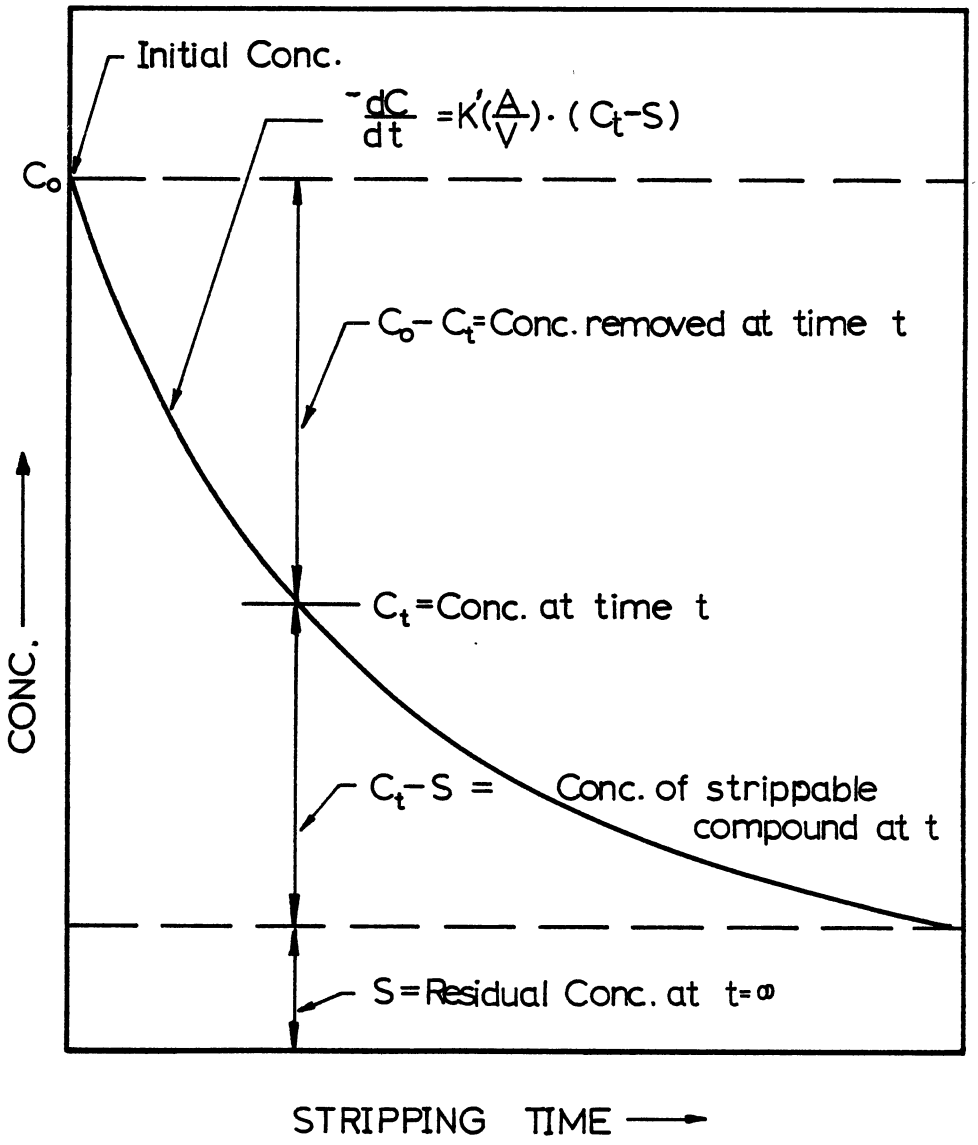



Figure 9. Schematic Diagram of Stripping Kinetics

The K constant is simply the slope of the line in Figure 9. K is compound specific and experimental condition specific. K, hereafter, will be referred to as slope or removal rate constant interchangeably.

Figures 10, 11, 12, and 13 present the results of the 1,2-DCE, 1,1,1-TCE, chloroform, and carbon tet investigations, respectively. Unlike Figure 9, the concentration term in these figures is expressed as a percentage of the initial concentration. It is seen that sonification did not improve the stripping efficiency of any tested compounds. As the sonification time increased, the specific compounds remaining decreased accordingly. The sound wave was such a powerful medium, it apparently acted as a stripping mechanism and removed the volatile compounds during sonification.

It is interesting to note that, for each specific compound, each sonification run (each line) had a different removal rate K (the slope). Attempts were made to correlate K to the initial concentration, Co. For both 1,2-DCE (Figure 10) and carbon tet (Figure 13), the line with the smaller slope (lesser slope) had the greater Co, meaning that the greater the initial concentration, the slower the removal rate of the compound. However, 1,1,1-TCE (Figure 11) and chloroform (Figure 12) did not exhibit this trend. In both cases, the slowest removal rate (the top line) had the lowest initial concentration.

Since no correlations were seen between K and Co, a relationship between K and the biomass (MLVSS) level was sought. This time, strong correlations were seen for all four compounds. With reference to Figures 10 to 13, it is seen that the lines with the smaller slope had the greater biomass concentration and, similarly, the line with the greatest slope (the left-most line) had the least biomass. The correlation is

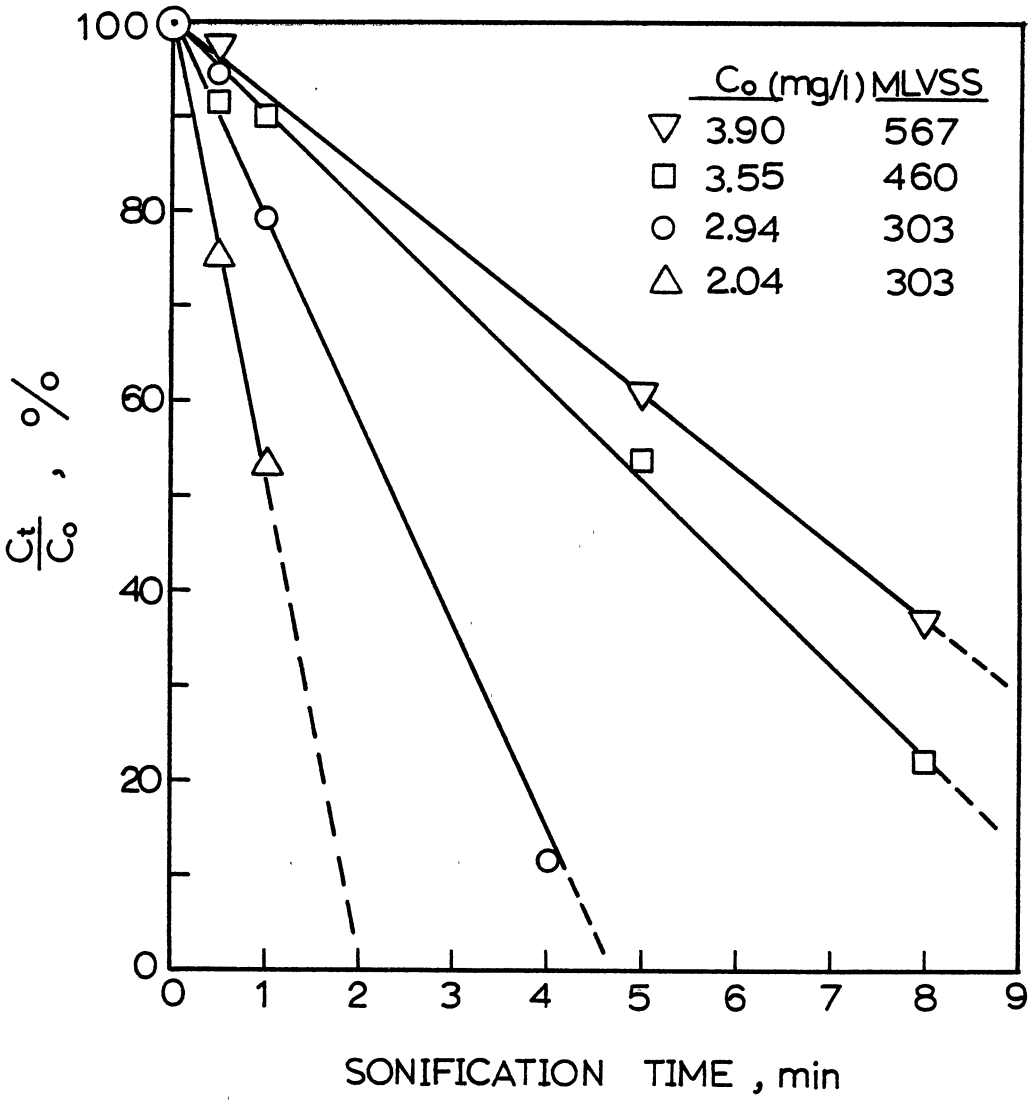



Figure 10. Sonification of 1,2-Dichloroethane, Arithmetic Plot

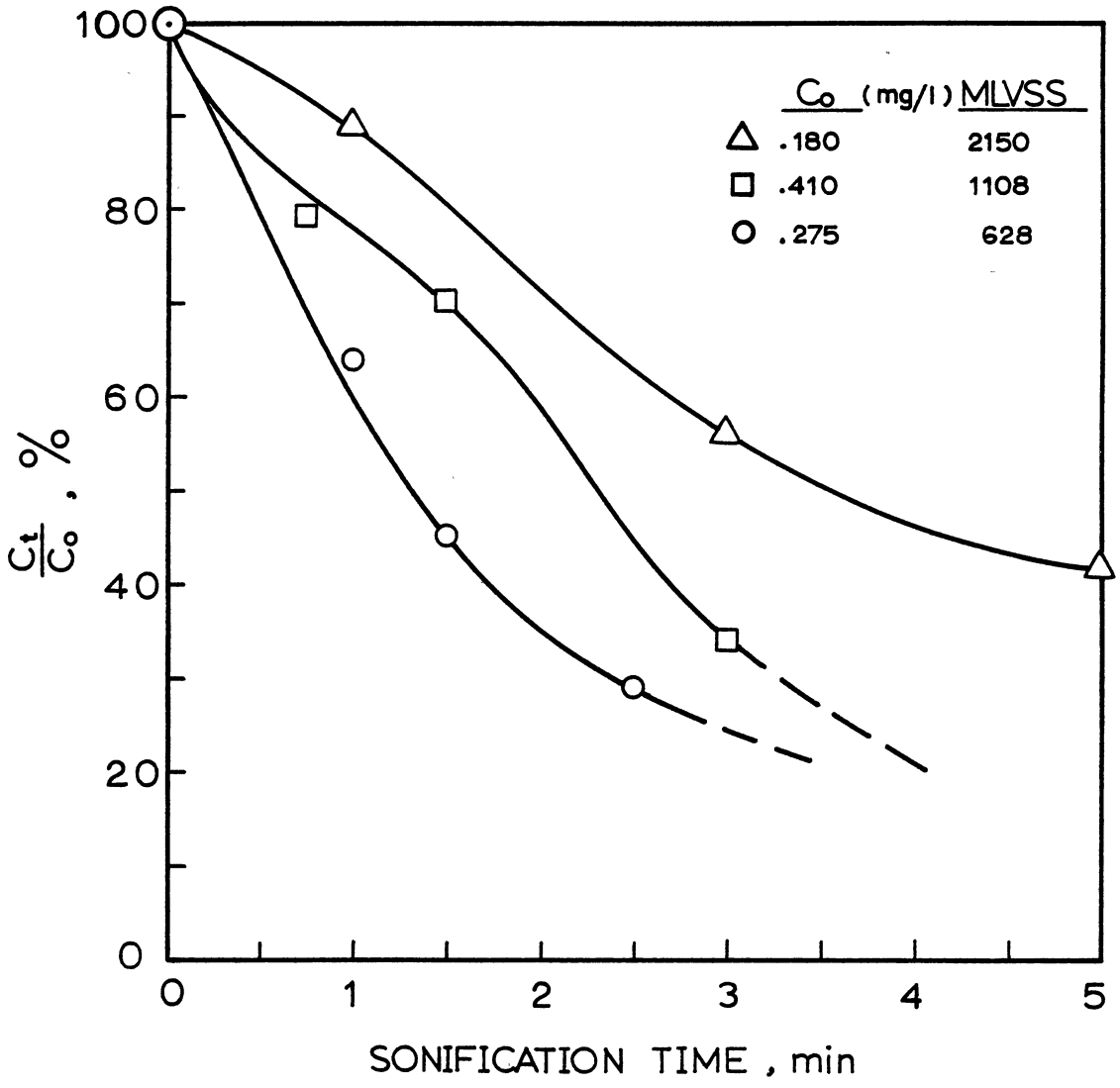



Figure 11. Sonification of 1,1,1-Trichloroethane, Arithmetic Plot

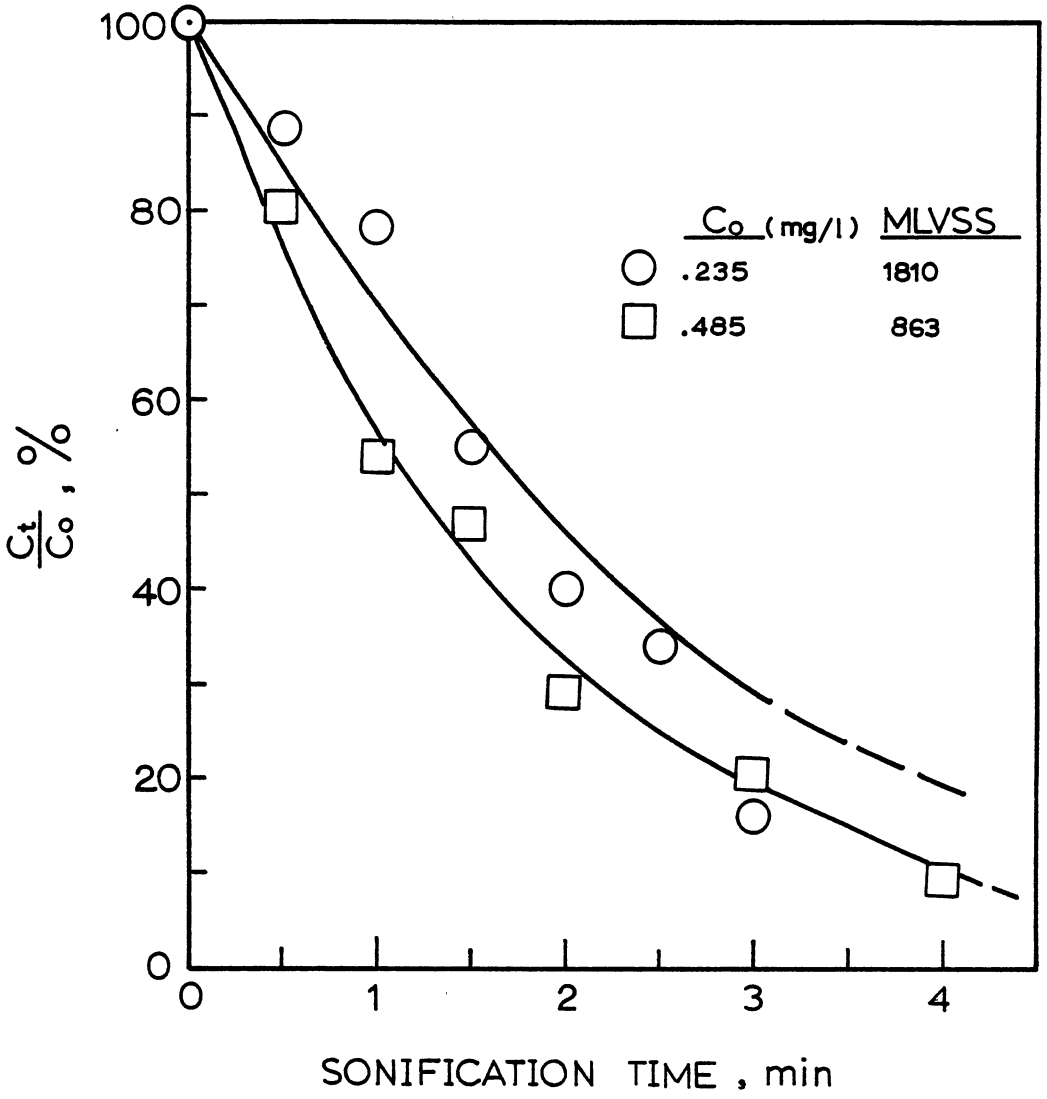



Figure 12. Sonification of Chloroform, Arithmetic Plot

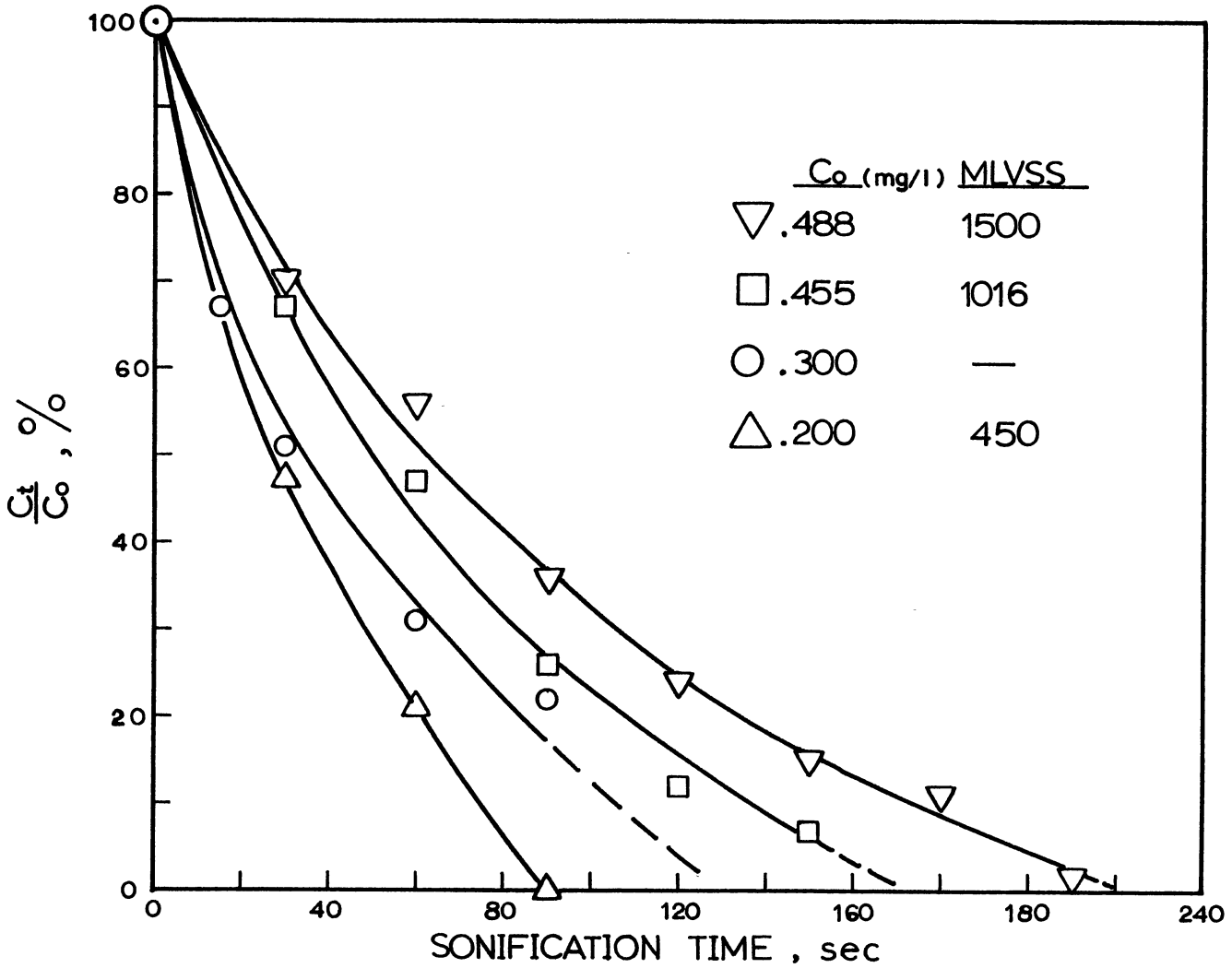



Figure 13. Sonification of Carbon Tetrachloride, Arithmetic Plot

perfectly logical considering that the biomass acted to resist the sound wave, as it did in the case of stripping. Therefore, the more biomass present, the greater the resistance to sonification, resulting in a smaller removal rate constant, K. The relationship between K and biomass level then indicates that K might be MCRT dependent.

Another point worth noting is that the 1,2-DCE concentration decreased linearly (Figure 10) while the other three compounds did not. To say that this discrepancy was compound specific would be the easy way out, therefore, no logical or technical explanation is offered here to account for the difference.

The linear relationship between concentration and time, given in Figure 10, is of major significance. It indicates that 1,2-DCE was probably sonified (stripped) in accordance with zero order kinetics, meaning that the removal rate was independent of the concentration reamining in the liquid at any time t. Figures 11, 12, and 13 were non-linear and, therefore, did not follow zero order kinetics. Attempts were then made to fit them to first order kinetics by plotting the data on semi-log coordinates.

The theory of first order kinetics simply states that the compound is removed at a rate which is constantly proportional to the concentration remaining at any time, t. The mathematical expression for first order kinetics can be easily derived. Equation (7) is rearranged such that $\frac{dC}{C_t} = -K \cdot dt$. Intergrating it between initial concentration, $C_o$, and any concentration, $C_t$, during the time period zero to t yields the equation

$$\ln \frac{C_t}{C_o} = -K \cdot t \qquad (8)$$

If a semi-log plot of concentration, $\frac{C_t}{C_o}$, against time, t, with a slope of K yields a straight line, then the reaction follows first order kinetics. Otherwise, it is non-first order.

Figures 14, 15, 16, and 17 give the semi-log plots of the four compounds. The curved lines of Figure 14 are an indication that 1,2-DCE was not removed according to first order kinetics. In other words, the rate of removal of 1,2-DCE was not concentration dependent. This confirms the finding of Figure 10 that 1,2-DCE was removed according to zero order kinetics. For the three other compounds, Figures 15, 16, and 17 show a combination of straight and curved lines, indicating that for each compound, some were removed in accordance with first order kinetics while others were non-first order. The one common trend among the three compounds was that the straight lines (first order kinetics) were indicative of those systems with the lowest MLVSS values. It seems to indicate that there was a threshold biomass level below which, removal rate became a function of the compound concentration, resulting in first order kinetics. When the biomass level exceeded that threshold level, then the removal rate became independent of compound concentration and, became a function of biomass level only. In such a case, nethier zero nor first order kinetics applys. Judging by the available data, for 1,1,1-TCE, chloroform, and carbon tet, the threshold biomass level was estimated to be approximately 860 mg/l.

In a further attempt at data fitting, the data were plotted on log-log coordinates. Since no correlations were observed, no graphs are presented here and a discussion is considered unnecessary.

Based on the results of this investigation, it was found that:

1. Sonification did not improve stripping efficiency.

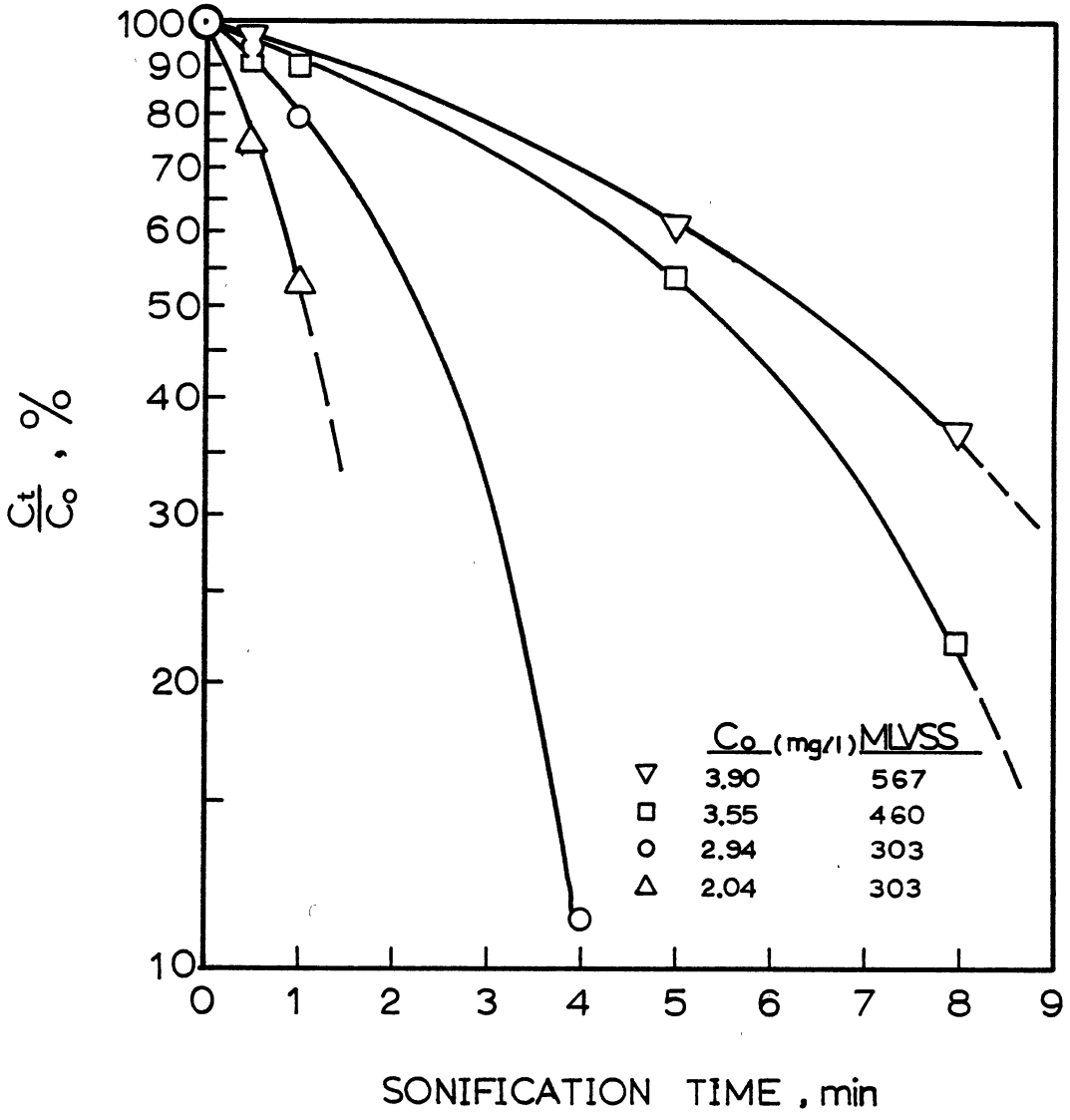



Figure 14. Sonification of 1,2-Dichloroethane, Semi-Log Plot

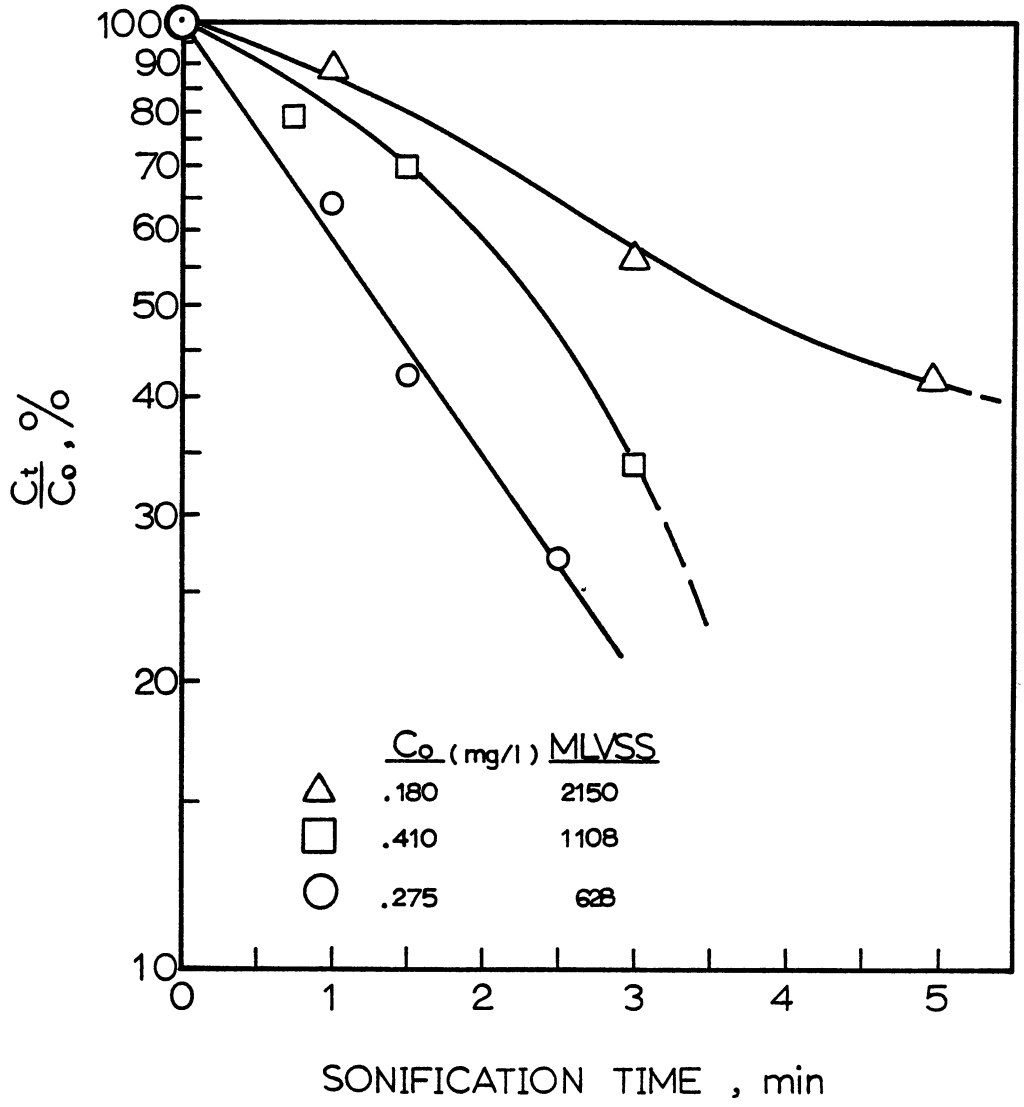



Figure 15. Sonification of 1,1,1-Trichloroethane, Semi-Log Plot

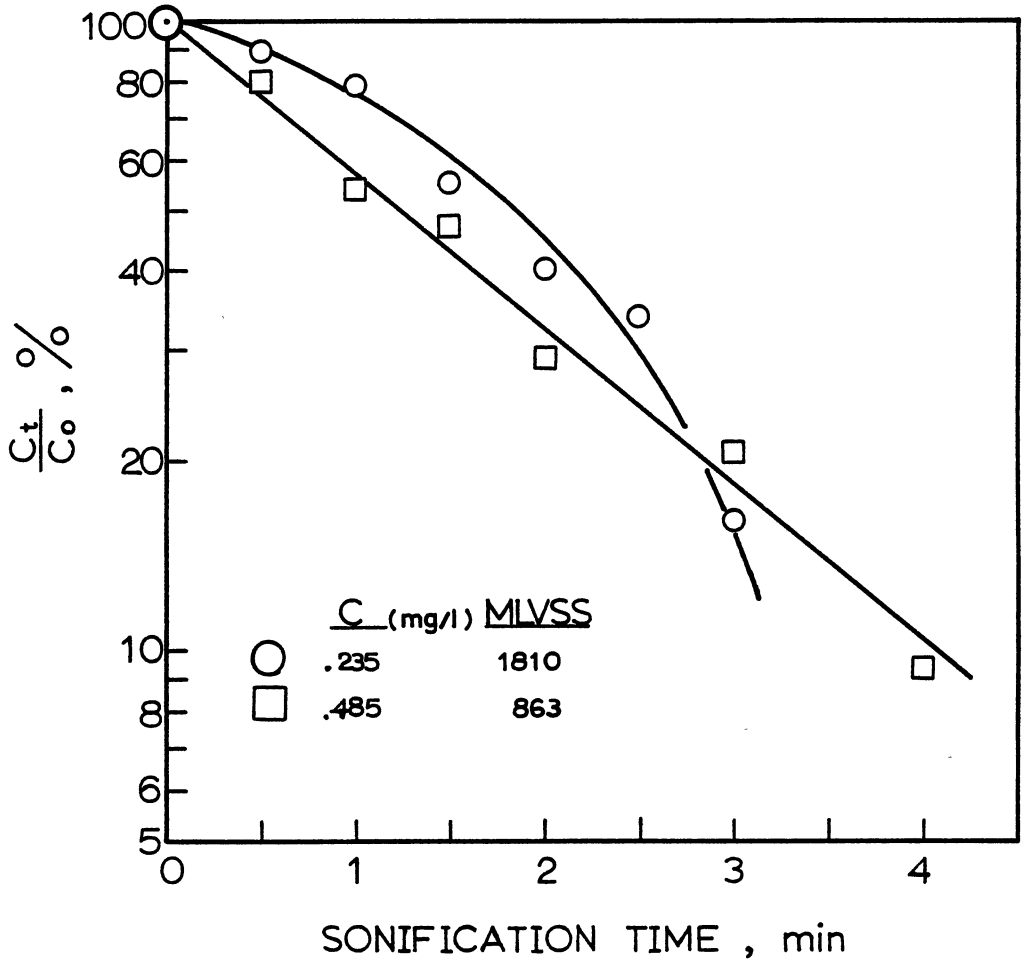



Figure 16. Sonification of Chloroform, Semi-Log Plot

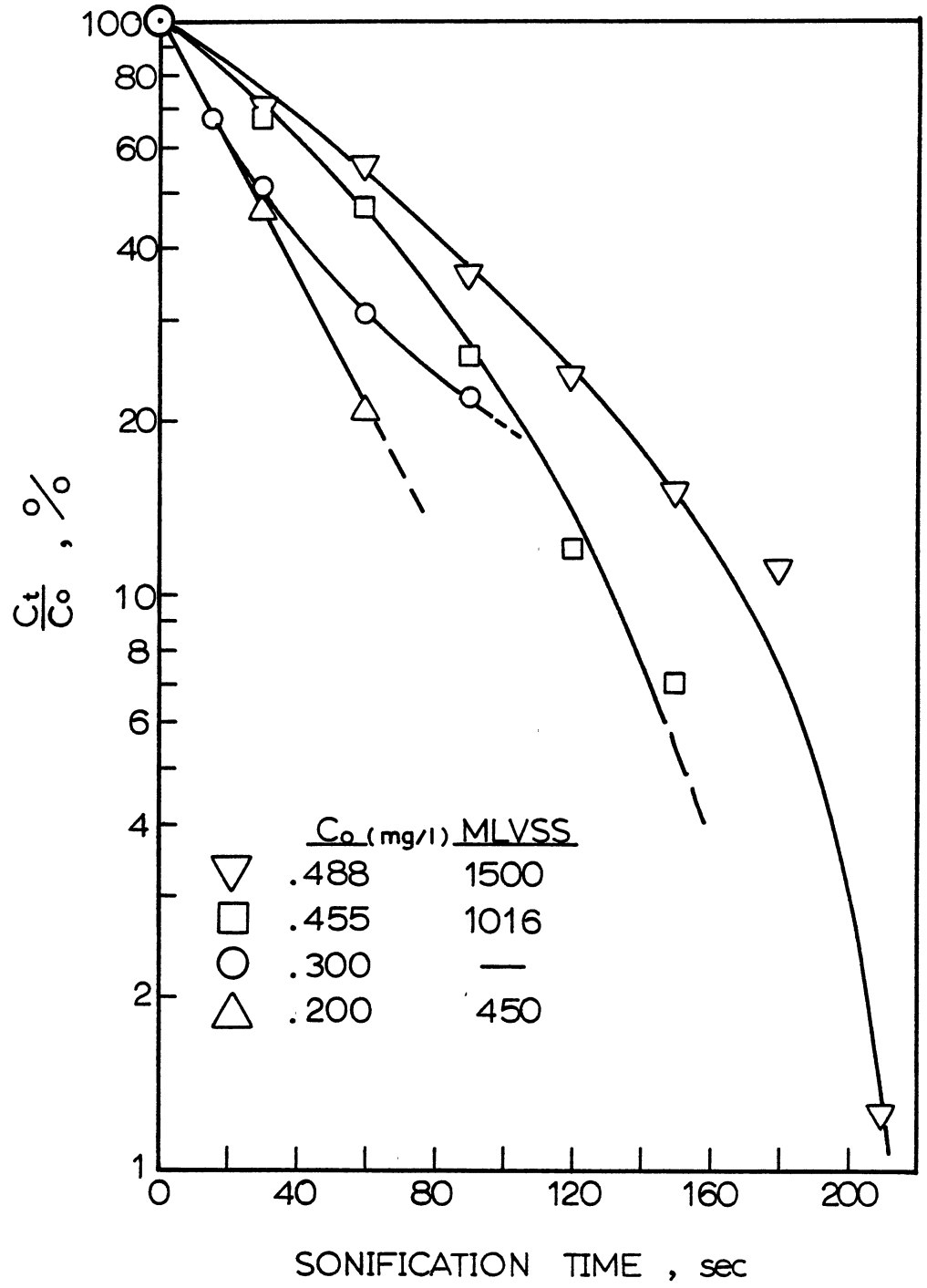



Figure 17. Sonification of Carbon Tetrachloride, Semi-Log Plot

2. The removal rate constant, K, was independent of the initial concentration $C_o$, but was a function of the biomass level, as the higher the biomass level the lesser the K values.

3. It can not be assumed that zero or first order kinetics characterized the sonification of all volatile compounds. The kinetic orders determined were compound specific, and cases existed which neither zero nor first order kinetics described the data well.

4. For some data points, such as that of carbon tet in Figure 17, a straight line could be obtained to fit first order kinetics if only a few points were moved up or downward slightly. This points out the difficulties of data reproducibility when using small samples. If possible, larger samples should be used.

## Purge Chamber Configurations

Two samples of equal volume and having the same concentration of specific compounds were introduced into two different purge chambers, they were then purged and quantified. The special chamber had a coarse porcelain sieve at the bottom which served as a diffuser, while the regular chamber had none. Otherwise, the two chambers were identical to one another in every respect. The dimensions and configuration of the chambers were given in the materials and methods section of this study.

The results given in Table XVI indicate that the quantities stripped were almost identical for both types of chamber; the differences were well within the limit of the 5 percent reproducibility/errors factor. Clearly, the special purge chamber was not superior to the regular type.

The special chamber had been expected to give higher results. The expectation was based on the assumption that, as the diffuser broke up

TABLE XVI

SPECIFIC COMPOUNDS CONCENTRATIONS OBTAINED
FROM DIFFERENT PURGE CHAMBERS

| Compound | Sample No. | Conc. (mg/l) | | Ratio |
|---|---|---|---|---|
| | | No Diffuser | Diffuser | No Diffuser:Diffuser |
| Chloroform | 1 | .545 | .490 | 1.11 |
| | 2 | .270 | .270 | 1.00 |
| | 3 | .293 | .295 | .99 |
| | 4 | .630 | .635 | .99 |
| | 5 | .425 | .440 | .97 |
| | 6 | .218 | .228 | .96 |
| | 7 | .540 | .570 | .95 |
| | 8 | .200 | .215 | .93 |
| Carbon Tet | 1 | .060 | .059 | 1.02 |
| | 2 | .254 | .250 | 1.02 |
| | 3 | .100 | .100 | 1.00 |
| | 4 | .220 | .224 | .98 |
| | 5 | .248 | .254 | .98 |
| | 6 | .052 | .055 | .95 |

the incoming stripping air, the finer bubbles formed would increase the gas-liquid interfacial area, thus enhancing the mass transfer of the volatile compounds from the liquid to the gas phase. In addition, the diffuser facilitated better mixing by spreading the bubbles outwardly and uniformly in the narrow cylindrical body of the chamber. The regular chamber had none of these attributes, but since there was no pressure reducer (the diffuser) in the chamber body, the intensity and stirring of air bubbles might have been greater. However, none of these factors apparently made any difference in the stripping of chloroform and carbon tet.

Based on the information of Table XVI, these conclusions are drawn:

1. Purge chamber configurations made no difference in the stripping efficiency of chloroform and carbon tet.

2. As long as sufficiently intense purging air is provided, factors such as pH and temperature become secondary, and stripping will go to completion regardless of the type of purge chamber used.

3. Some capital saving can be realized by employing the cheaper regular purge chamber with no sacrifice in stripping efficiency.

4. The above three conclusions also apply to 1,2-DCE, 1,1,1-TCE, and TCE, since the Henry's constants of the three compounds are all of the same order of magnitude ($10^{-3}$) as chloroform.

## Stripping (Purging) Time

Samples with identical concentrations were taken and purged for various time durations. The goals were to establish a relationship between the quantity of compound stripped and the purge time and to improve the stripping efficiency.

Figures 18 and 19 give the respective results of the two and six day chloroform tests. Figure 20 presents the six day carbon tet results. As expected in a batch system, the hyperbolic-shaped curves indicate that the quantity of compound stripped increases in direct relation to the purge time until 100 percent stripping has been reached. Note that the "minimum-purge-times" to achieve essentially 100 percent stripping were nine and six minutes for chloroform and carbon tet, respectively.

Four major observations were made from these three figures: 1) the specific compound concentration in the reactor varied according to the feed concentration, 2) the minimum-purge-time was compound specific but not MCRT specific, 3) Henry's constants were a good approximate measurement of compound stripability, and 4) the minimum-purge-time of a compound should be determined first for any PAT analysis. Each of these will be discussed briefly.

The hyperbolic-shaped curves for Figures 18, 19, and 20 were based on specific compound analyses and were obtained by varying the feed concentrations. Thus, higher feed resulted in a greater concentration in the ML. If the curves were BOD, COD, or TOC based, it is suspected that the concentrations in ML would not vary according to the feed concentrations, since chloroform and carbon tet exert little BOD, COD, or TOC.

The minimum-purge-times of the two and six day chloroform systems were both nine minutes. Though the minimum-purge-time of the two day carbon tet system was not determined, it is strongly believed that it was the same as that of the six day system, 6 minutes. This conclusion was derived by reason of deduction. Since carbon tet is more volatile than chloroform, what holds true for chloroform must also apply to carbon tet. The different minimum-purge-times of the two compounds

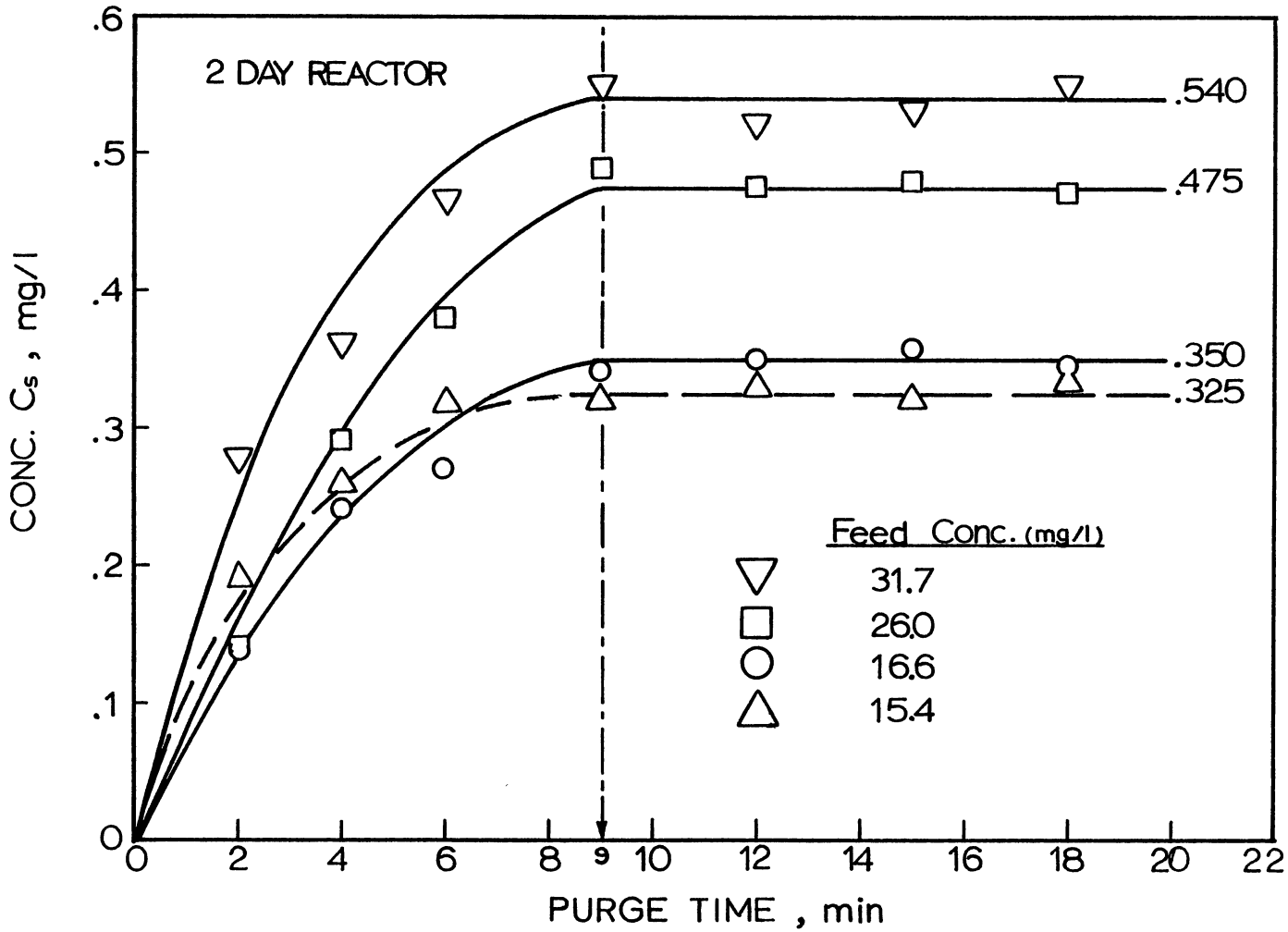



Figure 18. Chloroform Stripped in Various Purging Time, Two Day MCRT

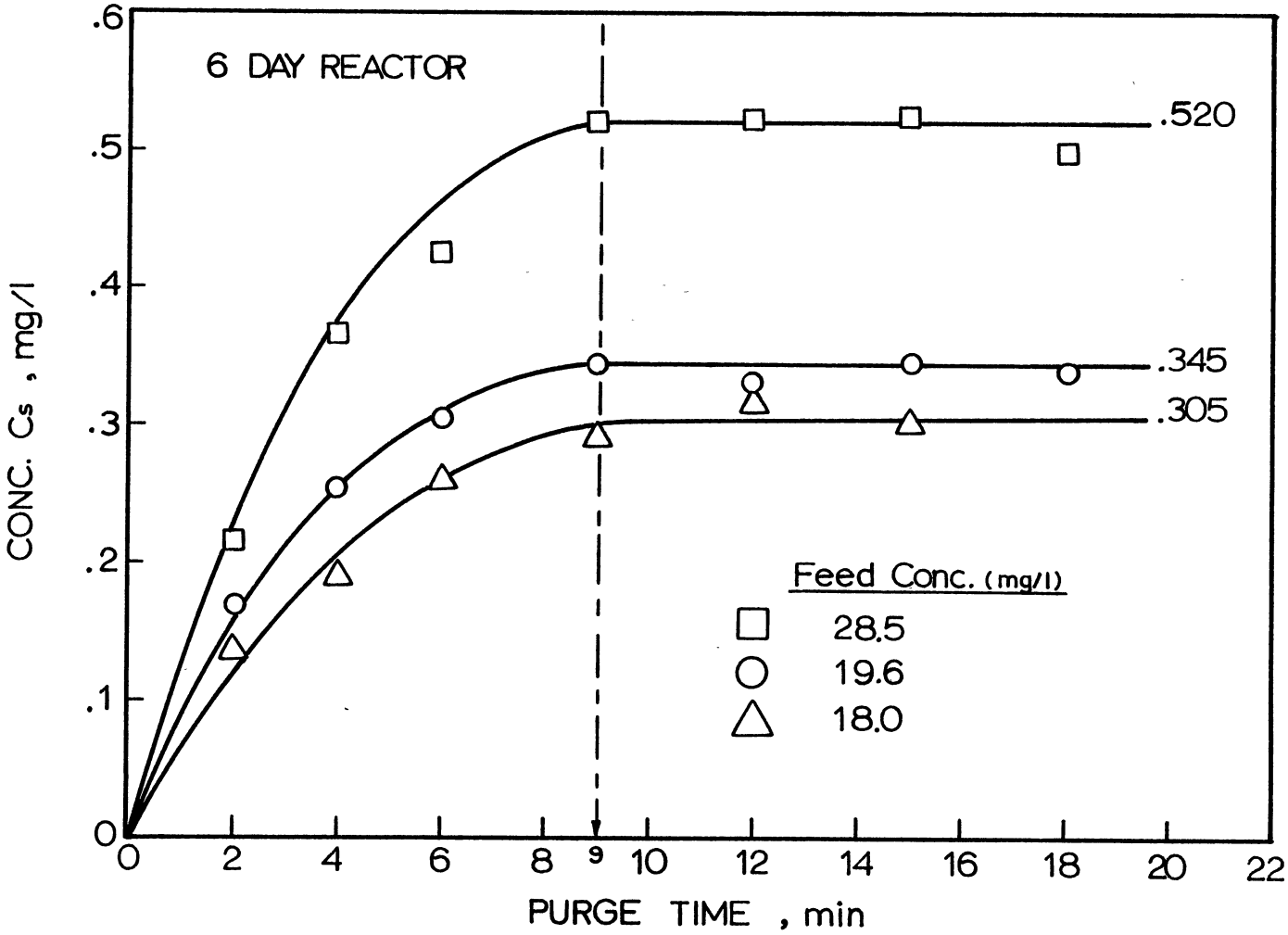



Figure 19. Chloroform Stripped in Various Purging Time, Six Day MCRT

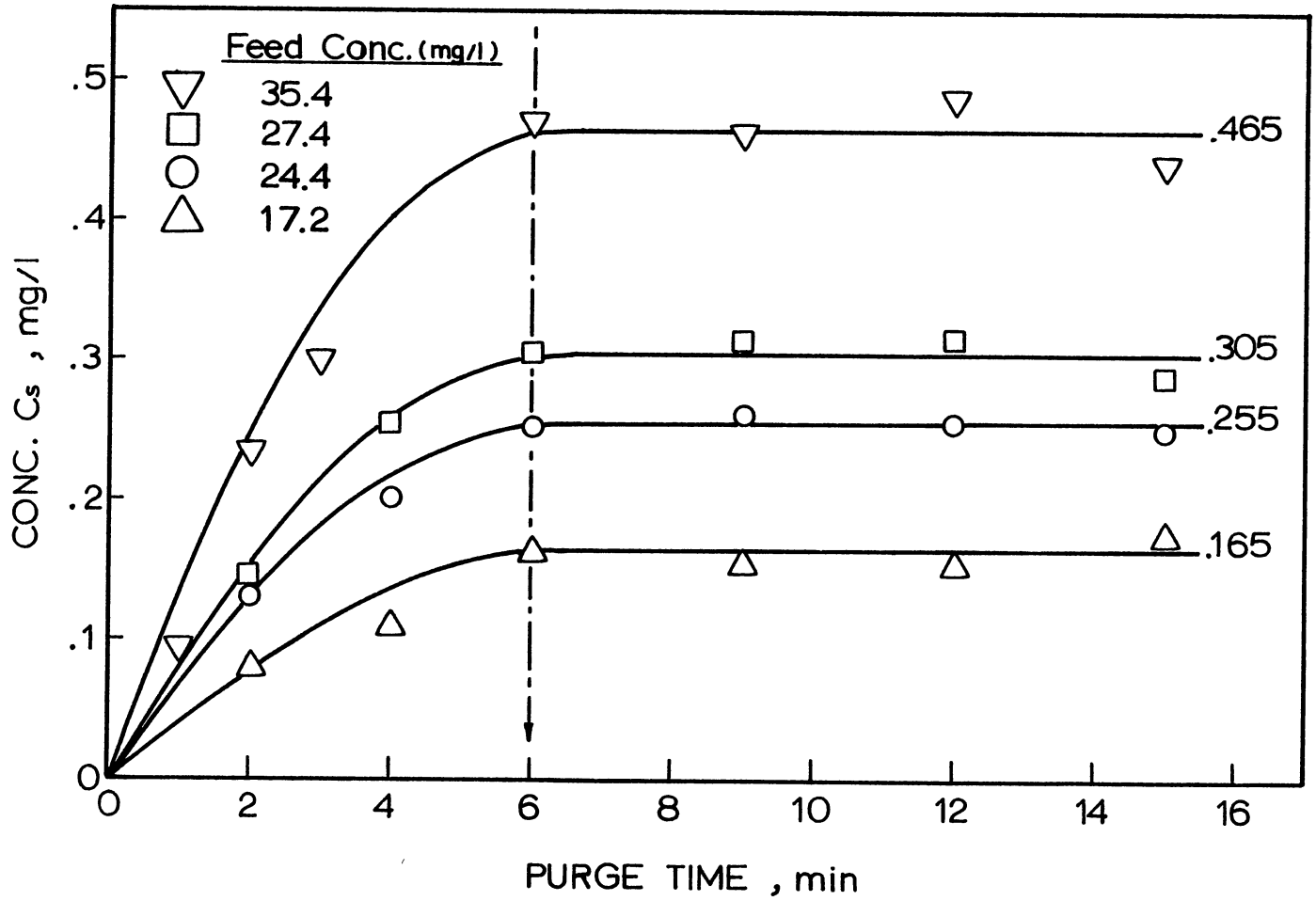



Figure 20. Carbon Tetrachloride Stripped in Various Purging Time, Six Day MCRT

clearly indicate that it was compound specific. But the minimum-purge-time of each compound was not MCRT specific, indicating that it was independent of biomass level. This is due to the very high air-to-liquid ratio used for purging in the PAT analyses. In this study, the PAT air-to-liquid ratio was 3.0 (60 ml/min air to 20 ml sample purged, 60/20 = 3.0), whereas the six day aeration reactor had a ratio of .67 (2 l/min air to 3 l ML, 2/3 = .67).

Henry's constant explains the different minimum-purge-times for the different specific compounds. Note that the Henry's constant of carbon tet ($3.0 \times 10^{-2}$) is about ten times the value of chloroform ($3.4 \times 10^{-3}$), indicating that carbon tet is far more volatile than chloroform. This explains why the minimum-purge-time of carbon tet was only six minutes, and chloroform, nine minutes. For 1,1,1-TCE, under the identical conditions, the minimum-purge-time should be slightly less than or equal to nine minutes, since its Henry's constant of $4.9 \times 10^{-3}$ is slightly greater than chloroform's $3.4 \times 10^{-3}$. By the same analogy, the minimum-purge-time for 1,2-DCE and TCE would be greater than nine minutes due to their slightly smaller Henry's constants ($1.1 \times 10^{-3}$ for 1,2-DCE, $1.2 \times 10^{-3}$ for TCE). Therefore, it may be concluded that Henry's constant is a good indicator of compound stripability.

The minimum-purge-time also raised concerns about the need to follow strict laboratory analytical procedures in accordance with the EPA guidelines. Bellar and Lichtenberg (17) recommended the following stripping parameters: purge time - 11 minutes, sample volume - 5 ml, $N_2$ purge rate - 20 ml/min. For Kincannon and Stover (5), the parameters were 12 minutes, 25 ml, and 40 ml/min, respectively. It should be

recognized that the purge time and purge rate are sample volume and concentration dependent, and also compound specific. No one set of operating parameters applies to all compounds. Therefore, it is recommended that the minimum-purge-time of a specific compound be determined before conducting any analysis by the PAT technique.

As part of the data fitting effort, the data from Figures 18, 19, and 20 were plotted on semi-log paper to determine if "exponential stripping" existed between purge time of zero and the minimum-purge-time. Since a straight line could not be drawn through the data points, it was concluded that exponential stripping did not take place for any of the compounds. The graphs are not shown here.

To determine if the stripping of the compounds followed first order kinetics, Figures 21 and 22 were plotted for chloroform and carbon tet, respectively. $C_o$ is the maximum quantity of compound stripped. $C_t$, the concentration remaining at time t, was obtained by subtracting $C_s$, the quantity stripped at time t, from $C_o$. It is seen that the six day chloroform data fitted the straight line fairly well, but two day chloroform and carbon tet did not. It was decided that the kinetic data lacked consistency to draw any definite conclusions. The kinetics could be interpreted as zero, first, or non-first order, depending on how one draws the line through the data points.

When the same data were plotted on log-log coordinates, a good fit was obtained for both chloroform (Figure 23) and carbon tet (Figure 24). A mathematical relationship could approximate the data points between the two minute purge time and the minimum-purge-time as:

$$C_s = c \cdot T^n \qquad (9)$$

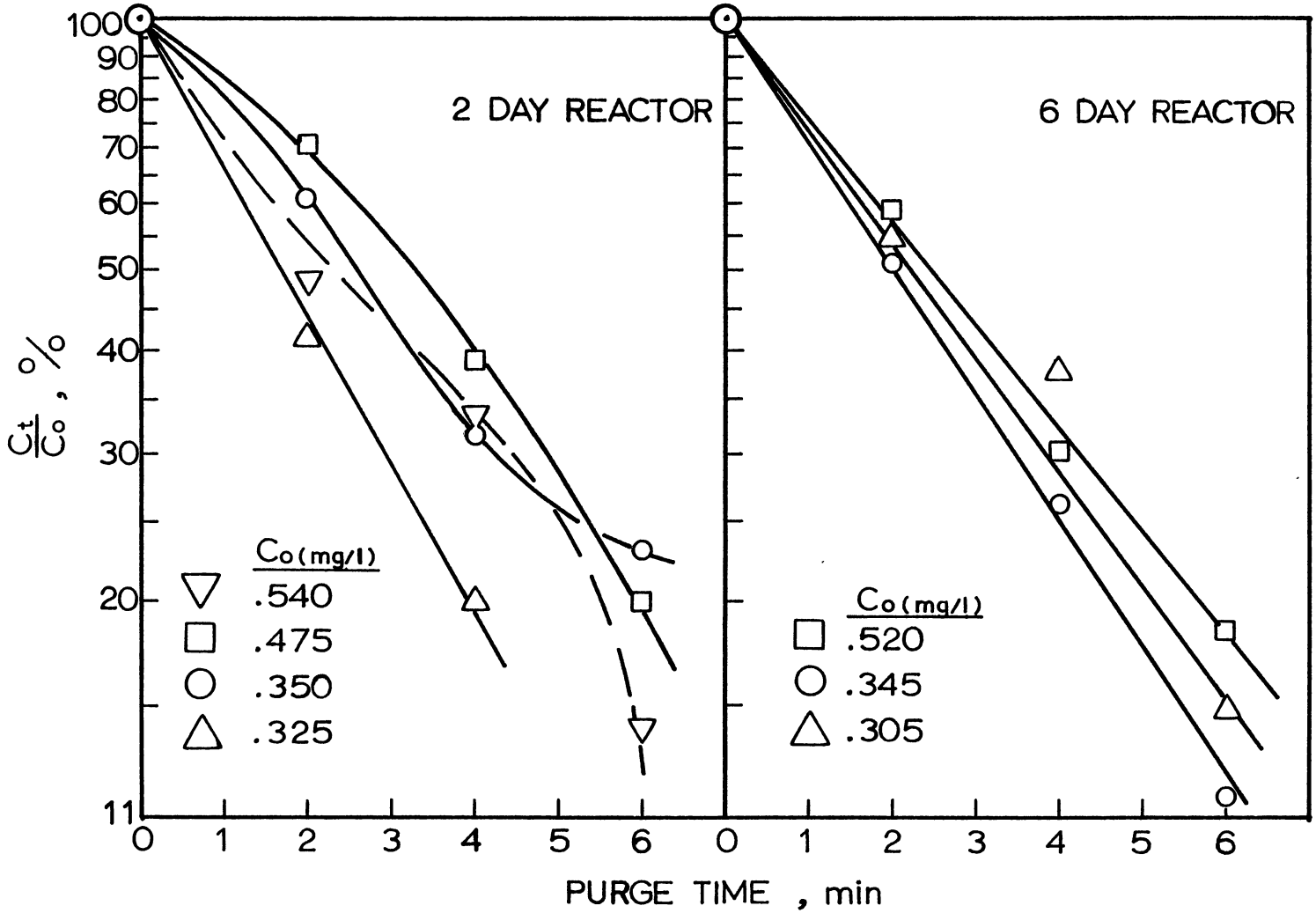



Figure 21. Stripping of Chloroform, Semi-Log Plot

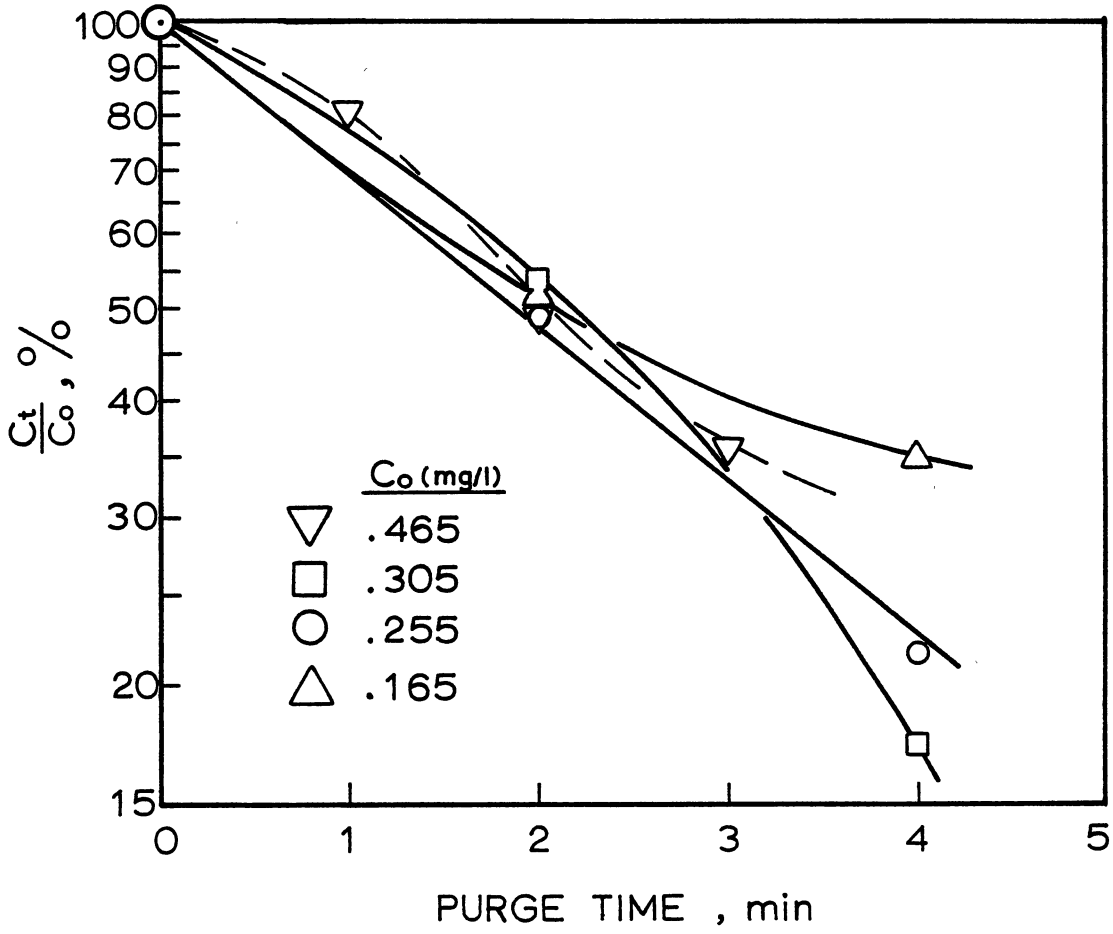



Figure 22. Stripping of Carbon Tetrachloride, Semi-Log Plot

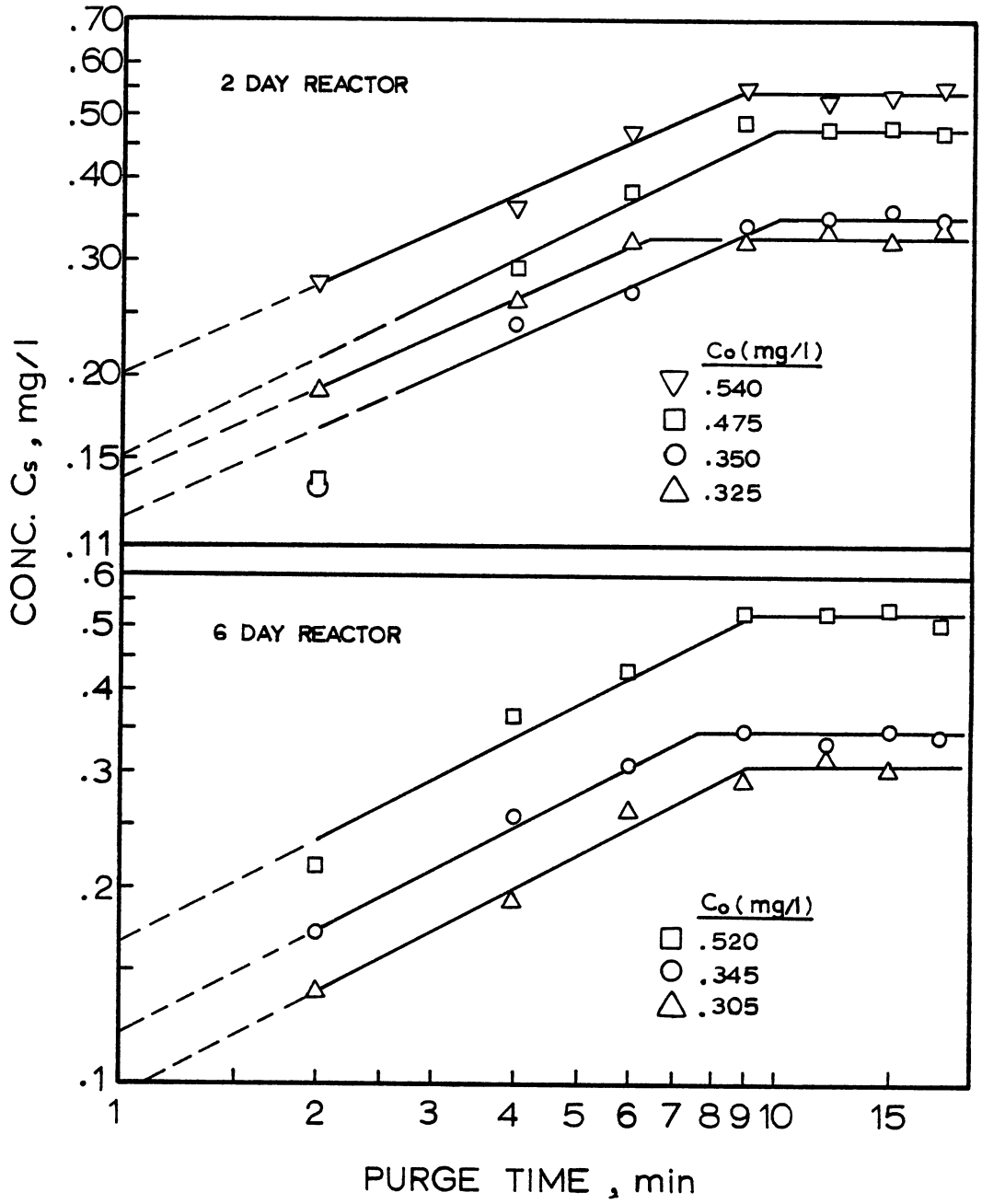



Figure 23. Stripping of Chloroform, Log-Log Plot

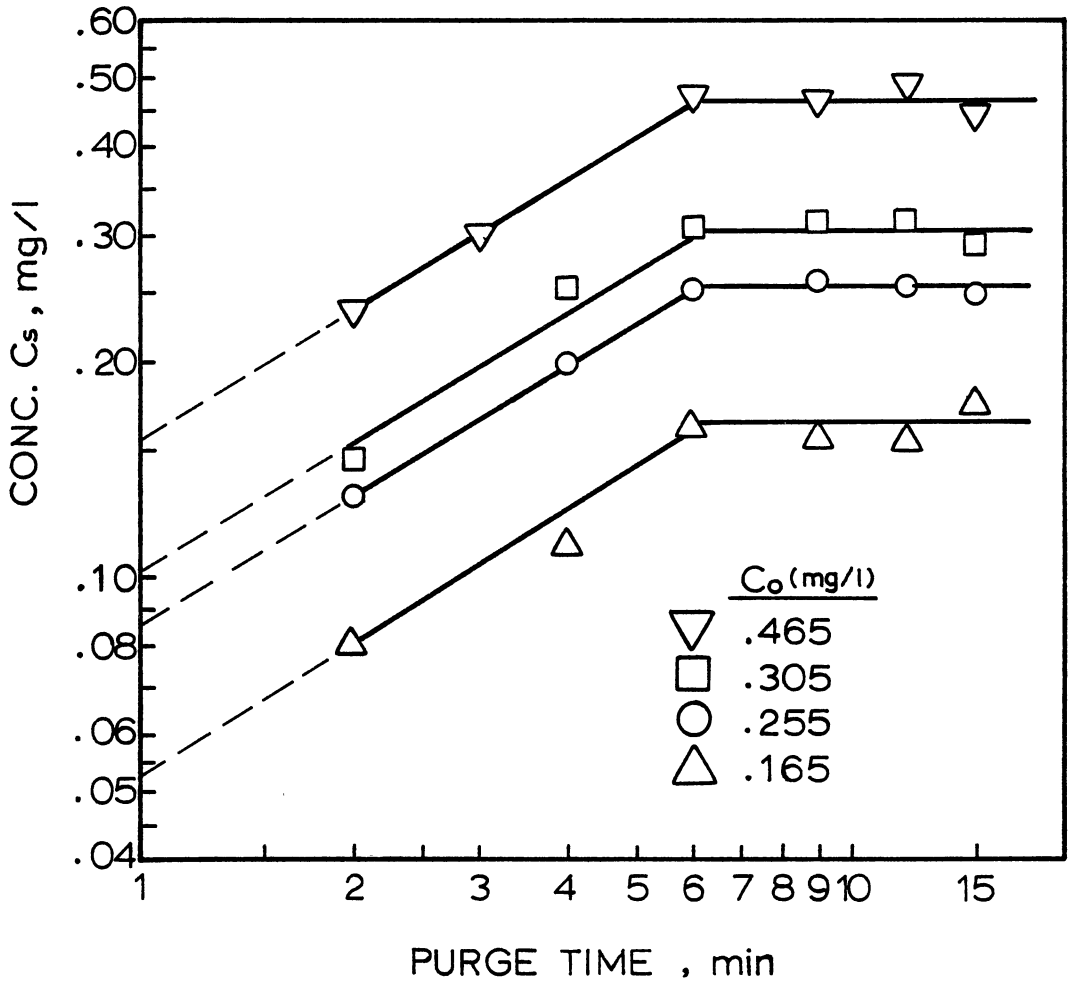



Figure 24. Stripping of Carbon Tetrachloride, Log-Log Plot

where $C_s$ is the compound quantity stripped at any time, t, c and n are constants, and T the purging time. By taking the natural log on both sides of Equation (9), the following expression is obtained:

$$\ln C_s = \ln c + n \cdot \ln T \qquad (10)$$

where n is the slope of the line, and c is the y-intercept in Figures 23 and 24. Table XVII gives the values of c and n computed from Figures 23 and 24. Note the n, the slope, is not only compound specific but also MCRT specific. C, however, does not remain constant for every experimental run of a compound at a specific MCRT. It is speculated that c, in addition to being compound and MCRT specific, may also be concentration dependent. The significance of this finding is that the stripping of volatile compounds by the PAT technique is not necessarily zero or first order, but rather, could be described by a simple mathematical expression such as that of Equation (9) stating that the quantity stripped, $C_s$, is a function of the stripping time, T, raised to some constant, n, and multiplied by a factor, c.

## Effectiveness of PAT Technique

Table XVIII gives the repurging results of three volatile compounds. It shows that the second purging of an once-purged sample had non-detectable amounts of compound remaining. The repurging test and other tests, such as those shown in Figures 6, 7, 18, 19, and 20, add support to the belief that the PAT technique was capable of completely stripping off the volatile compound in a sample, provided that sufficient purge air was provided.

TABLE XVII

STRIPPING CONSTRANTS c AND n

| Compound | $C_o$ (mg/l) | Slope n From Graph | c | |
|---|---|---|---|---|
| | | | From Graph | Calculated |
| Chloroform | .540 | .447 | .200 | .202 |
| Two Day | .475 | .500 | .150 | .150 |
| | .350 | .457 | .140 | .139 |
| | .325 | .449 | .121 | .122 |
| Six Day | .520 | .518 | .165 | .164 |
| | .345 | .521 | .119 | .120 |
| | .305 | .518 | .095 | .097 |
| Carbon Tet | .465 | .603 | .155 | .155 |
| Six Day | .305 | .600 | .102 | .101 |
| | .255 | .602 | .086 | .085 |
| | .165 | .623 | .053 | .052 |

TABLE XVIII

SPECIFIC COMPOUNDS RECOVERIES AFTER REPURGING

| Compound | Sample No. | Conc. (mg/l) | |
|---|---|---|---|
| | | First Purge | Repurge |
| 1,1,1-TCE | 1 | .195 | B.D.L.* |
| | 2 | .260 | B.D.L. |
| | 3 | .420 | N.D.** |
| | 4 | .430 | N.D. |
| TCE | 1 | .136 | B.D.L. |
| | 2 | .175 | B.D.L. |
| | 3 | .310 | B.D.L. |
| Carbon Tet | 1 | .160 | N.D. |
| | 2 | .383 | B.D.L. |
| | 3 | .440 | B.D.L. |

*B.D.L. = Below Detection Limit

**N.D. = No Detection

## Feed Variance and Tank Level

During the biosorption investigation, it was speculated that the specific compound concentration in the feed solution might vary according to the headspace available in the feed tank. The results given in Table XIX clearly indicate that the feed concentration of the chloroform and carbon tet did vary according to the feed tank level.

TABLE XIX

FEED TANK LEVEL VERSUS SPECIFIC COMPOUND CONCENTRATIONS

| Compound | Feed Batch No. | Tank Level (%) 100% = Full Tank | Feed Con. (mg/l) |
|---|---|---|---|
| Chloroform | 1 | 85 | 34.2 |
| | | 58 | 27.2 |
| | 2 | 67 | 37.0 |
| | | 33 | 32.6 |
| | 3 | 65 | 18.0 |
| | | 40 | 16.6 |
| | 4 | 60 | 28.5 |
| | | 53 | 26.0 |
| | | 31 | 23.0 |
| Carbon Tet | 1 | 100 | 22.0 |
| | | 60 | 20.0 |
| | 2 | 73 | 30.0 |
| | | 36 | 24.4 |
| | 3 | 69 | 56.6 |
| | | 38 | 41.0 |
| | 4 | 44 | 30.8 |
| | | 33 | 27.2 |

# CHAPTER V

## CONCLUSIONS

The results of this study lead to the following conclusions:

1. Biosorption did take place in the activated sludge reactor. The quantity of biosorption was insignificant when the error factor was taken into consideration.

2. The testing methods for determining biosorption appeared to be adequate.

3. pH alteration exerted no appreciable positive impact on stripping efficiency. With all other variables equal, alkalinity resulted in decreased stripping efficiencies.

4. Sonification had a negative impact on stripping efficiency. The sonification removal constant, K was independent of the specific compound concentration but related to the biomass level. High biomass levels resulted in lower K's. Also, it can not be assumed that all volatile compounds will be sonified in accordance with zero or first order kinetics.

5. Different types of purging chamber configuration had no impact on stripping efficiency.

6. Purging (stripping) time had a positive impact on stripping. As stripping time increased the quantity stripped also increased untill all compounds were depleted. It can not be assumed that all volatile compounds will be stripped in accordance with zero or first order kinetics. However, the quantity stripped may be expressed by a simple equation of $C_s = c \cdot T^n$

7. The PAT technique is capable of complete (100%) stripping. PAT is the best available technology (BAT) currently available.

# CHAPTER VI

## SUGGESTIONS FOR FUTURE WORK

1. Larger sample volume should be used by PAT technique to improve the reproducibility factor.

2. Effect of biomass level on concentration should be studied in depth by covering wider range of biomass in smaller increments.

3. Effect of biomass concentration on stripping should be investigated.

4. Combined effect of acidity and temperature should be studied in more detail.

5. Distillation as a means of improving the stripping efficiency should be investigated.

6. Off-gas analysis should be conducted in conjunction with all tests to gain a complete picture of the material balance.

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Candidate for the Degree of

Master of Science

Thesis: AN INVESTIGATION OF BIOSORPTION AND THE PURGE-AND-TRAP ANALYTICAL TECHNIQUE FOR SELECTED HALOGENATED HYDROCARBONS IN ACTIVATED SLUDGE SYSTEMS

Major Field: Bioenvironmental Engineering

Biographical:

Personal Data: Born April 28, 1955, in Taiwan, Republic of China, the son of Dr. and Mrs. Alan C.H. Hu.

Education: Graduated from Sumter High School, Sumter, South Carolina, in May, 1973; received Bachelor of Chemical Engineering Co-Operative Plan from Georgia Institute of Technology in June, 1978; completed requirements for the Master of Science degree in Bioenvironmental Engineering at Oklahoma State University in December, 1984.

Professional Experience: Co-operative Engineer, Columbia Nitrogen and Nipro Incorporated, 1973-1977; Environmental Engineer, FMC Corporation, 1978-1980; Graduate Research Assistant, Department of Bioenvironmental Engineering, Oklahoma State University, 1980-1983.