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SORPTION, DESORPTION, AND BIODEGRADATION OF NATURAL ORGANIC MATTER AND PESTICIDES ON SPENT GRANULAR ACTIVATED CARBON

Roger W. Babcock, Jr.
Veronica Ewald
Mitch Uehara

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Project Completion Report
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" Investigation of sorption, desorption, and bioregeneration of natural organic matter and pesticides on granular activated carbon used to treat contaminated drinking water "

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Principal Investigator: Roger W. Babcock, Jr.

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EXECUTIVE SUMMARY

More than fifty years ago, pesticide use in central Oahu began as Hawaii's agricultural economy was flourishing. These pesticides were necessary in order to prevent pests and other parasites from infecting or otherwise harming sugarcane and pineapple crops. Three of these pesticides (dibromoethane - EDB, trichloropropane - TCP, and dibromochloropropane - DBCP) caused a great deal of alarm in the early 1980s when trace amounts of each were identified in the well water supplies of central Oahu. Their presence rallied the State to find a solution to their source, containment, and treatment. The pesticide problem posed a unique challenge to the State and Federal governments since regulatory limits were not established for them. In 1992, the Hawaii State Department of Health (DOH) established maximum contaminant levels (MCLs) of 40 ng/L for EDB and DBCP and 800 ng/L for TCP.

In order to treat the contaminated water, the Board of Water Supply (BWS) reviewed several treatment schemes and chose to use granular-activated carbon (GAC) contactors. These contactors were designed and installed in Waipahu, Mililani, and Kunia. To date, all continue to operate and more contactors are being designed for installment in other areas. The contactors are extremely efficient in removing the pesticides from the water; however, spent carbon disposal has been a concern. The BWS has sought to find alternative means to disposal to prolong the carbon's useful life and minimize operating cost (currently, disposal and replacement costs are greater than $400,000 per year). It is this problem that is addressed by the study conducted here. This study incorporates both regeneration and biodegradation components in order to develop a complete bioregeneration process. The available literature has described several regeneration options; however, solvent regeneration was the focus here. Solvents included in this study were acetone and 2-propanol used in conjunction with hydrochloric, acetic, and formic acids and sodium hydroxide. Included in the regeneration portion of this study were separate experiments to determine competition between the pesticides and the natural organic matter (NOM) that exists in the water. This was a necessary objective in order to see if the NOM greatly interferes with pesticide adsorption which would cause premature breakthrough. Biodegradation studies were conducted in batch tests to determine the extent of biodegradation under aerobic, anoxic, and anaerobic conditions.

Current results have shown that pesticide removal from the spent carbon is effective using formic acid and acetic acid without additional solvents. Removal of the pesticides were upwards of 80% using acetic acid and over 95% using formic acid. However, neither removed more than 25% of the DBCP adsorbed onto the carbon. Hydrochloric acid removed about 50-70% of each pesticide and sodium hydroxide removed about 40% of each. When combinations of regenerants

were attempted, these percentages soared. When any of the acids or the base were used with either acetone or 2-propanol, removal percentages increased to almost 99% for all three pesticides. Though work in the field of solvent regeneration is not complete, these data show promise and it is hoped that one combination will be optimized to provide the practical balance between regeneration efficiency and cost.

From the long-term experiments to determine NOM competition, conclusive results have been difficult to draw. It seems that NOM is adsorbed, however, interference or competition for adsorption sites does not seem to have an extremely significant effect on pesticide breakthrough. There is evidence that NOM was adsorbed and then later desorbed during experimental filtration runs. When two columns were operated simultaneously (one with well water and the other with spiked deionized water containing the pesticides only), the column used to treat the spiked water did break through after the first, but only 2000 bedvolumes after the first one broke through. It was anticipated that the column would run much longer. These results seem to show that NOM interference, if any, is not a large problem. Again, further work is required to study NOM-pesticide competition.

In batch shake-flask tests, several bacterial cultures were tested under aerobic, anoxic, and anaerobic conditions. These experiments have shown that the pesticides are biodegradable, but the problem of volatilization has made it difficult to quantify the extent of biodegradation. Additional work in the biodegradation area continues to be conducted (with control of volatilization) and more conclusive data is anticipated in the future. Overall, promising progress has been made in both the areas of regeneration and biodegradation. On-going studies will produce additional results that will ultimately be used to develop a full-scale bioregeneration process for the BWS.

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INTRODUCTION

Overview

It has been almost 20 years since previously-used pesticides were discovered in the Pearl Harbor aquifer. Since this discovery in 1980, the State has sought to determine the best way possible to characterize the problem and find the most logical solution to correct it. The problem has now extended beyond the island of Oahu and has not diminished in scope. To date, the water in central Oahu's wells are still treated using granular activated carbon (GAC). This treatment process has proven to be a success; however, problems include a short useful life of the carbon and high operating costs. This study seeks to determine the adequacy of chemical regeneration as one method to extend the carbon useful life. It also seeks to characterize what competitive interaction may exist between natural organic matter (NOM) present in the water, silica, and the pesticides themselves. NOM is present in Hawaii's waters ranging in concentrations from 0.1 to 0.9 mg/L (Dugan et. al., 1995). Such background organic matter is not specific to Hawaii and is found in all natural water sources. NOM can cause decreased adsorption capacity for the pesticides, though the exact mechanism of competition is not well defined due to a variety of organic compounds that comprise NOM. These compounds vary in structure and size. Along with the NOM present in the water, Hawaii's well water does have the added presence of high silica (SiO_2) concentrations which is not uncommon in regions with soils of volcanic origin. Silica concentrations in Hawaii may vary anywhere from 20 parts per million (ppm) to 75 ppm (Davis, 1969). Through previous tests, the "basal groundwater" of Oahu was determined to possess an average of 44 ppm SiO_2 (Davis, 1969). Groundwater with even higher concentrations was suspected to have return irrigation water leaching into it. During periods of high rainfall, the silica concentrations increased even more. Other practices that may also contribute to increased silica content in the groundwater include agricultural practices such as the application of phosphates onto the soil which mobilizes silica and the burning of sugarcane which produces silica-rich ash (Davis, 1969). Because the role of silica and NOM have not been fully characterized, this study endeavors to find whether interference does occur. Understanding this behavior may provide some information as to: 1) why the columns exhaust when they do, 2) whether NOM and/or silica inhibits pollutant adsorption and 3) why one solvent or acid/base may regenerate the carbon better than another.

Background on pesticide contamination in central Oahu

Since the early 1980s, increasing concern over the quality of the groundwater on the island of Oahu has forced scientists and lawmakers alike to determine an adequate solution to monitoring,

containing, and preventing continued groundwater contamination by agricultural chemicals that have entered the water supply. Because of the boom of the pineapple and sugarcane industries in Hawaii which occurred almost a century ago, pesticide use was a common practice especially in central Oahu (Brennan, 1987). Though limited studies were conducted prior to 1979 as to the effects of pesticides on the workers and its interaction with the soil and pests, detection limits were quite high because of the incapability of the equipment at the time to detect concentrations at such low levels (Brennan, 1987). Detection limits were set at ppm to parts per billion (ppb) versus the current parts per trillion (ppt) range (Brennan, 1987). Those studies conducted prior to 1979 concluded that trace organics were typically retained in the soil column and only trace amounts of the more "refractory" chemicals (i.e., pesticides) would actually break through and leach into the basal lens (Eto, et al., 1967, Fischer, et al., 1977). In a 1971 survey of the primary municipal water sources on Oahu, tests showed that trace amounts of carbon-chloroform extracts (CCE) were present in the water; however in concentrations less than the standard (Zaidi, 1976). Because of the evidence found in these above-mentioned studies, more research as to the behavior of these trace organics was necessary in order to determine its interaction with Oahu's aquifer water supply. The pesticides focused on here are 1,2 - dibromoethane (EDB), 1,2,3 - trichloropropane (TCP), and 1,2 - dibromo-3-chloropropane (DBCP). Detailed discussion on their use in Oahu and specific health effects will follow.

Removal of Pesticides via Granular Activated Carbon (GAC)

Several studies were conducted to determine the best possible way to treat the contaminated well water. Use of granular activated carbon (GAC), thin-film volatilization, heat volatilization, as well as air stripping and cooling tower technologies to treat the water were all studied (Dugan et al., 1995). From these studies, it was concluded that GAC adsorption would be the most feasible even though it possessed the highest cost because: 1) its performance, when compared to the other evaluated processes, provided better results, 2) it provided the most stable performance even with varying influent conditions, 3) GAC seemed to be the most reliable among the processes studied, 4) the treatment was entirely enclosed which eliminated any health threats to workers and 5) adsorption via GAC produced no air emissions (GMP, 1984). GAC treatment facilities were constructed at three well sites: Kunia, Mililani, and Waipahu from 1986 to 1987. To date, GAC systems continue to treat water from all well sites in these three areas. Design and construction is also underway for several additional carbon contactors at other central Oahu sites.

Maximizing Useful Life of GAC columns

Despite the reliability of using GAC to treat the contaminated water, the Honolulu Board of Water Supply (BWS) wanted to find a way to prolong the useful life of the GAC columns because of the high operational costs. Preliminary work done by the Water Resources Research Center (WRRC) at the University of Hawaii studied the possibility of applying the rapid small-scale column test (RSSCT) to see what desorption methods could be used (Walton-Green, 1997). Primary desorption methods included use of heated water and organic solvents. Currently, the BWS operates 18 carbon contactors at the two Waipahu well sites, 16 contactors at the two Mililani well sites, and 8 contactors at the Kunia well site. Breakthrough occurs after approximately 11 months. Once breakthrough is reached, the "spent" carbon is disposed of and the contactors are repacked with virgin carbon at an estimated annual cost of greater than $400,000. This cost estimate is based upon data given in Leon-Guerrero et. al. (1994) and Kawata (1996) and was calculated for annual replacement of GAC in 19 contactors as follows:

Component	Unit Cost ($)	Annual Cost ($)
GAC purchase and replacement	1,938	368,220
GAC analytical testing	49	9,310
GAC disposal	60	11,400
Labor	154	29,260
TOTAL		**418,200**

Regeneration of GAC is a problem that extends beyond Hawaii. Since the 1950s, research has been conducted to determine what processes can be applied to remove volatile organic compounds (VOCs) from spent GAC (Modell, et. al., 1980). Such research was conducted due to the high cost associated with GAC use. For most applications, thermal regeneration is the process of choice because of its efficiency; however, drawbacks include loss of carbon capacity due to oxidation, frequent furnace breakdown, and high capital cost (Modell, et. al., 1980). Because of such disadvantages, there has been a growing need to find alternative regeneration processes to recycle spent GAC and prolong its useful life. Conventional solvents have been looked at as alternative means for GAC regeneration. There is still much work to be done in this area as well as debate over its adequacy. The objectives of this study include determination of the feasibility of using conventional solvents and acid/base combinations for GAC regeneration, determination of the competitive effects of NOM and silica upon pesticide adsorption using the RSSCT developed

by Crittenden, et. al. (1986), determination of the biodegradability of the target pesticides under aerobic, anoxic, and anaerobic conditions, and development of a complete bioregeneration process for GAC.

LITERATURE REVIEW

Contaminants

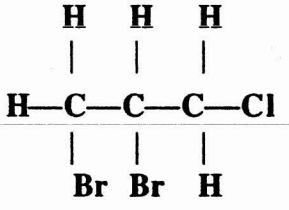
The pesticides focused on here are ethylene dibromide (EDB) or 1,2 - dibromoethane , 1,2 - dibromo - 3 - chloropropane (DBCP), and 1,2,3 - trichloropropane (TCP). These three pesticides were commonly used by the Del Monte Corporation on their agricultural land. They are also synthetic organic chemicals, and are therefore not known to occur as natural products. Their properties are listed in Table I. These contaminants are classified as halogenated aliphatic (straight chained) compounds, and as such are typically highly volatile. The thermal stability ranking (TSR) of DBCP and EDB are 214, 199, respectively, on a scale of 1 (highest stability) to 320 (lowest stability). The TSR of TCP falls within a range of 168 and 173 (Taylor et al., 1990). The TSR value can be translated into the temperature (°C) required for 99% destruction for a mean residence time of 2.0 seconds (T_{99}) (Table 1).

Table 1 - Properties of DBCP, EDB, and TCP.
(Verschueren, 1996; Howard, 1991; Taylor et al., 1990)

Property	DBCP	EDB	TCP
Molecular weight	236.36	187.88	147.44
Boiling point (°C)	196.0	131.6	156
Melting point (°C)	6.00	9.97	−14
T_{99}* temperature (°C)	560	545	625
Vapor pressure @ 20°C (mm HG)	0.58	11	2.0
Solubility in water (mg/l)	1,230 @ 20°C	4,310 @ 30°C	1,900 @ 25°C
Density @ 20°C (g/cm³)	2.09	2.18	1.39

** Temperature required for 99% destruction for a mean residence time of 2.0 seconds*

DBCP, a soil fumigant, was first introduced into widespread use on land in central Oahu in 1959 (Dugan, et al., 1995). It is an aliphatic or straight chain molecule whose structural formula is:



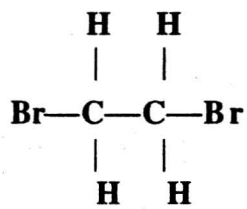
Use was discontinued in 1977 due to studies conducted on the possible detrimental health risks associated with prolonged exposure to the compound. If released into the soil, DBCP volatilization and leaching will occur. DBCP residues which have not volatilized or leached are very persistent in soil. DBCP near the soil surface have volatilization half-lives ranging from 0.6 days in dry soil

to 26.2 days in wet soil with high soil organic content (Howard, 1991). Leaching to groundwater is also expected due to its weak adsorption to soils.

Product studies of hydrolysis DBCP show the formation of two intermediates, 2-bromo-3-chloropropene (BCP) (~95%) and 2,3-dibromopropene (DBP) (~5%). Both intermediates produce a final hydrolysis product of 2-bromo-2-propenol, commonly known as 2-bromoallyl alcohol (BAA) (Burlinson et al., 1982).

DBCP has been classified as a carcinogen by the EPA and the U.S. Department of Health and Human Services. Public health effects include reproductive damage to males (EPA, 1979; EPA 1981; Torkelson, 1961), respiratory irritation, nausea, and central nervous system depression. Inhalation by animals also produced damage to their reproductive systems, stomachs, livers, brains, spleens, blood, and lungs (EPA, 1979; NIH, 1978; NCI/NTP, 1980). Human exposure to DBCP may result from ingestion of contaminated drinking water or inhalation of contaminated air. However, since DBCP use is no longer allowed as a nematocide and soil fumigant in the U.S., there is very little chance of the latter exposure route.

EDB, found typically in tetraethyl lead mixtures added to aviation fuel, was also used as a soil fumigant to control nematodes in pineapple fields. It, too, is an aliphatic hydrocarbon with the following structural formula:

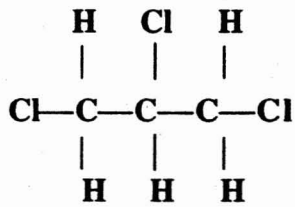


EDB use began in 1948 and increased use occurred as Dole Company chose it as its primary fumigant in 1978 after DBCP use was ceased in 1977 by the Hawaii Department of Agriculture (Dugan, et al., 1995). In 1983, the United States Environmental Protection Agency (US EPA) then announced that it would cancel registration of pesticide products containing EDB, allowing EDB use in central Oahu to continue until September 1, 1984; however, EDB application ceased by the end of 1983 (Dugan, et al., 1995). When released into the atmosphere, EDB is found to be resistant to atmospheric oxidation by peroxides and ozone. Its half-life for these reactions is typically in excess of 100 days (Verschueren, 1996). Manmade sources include gasoline engine exhaust when using leaded gasoline and agricultural fumigation.

In water, with a half-life of 5-10 days, EDB hydrolizes to ethyleneglycol and bromoethanol. In aqueous solution, dehalogenation occurs at 25°C and pH 7 with a half-life of 2.5 years (Verschueren, 1996; Vogel and Reinhard, 1986). EDB was readily lost from water samples exposed to the atmosphere, and heating enhanced losses (Isaacson et al., 1984).

Classified as a carcinogen by the EPA, EDB is known to cause redness, inflammation, skin blisters, mouth and stomach ulcers when ingested by humans. Human inhalation may cause severe irritation and damage to the upper respiratory tract. Animal testing on rats found EDB inhalation to cause reproductive problems, abnormal sperm, liver and kidney damage or death.

TCP, commonly known as a paint/varnish remover, was also used by the Dole Company initially as a soil fumigant then as a pre-plant nematicide with DBCP (Dugan, et al., 1995). Like the other two pesticides, it is also an aliphatic hydrocarbon with the following structural formula:



Under atmospheric conditions, TCP breaks down when exposed to sunlight with a half-life of 26 days. However, under aqueous conditions, TCP breaks down relatively slowly with a half-life of up to 2 years.

TCP is the only of the three target contaminants not to be classified for carcinogenicity by the U.S. Department of Health, U.S. EPA, and the International Agency for Research on Cancer. Human exposure resulted in eye and throat irritation. Animal testing on rats found that inhalation of low levels of TCP caused eye, nose and lung irritation, and liver and kidney disease. Ingestion of higher levels of TCP resulted in rats with blood disorders and stomach irritation, and death caused by liver and kidney.

By the early 1980s, concern over use of these three pesticides grew. On April 14, 1980, the Del Monte Corporation's Kunia well no. 2703-1 was found to have EDB and DBCP (Burch et al., 1982). Two years later, Mililani well water was also found to have DBCP (Brennan, 1987). DBCP concentrations were approximately 90 ppt which is well below the California standard of 1000 ppt; however, the public was not appeased and concern forced some major action to occur (Brennan, 1987). Later studies then showed that Waipahu wells were also contaminated. All three

well sites were shut down. Shortly after, TCP was detected in all three surveyed well sites (Dugan, et al., 1995).

After such findings, the State sought to determine how such contamination could occur. Contamination can occur through direct and indirect means. Direct contamination includes careless handling of the chemical and is often localized. Indirect contamination is the result of poor handling of containers, inadequate labeling, or poor maintenance of the chemical containers. Often times, corroded containers are left to sit and leakage of the chemical may occur over time. In addition to these two means of contamination, one must also consider the transport of the pesticides through the soil itself when it is applied onto a field. In a study conducted by Wong (1987), University of Hawaii researchers sought to determine how the pesticides filtered through the soil. EDB was the pesticide included in the study. Typically, EDB was applied at a rate of 12 gallons per acre, 10 - 12 inches below the soil surface and plastic mulch film (Wong, 1987). Because EDB was applied near the surface, a soil profile indicated that its concentration decreased quite rapidly with respect to time and depth. For example, two weeks after application, less than 10 % of the original EDB concentration remained in the soil and as soil depth increased, levels of EDB declined to undetectable levels (0.1 - 0.5 ppb). Such a sharp decline in concentrations was attributed to surface volatilization, chemical, and microbial degradation (Wong, 1987). However, during periods of high rainfall, residual levels of EDB were higher 10 to 30 feet below the surface than at the surface itself. It was determined that once below the surface, pesticide residuals could remain within the soil for an indefinite period of time and eventually leach into the aquifer.

Direct means may have been the cause of the Kunia well contamination in 1980. Three years earlier, roughly 500 gallons of EDB was accidentally spilled around the well area (Dugan, et al., 1995). This spill has been suspected to be the primary cause of the EDB contamination in the Kunia wells (Brennan, 1987). As to the presence of TCP and DBCP in the water, possible causes may be indirect which include improper handling and/or labeling (Brennan, 1987). Contamination may also be attributed to the application of the pesticides onto agricultural land. As stated above, groundwater movement through the soil may transport the pesticides to well below the surface shielding them from the effects of microbial degradation and surface volatilization. If this is the case, researchers speculate that the concentrations of pesticide will only increase in the aquifer instead of decline. Even with such plausible reasons for the presence of the pesticides in the wells, scientists agree that it is important to note that there are other uses for all three chemicals, and perhaps, these other uses attributed to the contamination, thus, the problem should not be labeled as pesticide contamination, but as organic chemical contamination.

When the pesticides were detected in the water samples, neither State nor federal regulations existed for EDB, DBCP, and TCP. Thus, the Hawaii Department of Health (DOH) established an interim limit of 20 ng/L (20 ppt) for both DBCP and EDB; however, since DOH did not have an action limit for TCP because of its assumed lesser risk, a limit for TCP was not established (Dugan et al., 1995). In 1989, US EPA proposed maximum contaminant levels (MCLs) for EDB and DBCP to be 50 ng/L and 200 ng/L, respectively (US EPA, 1989). In 1992, DOH established MCLs of 40 ng/L for EDP and DBCP and 800 ng/L for TCP. To ensure that trace pesticides were being removed, the State sought to determine the best, most efficient process to treat the contaminated water and thereby keep concentrations to well below regulated limits.

Competition between VOCs and Natural Organic Matter (NOM)

GAC has widely been used to remove VOCs and NOM from water. The question remains, however, on how these compounds interact with each other and how such interaction affects adsorption onto the carbon. NOM is a complex mixture of organic material found in varying concentrations in all natural waters (Newcombe, et. al., 1997a). In central Oahu's wells, NOM can vary anywhere between 0.1 - 0. 9 mg/L (Dugan, et. al., 1995). Though NOM composition can vary among water sources, some generalization can be made as to the compounds present. NOM can typically consist of small hydrophilic acids, proteins, amino acids, and larger fulvic and humic acids (Choudry, 1983). The larger fulvic and humic acids can consist of both aliphatic and aromatic compounds (Newcombe, et. al., 1997a). Because these larger compounds carry a charge, the entire solution can act polyelectrolytic (Ephraim, et. al., 1986).

NOM causes problems when GAC is used to treat water containing trace organic pollutants such as those found in central Oahu. Researchers have theorized that NOM can create a significant amount of competition with the trace pollutants, thus causing pollutant adsorption to decrease (Zimmer, et. al., 1989, Najm et. al., 1991). When GAC is used to treat contaminated waters, NOM "pre-adsorbs" onto sites and thereby decreases the carbon's capacity to remove the pollutants. This phenomenon is known as "carbon-fouling" (Zimmer, et. al., 1989).

According to Aiken and Cotsaris, the variation in NOM characteristics can affect pollutant adsorption in several ways and thus, predicting what may or may not happen can be quite difficult (Aiken and Cotsaris, 1995, Smith and Weber, 1985). Like other organic molecules, adsorption of NOM onto GAC depends on charge, size and polarity of the compounds, and the relationship between the adsorbate structure and carbon surface (Summers and Roberts, 1988). Researches have found that molecules of roughly the same size compete for sites on the carbon. There is also

a relationship observed between the pore size and adsorbate size. Adsorbates are likely to adsorb in pores of approximately the same size in which there are more contact points and more suitable adsorption energy (i.e., negative rG). It is also important to note that relative concentrations of NOM are much higher than the target pollutants, thereby exacerbating the problem. Several studies have sought to characterize the competitive behavior of the NOM with trace pollutants.

Preliminary studies by Jain and Snoeyink in 1973 showed that the greatest amount of competition arose between molecules of known similar structure. To further affirm this phenomenon of competition between similar compounds, Weber and Smith conducted several studies in 1989. They looked at the effects of three solution characteristics on trichloroethylene and *p*-dichlorobenzene adsorption. Their study incorporated adsorption of these two pollutants in the presence of NOM, in the presence of a known commercial humic acid, and with a mixture of three synthetic compounds. The greatest competitive effects were seen in the latter mixture, perhaps due to the similar structure of the two pollutants and three synthetic compounds (Newcombe et. al., 1997b). To quantify the competitive nature of organic compounds and NOM, Narbaitz and Benedek developed a mathematical model to describe competition between 1,1,2 - trichloroethane (TCEA) and NOM. They assumed that there are sites in which no competition existed and other sites where the compounds would compete. Their study showed that roughly 65-70% of the TCEA and 16% of the NOM were competing for the same sites. Other sites exhibited no competition whatsoever. Smith and Weber's work in 1985 applied this mathematical model in which they showed that the least amount of competition existed between the NOM and phenol and naphthalene. They attributed the lack of competition to specific adsorbate-carbon site interaction.

Other affects of NOM on carbon adsorption include alteration of the carbon's surface properties. This alteration may also cause fouling. In a study conducted by Newcombe et. al. in 1993, results showed a significant decrease in the surface area of the carbon as NOM adsorbed onto sites. The NOM altered the surface area by giving it a negative charge, thus, changing its characteristics and affecting pollutant adsorption. In another study conducted by Huang and Garrett (1975), they sought to determine the effects of pore blockage on pollutant adsorption. In the presence of polymer in the water, no competition was observed, leading them to conclude that large molecules (MW > 2,000,000) did not adsorb to sites and thereby did not compete with the pollutant phenol; however in the presence of humic acids, adsorption decreased. This decrease was thought to be attributed to a combination of factors: pore blockage and site competition with the acids themselves. To relate the competition of NOM with pollutants to changes in isotherms, Carter et. al. (1992) studied the effect of NOM versus trichloroethylene (TCE). Using the Freundlich

isotherm, Carter et. al. endeavored to quantify the heterogeneity of remaining adsorption sites by modifying the isotherm to the form below:

$$S_c = K(C_c)^n$$

where n refers to the heterogeneity of sites. The closer n reaches 1, the more homogeneous the site energies (Newcombe, et. al., 1997b). This means that as site energies become more uniform, capacity of the carbon for different compounds decreases. Testing this model, Carter et. al. preloaded carbon with NOM. Within two weeks of start-up, they found that site heterogeneity decreased as NOM took up high energy sites. This reaffirms the model and also reaffirms the idea of pore blockage. Kilduff and Weber (1994) also tested Carter's hypothesis by preloading carbon with humic acids of different molecular size. As humic acid size increased, its effects on TCE adsorption decreased. In solutions with smaller humic acid molecules, TCE adsorption decreased, thus reaffirming the competitive behavior between molecules of similar size. Using the Freundlich isotherm, Kilduff and Weber also found that n increased as the carbon was loaded with smaller humic acid molecules.

Application of the rapid small-scale column test (RSSCT)

1. Description of method.

The RSSCT is a method developed by Crittenden et. al. to simulate adsorption of a full-scale or pilot-scale column in less time. It is used to provide the engineer with an idea as to the affinity of the carbon for a specific pollutant to be removed and to provide design criteria for full-scale units. Advantages of the RSSCT include: 1) the decrease in operation time when compared to running pilot-scale tests, 2) the elimination of developing detailed mathematical adsorption models and running extensive isotherm/kinetic studies, and 3) the minimal volume of water required to run the test (Crittenden, et. al., 1987). The application of the RSSCT to a full-scale column process can be made by using simple equations. These equations establish a relationship between the carbon particle size in the full-scale and small-scale processes dependent on surface diffusivities. These equations will be discussed in detail in subsequent sections. Once applied, these equations will provide the dimensions for a properly-scaled mini-column that should produce a breakthrough profile similar to the full-scale column when plotted versus bedvolumes fed (Crittenden, et. al., 1987). Even with such promising results, however, the RSSCT is not recommended to completely replace pilot-scale tests due to the need for more work on the method. To date, literature has shown that numerous applications of this model have produced fairly good data that does mimic full-scale operation.

2. Important design criteria.

As mentioned above, the success of the RSSCT depends on the equations used to determine the dimensions and operating parameters for the mini-column. The set of equations established by Crittenden et. al. are based on the dispersed-flow, pore-surface-diffusion model (DFPSDM). In the DFPSDM, the following mechanisms are included: 1) advective flow, 2) axial dispersion/diffusion, 3) liquid-phase mass transfer resistance, 4) local adsorption equilibrium at exterior surface of adsorbent, 5) surface and pore diffusion, and 6) competitive equilibrium among solutes on the carbon surface (Crittenden, et. al., 1987). Dimensionless parameters are obtained from this model and applied to the mini-column. Important dimensionless parameters in this model include the Peclet, Reynolds, and Stanton Numbers. Along with these parameters, other operating criteria are calculated. These include the flow rate, column diameter, empty bed contact time (EBCT), hydraulic loading, and interstitial velocity (Crittenden, et. al., 1991). There are also guidelines that are to be followed when relating carbon particle size between the full-scale and small-scale columns. Application of the RSSCT depends on how one chooses to relate surface diffusivity between the full-scale and small-scale columns. Depending on this criteria, the equations chosen to size the column will vary slightly. For example, Crittenden et. al. tested their set of chosen equations by developing two general cases. These include: 1) identical surface diffusivity between the full-scale and small-scale columns and 2) proportional surface diffusivity dependent upon carbon particle size. Table 2 shows the properties of both cases:

Table 2 - Design criteria for the RSSCT based on surface diffusivity

Surface Diffusivity Identical in Full-Scale and Small-Scale Columns	Surface Diffusivity Proportional to Particle Size
Ratio of EBCTs equal to Square of Ratio of particle size	Ratio of EBCTs equal to Ratio of particle size
Peclet and Stanton Numbers equal	Peclet and Stanton Numbers Higher for Small Column
Minimum Reynolds Number = 1, but can be less if head loss and column length unacceptable	Minimum Reynolds Number = 1, but can be less if head loss and column length unacceptable
Bed void fractions, particle densities, influent concentrations equal	Bed void fractions and particle densities not required to be equal
Minimum column diameter to particle-size ratio $\leq$ 50 to avoid channeling	Minimum column diameter to particle-size ratio $\leq$ 50 to avoid channeling

3. Previous studies.

In the original study performed by Crittenden et. al., the RSSCT was applied to removal of TCE with background total organic carbon (TOC) present. They prepared columns in which operating and dimensionless parameters were based on identical and proportional surface diffusivity. The

data showed that the RSSCT based on proportional diffusivity resulted in a breakthrough curve most similar to the full-scale operation. Good results were also attributed to the difference in particle size between the relatively small TCE molecules and larger TOC compounds which reduced the competition between the compounds for sites. For the column designed assuming proportional surface diffusivity, the column and GAC characteristics were as follows: GAC particle radius = 0.0105 cm, EBCT = 61.4 seconds (s), interstitial velocity (v_s) = 3.96 m/h, flow rate = 6.27 cm^3/min, run time = 51.7 days. Average influent concentration of TCE was 70 µg/L. In another series of tests, the RSSCT was compared to pilot-plant operations on contaminated well water in Wausau, WI. Again, two columns were designed: one assuming identical diffusivity and another assuming proportional diffusivity. Poor results were obtained in the former case. There was a marked difference between the breakthrough curves for the pilot and small-scale columns. Discrepancies were attributed to differences in the influent concentrations between the columns, isotherm capacity, and intraparticle diffusivity. In contrast, the column designed assuming proportional diffusivity produced improved results. Breakthrough curves were similar. For the Wausau contaminated water tests, Table 3 displays the column characteristics for both constant and proportional diffusivity:

Table 3 - RSSCT Design Parameters from Crittenden, et. al. (1985) Field Studies

Column A: Constant Diffusivity	Column B: Proportional Diffusivity
EBCT = 9.54 s	EBCT = 12.28 s
GAC radius = 0.0105 cm	GAC radius = 0.0105 cm
Column diameter = 1.1 cm	Column diameter = 1.1 cm
Column length = 5.12 cm	Column length = 7.70 cm
Flow rate = 30.4 cm^3/min	Flow rate = 31.5 cm^3/min
v_s = 19.1 m/h	v_s = 22.4 m/h

Another series of tests conducted by Crittenden, et. al. (1991) involved predicting the removal of twelve different soluble organic compounds (SOCs) using the RSSCT and then comparing breakthrough curves with existing ones from pilot studies. Compounds ranged from weakly adsorbing trihalomethanes (THMs) to strongly adsorbing pesticides. Several water samples from around the United States were tested. Columns were sized according to both constant and proportional diffusivity. Three cases were also set up: 1) low background organic matter concentration (0.2 mg/L) and high SOC concentration (> 1 mg/L) , 2) adsorbable background organic matter with high SOC concentration, and 3) adsorbable background organic matter and low SOC concentration. In each case, carbon pulverized to No. 60 x No. 80 mesh was used. In case

1, the column sized assuming constant diffusivity was used. Results were quite good, though more dissolved organic carbon (DOC) removal occurred in the mini-column which may have been attributed to pre-adsorption in the column tests. Breakthrough curves between the pilot and mini-columns were similar and exhibited the same amount of "spreading" within the curve. This was attributed to the high SOC concentration and low DOC concentration. The low DOC concentrations did not hinder SOC adsorption and thus, external mass transfer was an important factor in the breakthrough behavior (Crittenden, et. al., 1991). In case 2, two columns were run: one assuming constant diffusivity and the other assuming proportional diffusivity columns. For the constant diffusivity case, the RSSCT also produced breakthrough behavior similar to that of the pilot column; however, the curve is much sharper and breakthrough occurs earlier. For the proportional diffusivity case, the breakthrough curve was much sharper and steeper than the curve for the pilot column. The sharper breakthrough curve was attributed to mass transfer resistance within the column. The proportional diffusivity design reduced the amount of "spreading" and thus, the curve appears steeper. In case 3, both constant and proportional diffusivity designs were applied. In this case, both designs produced breakthrough curves that were similar to the breakthrough curve for the pilot column; however, the mini-column seemed to exhibit a larger adsorption capacity. This seems to be the one drawback to using the RSSCT because there is difficulty in modeling the interaction between the SOCs (pollutants) and DOC (NOM). However, in case 3, it appeared that the column sized using proportional diffusivity produced much better results especially in the case where the SOC concentration is much lower than the DOC concentration (Crittenden, et. al., 1991). Results were better not only in terms of the RSSCT but also in adsorption capacity and kinetics (Crittenden, et. al., 1991).

In another test conducted by Cummings and Summers (1994), the RSSCT was used to predict the removal of disinfection by-products (DBPs) via GAC. Two experimental designs were set up: one with a bench-scale RSSCT in the laboratory and another with a field-scale pilot column. The raw water source was groundwater from Palm Beach, FL. The RSSCT was conducted using carbon pulverized to No. 60 x No. 100 mesh while the pilot column contained carbon size No. 12 x No. 40 mesh. Three mini-columns were set up, each with the same size carbon packed within them, the same flow rate (5.6 ml/min), EBCT (2 min) and bed depth (22 cm). All three were also designed assuming non-constant diffusivity. The study produced good results in which the mini-column breakthrough curves mimicked that of the pilot column. Breakthrough curves were, however, somewhat steeper than that of the pilot column. Time to breakthrough for the small columns was eight days in contrast to the nine-week run of the pilot column. Even with such promising results, problems were still encountered in the breakthrough behavior of the NOM. The RSSCTs did not predict this behavior accurately. Possible reasons for this were attributed to NOM

and DBP interaction and the difference in adsorption capacity between the small and pilot columns. Discrepancies may also have been attributed to the fact that the columns, though sized using non-constant diffusivity, were not truly designed assuming proportionality between surface diffusivities. If, perhaps, the columns were sized with this assumption, mini-column results may have been somewhat closer to the pilot-scale results.

In yet another series of analyses, the RSSCT was used by Bilello and Beaudet (1983) to predict THM removal using GAC. However, in this study, they sought not to scale the mini-column according to the equations used by Crittenden, et. al. and predict full-scale or pilot-scale column behavior but to determine the carbon's capacity for THM removal. In this study, Bilello and Beaudet also modeled their work not on Crittenden's research but on work conducted by Rosene et. al (1979). Rosene et. al. devised a mini-column technique using high-pressure liquid chromatography (HPLC). In this method, a high-pressure pump and small stainless steel diameter column ($\cong$ 2 mm) are used. Flow rates are set quite low (2 -3 cm^3/min) and the carbon is pulverized to a very small particle size (No. 200 x No. 325 mesh). The advantage of this very small column include a shorter mass transfer zone and longer service life prior to breakthrough (Bilello and Beaudet, 1983). In their study, the mini-column or dynamic mini-column adsorption technique (DMCAT) was applied to treatment of single component (benzene) and mulit-component (benzene, toluene, chlorinated-benzene) water samples. The DMCAT, like the RSSCT, is not proposed to replace pilot-studies. It is used to: 1) predict carbon usage rates and loading capacities, 2) determine the carbon's affinity for a target chemical, 3) determine feasibility for use in treating multi-component systems and predicting which component breaks through first, and 4) determine the applicability of GAC treatment for a specific water source. In Bilello and Beaudet's study, breakthrough curves were developed for all their raw water samples. These data were then compared to existing data on pilot-scale columns. Results were not compared to breakthrough curves from pilot studies, but were compared on the basis of carbon loading rates. The mini-column loading at breakthrough was calculated to be 0.185 and 0.190 mg/g, respectively. In comparison, for the pilot column, loading at breakthrough was calculated to be 0.182 mg/g. Loading rates determined from the mini-column technique predicted the pilot-scale behavior quite well. Even with good data, however, one may hesitate to use the DMCAT method because there does not appear to be mathematical or design criteria applied to the column dimensions and operating parameters. It seems to be a rapid method that minimizes cost and provides a rough portrayal of full-scale or pilot-scale behavior.

Regeneration Techniques

Regeneration of GAC certainly poses a problem because the most efficient technique may also produce un-desirable byproducts; however, work is important in this area because GAC use becomes extremely expensive if the carbon, once spent, is merely disposed of. Typically, thermal regeneration has been the choice for GAC regeneration. It has proven to be the most feasibly process for most GAC operations; however, it does have drawbacks. The capital cost is quite high. Also, carbon capacity is often lost due to oxidation. Multiple-hearth furnaces used in thermal regeneration are also subject to frequent furnace breakdown which forces plants to have back-up systems ready in case this does occur.

Another regeneration process that has had extensive studies performed on it is conventional solvent regeneration. Solvent regeneration has been thought to be an ideal alternative to thermal regeneration for the following reasons: 1) ease of performance, since it can be conducted in place, eliminating the problem of repacking and transportation of the spent carbon, 2) carbon attrition does not occur, 3) loss of carbon capacity due to oxidation is very minimal and only occurs after the first two regeneration cycles, thus, allowing carbon to be used for an indefinite amount of time, and 4) recovery of both adsorbate and regenerant is possible (Cooney, et. al., 1982). Regeneration using solvents can occur via physical displacement, reactivity of adsorbate and regenerant, and alteration of sorbent surface by the regenerant (Martin and Ng, 1983). In the early 1950s, the Carbon-Adsorption Method (CAM) was developed to quantify organics in industrial waste and drinking/surface waters. The method was revised and reintroduced in 1973 under the title Organics-Carbon Adsorbable (O-CA). In this revised method, spent GAC is dried and regenerated using chloroform and ethanol. The regeneration was performed over a 44-hr period using a Soxhlet apparatus. Subsequent solvent regeneration experiments were conducted and did not show a high degree of desorption of the adsorbates even over an extended period of time. Pahl et. al. (1973) performed regeneration experiments with ten solvents to desorb phenol from GAC. Carbon was initially loaded with 0.02 g/g of phenol. In a 2-hr period of continuous extraction, roughly 15% of the adsorbate was removed. The best solvent in that series of tests was dimethylformamide (DMF) which resulted in a 28% removal in the 2-hr period.

In another study conducted by Sutikno and Himmelstein (1979), fixed-bed regeneration tests were performed to remove phenol using acetone. After the first regeneration cycle, they calculated that 14% of the original carbon capacity was lost; however, after subsequent regeneration cycles, carbon capacity loss stabilized at about 17%. To confirm and also expand on the tests conducted by Sutikno and Himmelstein, Cooney et. al. (1982) performed an extensive series of batch desorption tests using many regenerants. They examined the adequacy of several organic solvents

and water to remove phenol from activated carbon samples. In these tests, 0.5 g of powdered activated carbon (PAC) was used. It was loaded with phenol via a batch test using conventional beakers and stirrers. The loading time was approximately 30 min, after which the carbon was filtered to remove all of the phenol solution. After filtration, the carbon was placed in a beaker with the regenerant solution for another 30 min. Fluid samples were then analyzed for phenol concentrations. Nineteen regenerants were chosen including DMF, 95% ethanol, acetone, methanol, distilled water, and acetic acid. From the batch desorption tests, it was shown that DMF removed the most adsorbed phenol (95%) while water only removed 18% of the adsorbed phenol. As a follow-up to these results, Cooney et. al. then ranked the solvents according to price per pound and solubility. From their data, they concluded that the most promising solvents were methanol, acetone, and DMF. Methanol is the cheapest solvent among the three costing about 10 cents/lb. These three regenerants were then subjected to a series of column tests using 1cm ID x 25.5 cm long chromatography columns. These columns were packed with 7.5 g of carbon, sieved to a size of 20 x 28. From these runs, DMF desorbed the greatest amount of phenol at 93%. Acetone and methanol desorbed 90% and 82%, respectively. Though methanol proved to desorb the least amount of phenol, it provided the most adequate characteristics among the three since it exhibited low adsorbability to the carbon as did DMF and acetone, but it also had a higher solubility in water, thus trace amounts of methanol were easily flushed from the column in the deionized water rinse post-regeneration. In successive regeneration/loading cycles in which all three solvents were subjected, loss of carbon capacity leveled off after the second regeneration, thus, reinforcing the idea that the carbon could be used for several cycles for an indefinite amount of time. Cooney et. al., concluded by recommending that an initial purchase prior to start-up of an extra 20-25% of carbon could minimize the loss due to regeneration even more.

Similar to the studies conducted by Cooney, et al., Martin and Ng (1983) also performed an extensive series of desorption tests using several types of regenerants: oxidizing agents, carboxylic acids, amines, heated water, alcohols, organic solvents, and acid/base mixtures (i.e., sodium hydroxide, hydrochloric acid). Tests were divided into two phases: phase I tests were performed using nitrobenzene as the adsorbate, phase II tests were performed using several mono-substituted benzene compounds in order to determine the effect of functional groups. In both phases, batch tests were performed to both load and regenerate the carbon. In phase I, it was observed that carboxylic acids restored an average of 55% of the original carbon capacity. For the carboxylic acids forming true "solutions" in water (i.e., formic, acetic, and propionic), regeneration efficiency was quite poor averaging only 50% while the acids forming suspensions (i.e., n-Butyric, iso-Butyric, and n-Valeric) exhibited higher regeneration efficiencies averaging around 80%. According to Martin and Ng, this discrepancy can be attributed to the acids' behavior

in water. The acids forming suspensions acted as globules trapping the carbon granules among them which, in effect, produced a 100% regenerant regardless of concentration. In contrast, acids such as formic and acetic have higher solubilities in water. When introduced to the spent carbon with nitrobenzene, the acids tend to stay in the water phase while the nitrobenzene tends to stay on the carbon because of its low solubility in water, thus, resulting in low regeneration efficiencies. When the acids are increased in concentration up to 100% acid, regeneration efficiency also increases. When methanol and ethanol were tested to remove the nitrobenzene, results were not so good. Regeneration efficiencies were 31% and 32%, respectively. Low efficiencies were attributed to the alcohols' solubility in water. For the alcohol to physically displace the adsorbate, energy would be required to first break a water-alcohol bond. According to Martin and Ng, these strong bonds were the most likely reason for the poor regeneration. Using acetone, regeneration efficiencies averaged about 45%. Such a low efficiency was atttributed to residual acetone on the carbon. When oven-drying was performed, regeneration efficiency increased to about 52%. At concentrations of 100% acetone (with oven-drying), up to 85% of the original carbon capacity was regained. In the phase II studies, five mono-substituted benzene compounds were tested as adsorbates. When boiling water was used as a regenerant, regeneration efficiencies up to 80% were observed. Regeneration efficiencies also increased with prolonged boiling time; however, results stabilized at boiling times of about 4 _ hrs. The highest carbon capacity was regained with sample exhausted with phenol. The lowest capacity was regained with carbon exhausted with aniline. According to Martin and Ng, this observation correlates to the solubility of the adsorbate. If the carbon's affinity for the compound is high, regeneration efficiency is low and vice versa. When oxidizing agents were tested as regenerants ($K_2Cr_2O_7$, $KMnO_4$), regeneration efficiencies were low and in some cases negative. These poor results were attributed to the alteration of the carbon surface itself. Strong oxidizing agents tend to increase the surface oxide concentration of the carbon, thus, decreasing its adsorption capacity. These oxidizing agents may also produce other end products which ultimately block the carbon pores inhibiting the removal of the adsorbates. In phase II, carboxylic acids were again used as regenerants. Unlike the phase I results, regeneration of the mono-substituted benzenes occurs via physical displacement, and therefore, molecular weight (MW) plays a larger role here. Martin and Ng concluded that the more optimum regenerant would possess a smaller MW than the adsorbates allowing them to penetrate the carbon micropores. For example, formic acid with a MW of 46.03 restored over 90% of the carbon capacity for samples exhausted with benzyl alcohol, benzaldehyde, and phenol, while iso-butyric acid (MW = 88.11) only restored only 50% of the carbon capacity for samples treated with benzyl alcohol and benzaldehyde, and only 74% for carbon samples treated with phenol. When HCl and NaOH were used as regenerants, it was observed that the NaOH performed better. HCl restored only 25% of the carbon capacity for carbon samples exhausted with benzyl alcohol and

10% for samples exhausted with benzaldehyde and nitrobenzene. Such low regeneration efficiencies could be attributed to several factors. One reason for the low efficiencies is the dissociation of the acid into its component ions which could invariably occupy sites and reduce carbon capacity. On the other hand, weak solutions of NaOH (1 and 3M) performed quite well when regenerating the exhausted carbon in contrast to highly caustic solutions of NaOH. According to Martin and Ng, this may be so due to the dissociation of the ions in the stronger solution which could then occupy sites on the carbon. For alcohols tested in phase II (methanol, ethanol, 1 and 2-propanol, and 1 and 2-butanol), no discernible relationship between MW and adsorbate could be delineated, partly due to the fact that all the alcohols were much smaller than the adsorbates. Because of this, one would expect high regeneration efficiencies. For the phase II adsorbates, efficiencies were quite high ranging from 68% to 100%. In addition to phase II tests, Martin and Ng also conducted an additional series of tests designated as phase III. For these tests, five more compounds were chosen as adsorbates. These compounds were similar to those in phase II with the addition of a second benzene ring. All the regenerants remained the same. Similar to phase II results, MW seemed to be the governing factor. Regenerants with MW smaller than the adsorbates exhibited high regeneration efficiencies.

Other desorption work has been conducted using inorganic and organic regenerants that applies similar methods like that described above to treat spent carbon from fertilizer waste slurry. Srivastava and Tyagi (1993) performed desorption tests on fertilizer waste slurry in India. Target adsorbates were also phenol-type compounds. In this particular series of tests, regenerants were recycled up to 20 times to determine if regenerant solution could be reused and still maintain the high regeneration efficiencies. Batch tests were performed using small flasks. Carbon was loaded with a specified solution of phenol and subsequently regenerated and reloaded up to 28 cycles using one regenerant solution. Regenerants tested were organic solvents (methanol and acetone), inorganic desorbents (HNO_3 and NaOH), and acids (acetic acid). From their desorption studies, Srivastava and Tyagi observed that regeneration efficiencies dropped sharply when reusing the regenerant. This was attributed to displacement of the adsorbate with regenerant. Any residual regenerant would hinder adsorption of the phenols in proceeding loading cycles. After the 8^{th} cycle, fresh regenerant was applied, thus, improving regeneration efficiencies overall. From the above-listed group of regenerants, acetone and acetic acid seemed to prove very effective with regeneration efficiencies near 100%. Methanol proved to be less effective a regenerant than both acetic acid and acetone, perhaps due to bonding with water. These bonds would need to be broken before the methanol could displace any adsorbed phenol. The inorganic regenerants were found not to be as effective, possibly due to "steric hindrance" (Srivastava and Tyagi, 1993). Steric hindrance arises from the effect of the oxidizing agent on the adsorbent or from the possibility of

oxidation of the adsorbate itself. Though aqueous solutions of the organic and acidic compounds proved to be less than effective, aqueous solutions of NaOH seemed to be quite good at desorbing the phenol and produced high regeneration efficiencies (near 85%) at low concentrations. Similar to the work by Martin and Ng, Srivastava and Tyagi attributed these high regeneration efficiencies to the formation of the soluble salt which could easily be carried by the regenerant solution. At higher NaOH concentrations, regeneration was not as good, perhaps, due to the dissociation of the NaOH into its ion species which could occupy sites on the carbon.

Though extensive research has been performed on the use of organic and inorganic regenerants, little has been written on the application of hot water. Its use has been included in the study conducted by Martin and Ng; however, focus is typically on the organic solvents or aqueous solutions of NaOH and acids. A small project was conducted by Bercic, et. al. (1996) on the application of hot water to desorb phenol from activated carbon. Bercic et. al. sought to determine the efficacy of water as a regenerant and also endeavored to develop sorption isotherms to describe the sorbent/sorbate interaction. Bercic et. al. conducted their tests using small columns loaded with phenol at 25°C then regenerated with water at high temperatures. Heated water in a range from 110°C to 190°C was used. As temperature increased, regeneration efficiencies also increased; however, even at 110°C, regeneration efficiency reached a high of 95%.

Along with the work completed by Martin and Ng above, other research has been conducted on the use of HCl as a potential regenerant. In a series of tests conducted by Leng and Pinto (1996), they sought to test 5% HCl solutions on GAC exhausted with aniline. They obtained a regeneration efficiency of 70%. They concluded that strongly acidic solutions are better than water as regenerants because of the alteration of the surface charge on the carbon. Strongly acidic solutions can alter the surface charge so that it becomes very positive causing the neutral organic compounds to desorb. It is also important to note that regeneration efficiency will vary depending on the nature of the adsorbate. Though regeneration efficiency is high for aniline, results using HCl are still not as consistent as testing an alcohol or carboxylic acid as a regenerant. Still, HCl does provide desirable characteristics and the necessary results when regenerating carbon. For example, a series of tests were conducted on spent GAC from the Upper Occoquan Sewage Authority (UOSA) in Virginia. There, a counter-current GAC adsorption unit is used to further treat tertiary effluent prior to discharge into Bull Run Creek. Spent GAC is regenerated via thermal regeneration. In tests conducted by Sebastiani, et. al. (1994), acid-washing the spent GAC was performed prior to thermal regeneration. It was concluded that acid-washing reduced the rate of mass loss for all tested GAC samples. With in-furnace regeneration alone, 5-10% of carbon volume was lost. In comparison, when the GAC samples were acid-washed, then introduced to the furnace, losses

were reduced to 1-2.5%. Sebastiani et. al. concluded that acid-washing GAC aided in improving micropore volume and surface area.

Aside from extensive solvent regeneration studies using organic solvents, much work has been done on the efficacy of sodium hydroxide (NaOH) in solution. Previous studies have shown the effectiveness of using a 4 % solution of NaOH to remove phenol from carbon (Himmelstein et. al., 1973; Fox, et. al., 1970). The phenol reacts with the caustic soda to form sodium phenate which could easily be desorbed and carried out with the regenerant solution. The effectiveness of NaOH as a regenerant has also been demonstrated in combination with the use of a conventional solvent. For example, in a study conducted by Rovel (1972), 2-propanol was used to regenerate spent carbon. Improved desorption was obtained when the spent carbon was pretreated with a 10% solution of NaOH. Overall, the carbon capacity was restored to within 80% of the original. Beccari et. al. (1977) also confirmed the usefulness of NaOH in conjunction with a conventional solvent. When acetone alone was used to regenerate GAC exhausted with peptone, only 49% of the carbon's original capacity was regained; however, when the carbon was pretreated with a 6M NaOH solution at 80°C, carbon capacity was improved to 78%. When used alone, the NaOH solution recovered up to 50% of the carbon capacity.

It seems as if slow desorption is the largest problem associated with solvent regeneration; however, others include cost of solvents, recovery of the desorbent for reuse, and potential health hazards of the solvents themselves (Modell, et. al., 1980). For an ideal solvent desorbent, favorable characteristics include: 1) high solubility, 2) good mass transfer, and 3) high volatility for adequate separation proceeding regeneration. Even with these drawbacks, however, solvent regeneration seems to be a technique of great interest because solvents are readily available and can be obtained fairly easily.

A compromise between conventional solvent desorption and high solubility characteristics is the use of supercritical carbon dioxide (CO_2). Supercritical CO_2 is a fluid that is above its critical temperature and pressure. It exhibits excellent solubility, while retaining characteristics common to liquids, and possesses high mass transfer and diffusivity (Modell, et. al., 1980). In a laboratory study, supercritical CO_2 was used to desorb phenol from loaded carbon columns. Results showed that after 90 min, over 90% of the adsorbate is removed. This is, of course, a great improvement over the Pahl, et. al. study in which a maximum of only 28% of adsorbate was removed. In other supercritical CO_2 studies, it did prove to remove a variety of adsorbates successfully including naphthalene, stearic acid, octadecanol, and polyvinyl chloride. Separation of the solutes from the supercritical CO_2 also proved to be easy. This is a liquid that can be recycled without a great

amount of difficulty. Ease of separation is attributed to the characteristics of the fluid itself because any changes in temperature or pressure alter the density of the fluid greatly, and thus, the solutes' solubility is affected (Modell, et. al., 1980). Comparisons as to cost are not given between conventional solvent regeneration and supercritical CO_2; however, when compared to thermal regeneration, the cost should be lower. The largest capital costs are for the desorption vessels and compressors which cost much less than multiple-hearth furnaces. Work continues in the field of using supercritical fluids and applying it to full-scale regeneration processes.

Degradation of DBCP

1. Anaerobic Transformations

Anaerobic degradation of DBCP in suspensions of soil have resulted in conversion to organic products, but not CO_2, but no conversion was observed in groundwater or aquifer solid samples (Bloom and Alexander, 1990). DBCP studies were complicated by its volatility, lower solubility, and ease with which it was taken up in bottle cap liners and rubber serum caps (Castro and Belser, 1968). Despite difficulties, the study found that maximum DBCP conversion to *n*-propanol was 63% by soil water cultures after 4 weeks at pH 7.5 as presented by the following reaction:

$$CH_2Br—CHBr—CH_2Cl \longrightarrow CH_3— CH_2 —CH_2OH + 2Br^- + Cl^-$$

(Castro and Belser, 1968)

2. Aerobic Transformations

Degradation of DBCP have been unsuccessful in aerobic soil columns within 25 days (Wilson et al., 1981). Significant levels of DBCP have been found in soils whose last known application of the pesticide was six to seven years prior to the testing (Nelson et al., 1981). This persistence in soils implies that biodegradation of DBCP is probably an extremely slow process. However, in a recent study, Bloom and Alexander demonstrated that DBCP can be aerobically transformed to organic products and inorganic halogen by individual microorganisms in the presence of methane (Bloom and Alexander, 1990). Biodegradation aerobically did not occur without methane. Biohalogenation of DBCP was studied in static cultures of *Pseudomonas putida* which resulted in successful degradation, though the intermediate products were not determined (Lam and Vilker, 1987).

3. Anoxic Transformations

Attempting to replicate groundwater environments, experiments were performed under anoxic conditions and found that DBCP was susceptible to biodegradation under specific conditions. The

experiment involved the use of anoxic biofilm columns under conditions of methanogenesis, denitrification, and sulfate respiration (Bouwer & Wright, 1988). Data from these experiments suggests that DBCP is biodegradable in groundwater anaerobically (Bouwer & Wright, 1988). DBCP was transformed under all three conditions, as shown in the following table (TABLE 4):

Table 4 - Removal of DBCP in methanogenic, sulfate reducing, and denitrifying biofilm columns with 2.5-day detention time (Bouwer & Wright, 1988)

Condition	Accl. period	Influent (µg/L)	Effl. % removal
Methanogenic	9–12 wks	17 ± 2	> 99
Sulfate reducing	< 2 wks	12 ± 4	98 ± 7
Denitrifying	——	37 ± 3	14 ± 11

[a]One standard deviation of the mean values given.
Accl. = Acclimation

The small decrease in effluent concentration under denitrifying conditions was not conclusively attributed to transformation.

4. Non-biological Degradation

Non-biological degradation studies have been found to successfully and quickly transform DBCP to propane. According to Siantar et. al., zero-valent iron (Fe^0) powder and hydrogen with a palladium catalyst (H_2/Pd-alumina) have the ability to hydrodehalogenate DBCP contaminated water (Siantar et. al., 1996). This treatment process, unlike air stripping or GAC contacting, does not require additional treatment of the secondary waste stream, which typically results in additional treatment expenses. Dehalogenated hydrocarbons (RX) may be reductively dehalogenated according to the following equations:

$$RX + H^+ + 2e^- \rightarrow RH + X^- \qquad \textbf{(a)}$$

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \qquad \textbf{(b)}$$

$$Fe^0 + RX + H^+ \rightarrow Fe^{2+} + RH + X^- \qquad \textbf{(c)}$$

Vogel et. al. stated that the reaction equation (a) is thermodynamically favorable for several brominated and chlorinated methanes, ethanes and ethylenes under water treatment conditions (Vogel et al., 1987). Since DBCP is structurally similar to these compounds, and thus, favorable reductive dehalogenation was expected. Since the oxidation in equation (b) is thermodynamically favorable (Weast, 1983-1984), the reduction of DBCP in equation (c) was also expected to be favorable (Siantar et. al., 1986).

According to Rylander, hydrodehalogenation of RX is possible when in the presence of hydrogen gas and a suitable metal catalyst (M) such as Rd, Ni, Pt (Rylander, 1979), or possibly Fe^0 by the following equation:

$$H_2 + RX^M \rightarrow RH + H^+ + X^-$$

Zero-valent iron experiments were conducted using 125 mL glass serum bottles filled with iron powder and solution, which were autoclaved and spiked with DBCP and shaken at 400 r.p.m.. Hydrodehalogenation experiments were conducted using Pd and catalyst added to solution, spiked with DBCP. Samples were analyzed for DBCP and propane using gas chromatography.

Both Fe^0 powder and H_2/Pd catalyst successfully transformed DBCP to propane with propene as an intermediate. Siantar et. al. concluded that zero-valent iron reductive halogenation is more useful as an *in-situ* treatment method, while Pd-catalyzed hydrodehalogenation is more useful and practical as an above ground, DBCP contaminated, water treatment process (Siantar et. al., 1996).

5. Synthesis of Findings

Due to the highly volatile nature of DBCP, aerobic experimentation would not be an acceptable method of determining its degradability. It is unclear if anaerobic degradation will provide sufficient decrease in DBCP concentration based on the 63% reduction in four weeks by soil-water cultures. The most promising method of degradation is sulfate reducing biofilm columns which reduced substrate concentration by 97%, requiring a acclimation period of only two weeks. Non-biological methods of dehalogenation, such as zero-valent iron powder and hydrogen with a palladium catalyst, will not be considered as a possible alternative.

Degradation of EDB

1. Anaerobic Transformations

A study by Wilson et al. examined the fate of EDB using diverse and metabolically active microorganisms, found in both shallow and deep aquifers, under methanogenic conditions (Wilson et al., 1986). Results showed that biodegradation reduced EDB concentration to 27% of the control concentration or less in 7 weeks. In 16 weeks, the concentrations were below detectable limits. Previous studies has shown transformation of EDB to ethylene and bromide in soil-water cultures by the following equation (Castro and Belser, 1968):

$$BrCH_2CH_2Br \xrightarrow[\text{pH above 7.0}]{\text{Soil-H20}} CH_2{=}CH_2 + 2Br^-$$

While methanogenic cultures and biofilm columns has shown transformation to a hydrophilic intermediate such as bromoethanol and a very volatile end product (Bouwer and McCarty, 1985). Of the five aliphatic halogenated hydrocarbons tested by Wilson, EDB was one of two that did not require long lag times before the onset of degradation (Wilson et al., 1986).

2. Aerobic Transformations

Aerobic degradation experiments have shown EDB to be degradable by ammonia-oxidizing bacterium *Nitrosomonas europaea* (Vannelli et al, 1990). This soil and water dwelling nitrifying bacteria are obligate autotrophic aerobes which oxidize ammonia by ammonia monoxygenase by the following equation:

$$2H^+ + 2e^- + O_2 + NH_3 \longrightarrow NH_2OH + H_2O$$

This study reports that *N. europaea* is capable of degrading many halogenated aliphatic compounds. Degradation of many substrates were observed without the inclusion of ammonia, however the degradation rates and extent of degradation were generally greater with ammonia. With the inclusion of ammonia using *N. europaea*, EDB substrate remaining dropped from 92 to 16% (Vannelli et al, 1990).

3. Anoxic Transformations

Bouwer and Wright examined the transformability of EDB under conditions of denitrification, sulfate respiration, and methanogenesis using anoxic biofilm columns. Acetate was the primary substrate to support microbial growth. Eight weeks of column operation were required to develop an active methanogenic culture. EDB was transformed under all three conditions, as shown in the following table (TABLE 5):

Table 5 - Removal of EDB in methanogenic, sulfate reducing, and denitrifying biofilm columns with 2.5-day detention time (Bouwer & Wright, 1988)

Condition	Acclimation period	[illegible]	Effluent % removal
Methanogenic	< 2 wks	20 ± 4	> 99
Sulfate reducing	< 2 wks	19 ± 3	63 ± 9
Denitrifying	——	30 ± 2	23 ± 7

**One standard deviation of the mean values given.*

Under denitrifying conditions, the scant EDB decrease in effluent concentration could not be conclusively attributed to transformation. The intermediate product of EDB was found to be highly

volatile, more so than EDB itself, under sulfate reducing and especially under methanogenic conditions. Previous studies suggests this product to be ethylene (Bouwer and McCarty, 1985; Castro and Belser, 1968).

4. Synthesis of Findings

Since aliphatic halogenated compounds are typically highly volatile, aerobic biodegradation is not thought to be feasible. However, Vannelli et al. successfully biodegraded EDB to 16% of the initial value using the ammonia-oxidizing bacterium *Nitrosomonas europaea* in 24 hours. It is uncertain according to his 1990 published study, how Vannelli et al. overcame the high volatility characteristic of EDB. Anaerobic degradation was also successful whereby EDB was degraded to 27% of the control concentration in seven weeks, and to undetectable levels in 16 weeks. Successful anoxic degradation occurred under sulfate reducing and methanogenic conditions. Since detailed experimental procedures for aerobic degradation were not provided, the best course of action appears to be anoxic degradation under methanogenic conditions, or possibly sulfate reducing conditions.

Degradation of TCP

1. Aerobic Transformation

As in the aerobic degradation experiments performed on EDB, Vannelli et al. examined the potential of the ammonia-oxidizing bacterium *Nitrosomonas europaea* to degrade the halogenated aliphatic compound, TCP. Again, with the addition of ammonia, the substrate remaining decreased from 91 to 77% of the initial value after 24 hours (Vannelli et al., 1990). Intermediate and final products were not determined.

2. Synthesis of Findings

There is a general lack of prior biodegradation experimentation on TCP. The Vannelli study indicates that aerobic degradation relative ineffective. The best course of action appears to be to try the same conditions proposed for EDB and DBCP.

Degradation of Ethylene and Propane

The nitrifying bacterium *Nitrosomonas europaea* is capable of oxidizing methane than can serve as a substrate for the ammonia oxidizing enzyme, ammonia monooxygenase (Hyman and Wood, 1983). Ethylene was also thought to be a suitable substrate for this enzyme. A subsequent 1984

study by Hyman and Wood found that *N. europaea* incubation with ethylene led to the formation of ethylene oxide (Hyman and Wood, 1984). Ethylene seemed to be a substrate for the ammonia oxidizing enzyme, ammonia monooxygenase. If an inhibitor of NH_4^+ oxidation was used, ethylene oxide was not produced. Ethylene oxide was also not formed under anaerobic conditions. These observations concerning ethylene oxide production are consistent with the product being an alternative substrate for the monooxygenase, but with a much lower affinity than ethylene (Hyman and Wood, 1984).

In a similar study, Hyman et al. examined the ability of *N. europaea* to oxidize a range of straight chain alkanes and alkenes (Hyman et al., 1988). Propane, a possible transformation product, was one of the substrates tested in this study. The oxidation of propane by whole cells of *N. europaea* produced propan-1-ol and propan-2-ol (Hyman et al., 1988). The rate of oxidation is influenced by the choice of reductant, incubation period, solubility of the substrate and the affinity of ammonia monooxygenase for the substrate (Hyman and Wood, 1983 and 1984).

Summary of biodegradation studies from the literature

The most effective methods for biodegradation of DBCP and EDB were sulfate reducing and methanogenic biofilm columns, respectively. TCP was not included as one of the test chemicals in the study by Bouwer and Wright, however it is likely that the transformation of other aliphatic halogenated compound would have occurred. EDB was degraded successfully via sulfate reducing biofilm columns, though not as effectively as methanogenic columns. The same cannot be said for the effectiveness of DBCP degradation via methanogenic conditions. Therefore, further biodegradation testing should utilize sulfate reducing conditions as a first step to dehalogenate and perhaps further degrade these pesticides. Aerobic biodegradation tests should be used for the effluent from the sulfate reducing conditions since ethylene, propane, and their alcohols are aerobically degradable.

EXPERIMENTAL AND ANALYTICAL METHODOLOGY

Objectives

To date, work has been conducted on the application of the RSSCT to mimic and design full-scale carbon columns. These extensive studies have resulted in very promising results. At the same time, due to the growing need for alternative carbon regeneration methods, researchers have investigated several processes. It is in the field of carbon regeneration that the BWS seeks an alternative to their current practice of disposal once breakthrough of any of the three pesticides is obtained. The BWS also endeavors to gain a better understanding of the breakthrough phenomenon and what type of competition exists among the pesticides, the NOM, and silica. It is hoped that such an understanding will assist in choosing a regeneration technique. Other questions that are also to be investigated will be feasibility of the method chosen and cost. This study seeks to apply the RSSCT model to qualify the competitive interaction of the pesticides, NOM, and silica. The RSSCT will also be used to conduct several column tests applying many desorbent schemes. In these short-term tests, "real" conditions will be used as spent carbon from the BWS will be packed into the mini-columns. The spent carbon is used in order to include interference from NOM and silica. It is hoped that the short-term tests will provide a logical blend between adequate regeneration efficiency and a practical, readily-available regenerant method.

Because of the regenerant waste stream that will be produced, it is also hoped that a series of biodegradation studies will be conducted to break down the pesticides and reclaim any usable solvent. This, of course, is the larger goal of this research. Both sections will hopefully be combined to develop one bioregeneration process for GAC. For the biodegradation studies, two objectives will be examined: 1) developing two bacterial cultures (non-specific and nitrifying) to degrade EDB, TCP, and DBCP and 2) testing these bacterial cultures under various conditions (aerobic, anaerobic, and anoxic). For these biodegradation experiments, bench-scale reactors will be utilized.

General Materials and Methods

1. Liquid-Liquid Microextraction

1. 35 mL of sample were poured into a glass 40 mL volume Kimax tube fitted with a teflon-lined plastic screw cap. Prior to each use, these Kimax tubes were soaked for 24 hours in a soap/water solution, then rinsed with distilled, deionized water, then acetone. They were then

allowed to dry in a 135°C oven for another 24 hours. All glassware used for this study was cleaned in this manner.

2. To each Kimax tube, 2 mL of reagent-grade hexane was added. The Kimax tube was then sealed tightly with a teflon-lined screw cap. The tube was then shaken vigorously by hand for 2 minutes. At the end of 2 minutes, the tube was allowed to sit with the cap loosened. This allowed the hexane and water layers to become easily distinguishable, thus, facilitating collection of the top hexane layer.

3. Then using a Pasteur pipette, the hexane layer was carefully transferred to a centrifuge tube made of glass with a maximum volume of 15 mL. To each centrifuge tube, a little sodium sulfate was added (this removes any remaining water). The centrifuge tube was then shaken.

2. Gas Chromatography Method

1. All column samples were analyzed using the GC. In this study, two types of GCs were used.

2. The first GC used was the Hewlett Packard Model 5700A. The following were the necessary parameters for this GC: electron capture detector required with temperature = 300°C, injection port temperature = 250°C, oven temperature = 135°C, flow gas = 30 mL/min, Argon-Methane carrier gas at pressure = 60 psi (95% Ar, 5% CH_4), column type: J&W Scientific model # DB624, 75 m in length, column temperature = 100°C, and 5 µL injection of sample, integrator model HP series 3390A. For this GC, modifications were also performed halfway through the project. New parameters were established according to the column installed. The second set of parameters were: electron capture detector required with temperature = 300°C, column type: JW scientific model #1701, column length = 30 m, 2 µL injection, oven temperature = 85°C. Retention times for this column were as follows: EDB = 0.70 min, TCP = 1.39 min, and DBCP = 3.70 min. Carrier gas flow, gas pressure, and injector temperature were not changed.

3. The second alternative GC was the Hewlett Packard Model 5890 Series II. The following were the necessary parameters for this GC: electron capture detector required with temperature = 325°C, injection port temperature = 210°C, two types of carrier gas: Helium at pressure = 60 psi, Argon-Methane at pressure = 28 psi, flow = 40 mL/min, column head pressure = 5 psi, septum purge = 3 mL/min, column flow = 2.5 mL/min, column type: J&W Scientific model # DB624, 30 m in length, integrator model HP series II 3396.

4. When using both types of GCs, a standard solution was always analyzed prior to running any samples. These standards were prepared ahead of time and stored at the end of each day in the refrigerator. Between each injection of sample or standard into the GC, the syringe was rinsed thoroughly with solvent (either methanol or hexane (both reagent grade)). For standard solutions, rinsing solvent should be methanol since standards were prepared in methanol. For samples, rinsing solvent should be hexane since samples were extracted into hexane.

5. For the GC model type 5700A, peak heights were measured by hand. These peak heights were then used to determine the concentration of pesticide in a sample. However, for column type JW Scientific model #1701, peak areas were used to quantify pesticide concentrations. For the GC model type 5890 A, the integrator prints out a record of peak areas at the end of each run. These areas were then used to determine the concentration of pesticide in a sample.

Materials and Methods - Regeneration/RSSCT

1. Carbon Preparation

1. No. 12 x No. 40 mesh virgin GAC was obtained from the BWS. The carbon was then placed in a blender - Waring Deluxe model 702B (enough to produce a layer that covers _ of the blender length was poured). The carbon was then pulverized for 5 minutes. After 5 minutes, it was poured onto a No. 80 sieve, placed over a No. 100 sieve. A brass pan was also placed below the No. 100 sieve to catch any fines. Sieving was done by hand, shaking the sieve pans vigorously for a few seconds at a time. Any pulverized carbon remaining on the No. 80 sieve was returned to the blender and pulverized further. This process of sieving and pulverizing any carbon retained on the No. 80 sieve was repeated until an adequate amount of carbon was retained on the No. 100 sieve.

2. Once enough carbon was retained on the No. 100 sieve, it underwent a series of rinsing/settling. It was first rinsed with deionized water to allow any fines to pass through the sieve, then carefully transferred to a 500 mL beaker using a spatula.

3. Once the carbon had been placed in the beaker, deionized water was poured up to the 500 mL mark. The carbon/water mixture was then stirred and allowed to settle for 15-20 minutes. The supernatant was then discarded carefully so as not to lose any carbon. Deionized water was again added and the carbon allowed to settle for another 15-20 minutes. The supernatant was then poured off. This rinsing/settling procedure was repeated until a fairly clear supernatant layer was produced. Once supernatant appeared to be quite clear, the water was drained off and

no more was added. The carbon was then covered with foil, pricked with holes and placed in a 135°C oven for 24 hours.

4. After 24 hours, the carbon was removed from the oven and cooled in a desiccator until cool enough to the touch. The above-mentioned rinsing procedure was again performed several times until the supernatant appeared clear. The carbon was then covered with foil and returned to the oven for at least 8 hours (until carbon was completely dry).

5. After the carbon dried completely, it was removed from the oven and allowed to cool in a desiccator. Once cooled, it was transferred to an opaque 50 mL bottle with a teflon-lined cap. It was then properly labeled and placed in a desiccator until the columns were ready to be packed.

2. Column Preparation

1. Please refer to Figure 2 in Appendix for column set-up.

2. Before packing the column, it was washed thoroughly with tap water, followed by rinsing in distilled and deionized water and acetone. It was then allowed to dry in a 135°C oven for 24 hours.

3. After 24 hours, the column was cooled in a desiccator.

4. To prepare the column, it was first packed with glass wool (starting from the effluent end). The glass wool was packed in the column securely (1/2 inch deep) using a slim stainless steel rod with a teflon tip or plastic tip to push it up into column. A teflon or plastic tip was recommended so as not to scratch the carbon causing flow bypass.

5. After adding glass wool to the bottom of the column, glass beads were carefully poured into the top opening to produce a layer about 1/4 inch in depth. The column was tapped gently on its side to ensure loose particles did not adhere to the sides of the column. After the layer of glass beads, glass wool was layered on top, again using the steel rod to press it firmly into the column. About 1/4 inch of wool in depth was added. At this point, the column was weighed. A balance was set to zero to ensure that the exact weight of carbon added could be measured. Pulverized carbon was added slowly. Each time, the column was tapped gently to loosen particles from the column sides and also weighed to determine when desired mass was

reached. Carbon depth was also measured. Once the desired depth was reached, the column was weighed and the carbon mass recorded.

6. Once all carbon had been added and packed neatly, a top layer of glass wool was added. This was packed down gently.

7. After the column was prepared properly, it was then set up with the pump and influent/effluent lines as shown in Figure 3. To ensure adequate flow rate, all air bubbles were removed from influent and effluent lines. The flow rate was then set at 1 mL/minute.

3. Column rinsing/cleaning

1. To ensure that any residual pesticide was removed from both the influent and effluent lines, a rinsing process was performed between all runs after regeneration and at start-up.

2. A 50/50 (by volume) mixture of methanol and deionized water was prepared and pumped through influent and effluent lines for 24 hours. At the end of the 24 hour period and prior to the deionized water rinse, 35 mL of methanol rinse was collected in a graduated cylinder. Microextraction was performed on this rinse sample to determine if residual pesticide remained in the influent/effluent lines. If none was present, a new column experiment was performed; however, if residual pesticide appeared on the GC chromatogram, the rinsing procedure continued for another 24 hours.

3. After this solvent rinse, the column was flushed with deionized water for 24 hours. Again, after the 24 hour period, an effluent sample was collected and analyzed for residual pesticide concentrations via GC. It was observed that a 48 hour rinse was more than adequate to remove any residual pesticide from the influent and effluent lines.

4. Column Loading

1. After the influent and effluent lines were free of any residual pesticide, the column was then set up as shown in Figure 3. Prior to passing any contaminated water through the column, deionized water was pumped through them for 24 hours to wet the carbon and also ensure that the set up was correct and free of leaks.

2. When loading experiments using spiked deionized water were conducted, influent concentrations were increased each day incrementally according to the following scheme: for day 1, EDB and DBCP at 200 ng/L and TCP at 2000 ng/L. Each day after, concentrations were increased by 5x, 10x, 50x, 200x, 1000x, 5000x. By the time the influent concentrations were increased to 5000x original, effluent samples showed signs of breakthrough. Once distinct breakthrough was observed, the column was shut down and regeneration followed. This procedure was used for experiments using 50%, 70%, and 100% acetone regeneration. This loading scheme was followed in order to achieve breakthrough early, otherwise, column operation would continue for too long a time period. Each day of operation, effluent was measured out to determine the amount of water treated. Effluent and influent samples were also tested via microextraction and GC each day to determine pesticide concentrations.

3. When conducting the experiment to determine effect of NOM on adsorption of pesticides, a spike of deionized water with pesticides was also prepared and treated along side the natural water in its own separate column. For this experiment, however, no increase in loading was required. Concentrations of the pesticides for the spiked deionized water were prepared according to concentrations found in the natural well water. Again, effluent and influent samples were collected each day to determine pesticide concentrations. Effluent volumes were also measured each day to determine amount of water treated. Natural well water samples were also set aside each day for total organic carbon (TOC) and silica analyses to determine if the carbon removed either. TOC samples were saved in small glass tubes (minimum volume = 10 mL) with a couple drops of H_2SO_4 added according to Standard Methods while silica samples were saved in similar tubes with HNO_3 instead.

5. Long-term experiments: regeneration of GAC loaded with spiked deionized water

1. The solvent mixture was prepared according to the chosen percentage (i.e., 25, 50, 75, %) with deionized water. As stated above, 50%, 70%, and 100% acetone by volume were used.

2. The solvent mixture was prepared in the influent bottle and then allowed to pass through the column. Effluent was collected in a graduated cylinder. Each 35 mL of effluent collected was analyzed for pesticide concentrations.

3. To adequately compare the regeneration efficiency between different solvents and different percentages, regeneration was run until 13 x 35 mL samples were obtained. This did require many bedvolumes of desorbent running through the column; however, running the

regeneration process for an extended period was necessary to show dwindling pesticide concentrations. Though the first 35 mL collected always displayed the most amount of pesticide, residual would continue to desorb for another 5 - 6 samples or so. Thus, allowing the regeneration to run for a long enough time was necessary.

4. For the regenerations with 100% acetone, successive loadings were conducted in order to determine if the carbon regained its original capacity after more than one regeneration. In this experiment, two regenerations were performed.

6. Short-term experiments with spent carbon

1. These were a separate set of experiments designed to operate over a short term and to analyze several combinations of desorbents. For these experiments, the same mini-columns as described above were used; however, spent carbon from the BWS was used in place of the sieved/pulverized virgin carbon. The spent carbon was not pulverized or altered in any way. It was loaded into the columns as is and according to the column preparation procedures listed in section 2 above. The only difference was carbon bed depth for these experiments - it was 15 cm instead of 11 cm. A 15 cm bed depth was chosen randomly. It was intended that a maximum amount of carbon be placed into the column. Once the glass wool and beads were packed into it, 15 cm of carbon seemed to allow just enough headspace at the top of the column to pack about _ - _ inch of wool. Thus, 15 cm became the standard depth for all columns in this portion of the study. Prior to loading carbon into the column, ultrasonic extraction was first performed on a small portion of the carbon to determine concentrations of the pesticides on it. Ultrasonic extraction procedures are listed in the proceeding section.

2. Once the column was prepared, it was set up according to Figure 3. To determine the carbon's ultimate capacity, a solution of spiked deionized water with 1000x original pesticide concentrations (i.e., 1000 x 200 ng/L for EDB, DBCP and 1000x 2000 ng/L for TCP) was prepared. This solution was then allowed to run through the column for at least 12 hours. At the end of the 12 hour period, the effluent volume was measured. Influent and effluent samples were also collected and analyzed for pesticide concentrations. This data was then used to create a mass balance around the column and determine the carbon's adsorption capacity for the pesticides.

3. The matrix in Table 6 was developed to see what desorbent combinations would adequately remove the pesticides from the carbon. For this matrix, the following parameters were

developed: Acid/base volumes = 10 bedvolumes, acid concentrations = 60% by volume with deionized water, NaOH concentration = 3 M. For regenerations in combination with acetone or 2-propanol, the solvent was passed through the column according to the following: 1st cycle - 52 bedvolumes (3 x 35 mL samples), 2nd cycle 36 bedvolumes (2 x 35 mL samples). After any acid/base rinse, a deionized water rinse followed at a volume of 10 bedvolumes. These criteria were set in order to: 1)achieve continuity between each short-term experiment, 2) provide a basis for comparison between each regenerant combination and 3) to allow for timely completion of this portion of the study.

4. After each regenerant combination was finished, the carbon was removed from the column and subjected to ultrasonic extraction to determine if residual pesticide remained on it.

Table 6 - Desorbent Aid Matrix for Short-term Loading/Regeneration Experiments

EXP	Solvents Used			Acids Used			
	Acetone	2-propanol	Water	Acetic	HCl	NaOH	Water
1a	X		X				
1b	X		X				
1c			X				X
2a	X			X			
2b	X			X			
2c				X			X
3a	X				X		
3b	X				X		
3c					X		X
4a	X					X	
4b	X					X	
4c						X	X
5a		X	X				
5b		X	X				
6a		X		X			
6b		X		X			
7a		X			X		
7b		X			X		
8a		X				X	
8b		X					

Key:

a = ASAS
b = SAS
c = AW
A = acid/base
S = solvent
W = Water
** *all solvents in 100% concentrations*
** *acids in 60% by volume concentrations*
** NaOH in a 3 M solution

7. Ultrasonic extraction

1. 0.2 grams of spent carbon were measured and placed into a Kimax tube (20 mL total volume). It was then carefully filled with reagent grade methanol to the rim. The total amount of methanol added was measured and recorded. Once filled, the Kimax tube was sealed tightly with a teflon-lined screw cap. The Kimax tube was then placed in the ultrasonic unit (Branson model # 3200) for 30 minutes. Every 5 minutes, the tubes were removed from the bath and inverted several times to distribute the carbon.

2. After 30 minutes, the tubes were removed from the bath and placed in the centrifuge (Fisher Scientific model 255) for 15-20 minutes allowing adequate separation between the methanol layer and carbon.

3. 5 mL of the methanol were then transferred to a centrifuge tube and analyzed via GC.

Materials and Methods - Biodegradation

1. Development/maintenance of activated sludge bioreactors for non-specific bacterial culture.

Development of non-specific bacterial culture

The non-specific bioassay seed culture was provided by two bench-scale bioreactors (Figure 4). The bioreactors were constructed of 3/16 " thick acrylic plastic. The reactor faces were made of clear acrylic to make interior observation possible. The remaining sides of the reactors were made of black acrylic to prevent light penetration which may promote the growth of photosynthetic organisms and/or chemical breakdown of cosubstrates. Aeration and mixing were provided by compressed (house) air through twin, fine bubble diffuser stones with flows of 15 SCFH to each reactor which was sufficient to provide thorough mixing. The reactors were operated and maintained at ambient air temperature ranging between 20 and 25°C.

Waste activated sludge (WAS) collected from the Schofield Barracks Wastewater Treatment Facility on June 20, 1997 at 2 PM was used to inoculate the bioreactors. The WAS was left to settle for approximately one hour and the supernatant drained. Each reactor received three liters of WAS and 12 liters of tap water. The bioreactors were then fed and aerated.

The mean cell retention time (MCRT) of the reactors was 10 days on a 24 hour cycle. The cycle consisted of 22 and one half hours of aeration, one hour of settling and one half hour for

supernatant draining and reactor feeding. Approximately two retention times were necessary for the reactors to stabilize.

The VSS in the batch reactors were completely made up of the bacterial culture. Typical VSS values for batch reactors in the field are between 1100 and 2500 mg/L (Tchobanoglous & Schroeder, 1987). Therefore a feed solution was needed to maintain the typical VSS concentration. The original feed solution, based on previous work done by Babcock et al., (1992) (Table 17), was altered by increasing the carbon and nitrogen sources, which includes the bacto peptone, yeast extract, and ammonium sulfate, by a multiple of five. This adjustment brought about a series of problems, such as foaming and temperature variations, which were resolved by Long (1997) via temperature corrections and additional feed adjustments. The final altered feed solution components and concentrations are reported in Table 18.

The reactors required daily maintenance which simulated an activated sludge system. The maintenance included removing waste activated sludge, allowing the bacterial culture to settle, draining the supernatant, and feeding the culture. Since attached growth contains an undesired population of microorganisms than that of mixed liquor, the maintenance required thorough cleaning of the internal surfaces to prevent the growth of attached growth.

Tests were performed on each reactor from the initial creation till equilibrium of the cells was reached within the reactors. The tests included total and volatile suspended solids, pH, temperature, and dissolved oxygen, all which were performed in accordance with Standard Methods (1995).

Maintenance of activated sludge bioreactors for non-specific bacteria cultures

The following list contains the complete details of the daily reactor maintenance process of the activated sludge bioreactors for non-specific bacterial cultures:

1. Safety glasses, gloves and apron were used whenever working with the reactors. All spills or splashes were cleaned using paper towels and a 1% amphyl solution.
2. Aeration typically generate cells to be suspended above the water level and therefore requires brushing into the mixed liquor. The insides of the reactors were also brushed and cleaned to remove all attached cell growth. Additional tap water was added to the mixed liquor to the 15 liter level to compensate for evaporation that occurred throughout the 24 hour period.
3. Remove 1.5 liters (10% of the reactor volume) of mixed liquor from each of the reactors.
4. Shut down the airflow to the reactors and allow solids to settle for an hour.

5. Remove the clamp on the drain hose located on the back of the reactors and allow supernatant to drain.
6. Reattach the clamp and add 67.5 milliliters of feed into each of the reactors.
7. Add tap water into the reactor until the water level reaches the 15 liter mark.
8. Adjust the airflow until 15 SCFH is attained.

2. Development/maintenance of activated sludge bioreactors for nitrifying bacterial culture

Development of nitrifying bacterial culture

The nitrifying bacterial culture differs from the non-specific culture because of its ability to degrade ammonia nitrogen. Studies have found that nitrifying bacteria have the ability to rapidly degrade aliphatic halogenated compounds (Vannelli et al, 1990).

The nitrifying bioassay seed culture was provided by a bench-scale bioreactor (Figure 4). The bioreactor used for creating the nitrifying culture was identical to the non specific bacterial reactors. Similarly, WAS was collected from the Schofield Barracks Wastewater Treatment Facility on June 20, 1997 at 2 PM which was used to inoculate the bioreactor. The nitrifying bioreactor received three liters of WAS and 12 liters of tap water. The MCRT of the nitrifying reactor was 20 days on a 24 hour cycle. The cycle consisted of 22 and one half hours of aeration, one hour of settling and one half hour for supernatant draining and reactor feeding. Approximately two retention times were necessary for reactor stabilization.

The reactors required daily maintenance which simulated an activated sludge system. The maintenance included removing waste activated sludge, allowing the bacterial culture to settle, draining the supernatant, and feeding the culture. The nitrifying bacteria feed solution was also based on previous work by Babcock et al., (1992) and was altered by Lam (1997). The final altered nitrifying bacteria feed solution components and concentrations are reported in Table 19. The nitrifying bacterial culture required the addition of ammonia nitrogen.

Ammonia nitrogen was added along with the feed in the form of ammonium chloride. The ammonia-nitrogen concentration initially added was 50 mg/L. When the bacterial culture was able to degrade this concentration to the point at which less than 1 mg/L remained after 24 hours, the ammonia concentration was increased by 20 mg/L. This was repeated until the culture was able to degrade approximately 200 mg/L. This final culture was then used for experimentation.

Tests were performed on each reactor from their initial creation until stabilization of the cells was achieved within the reactors. The tests included total and volatile suspended solids, pH, temperature, dissolved oxygen, and ammonia nitrogen. All were performed in accordance with Standard Methods (1995).

Maintenance of activated sludge bioreactors for nitrifying bacterial culture

The following list contains the complete details of the daily reactor maintenance process of the activated sludge bioreactors for nitrifying bacterial culture:

1. Safety glasses, gloves and apron were used whenever working with the reactors. All spills or splashes were cleaned using paper towels and a 1% amphyl solution.
2. Aeration typically generate cells to be suspended above the water level and therefore requires brushing into the mixed liquor. The insides of the reactors were also brushed and cleaned to remove all attached cell growth. Additional tap water was added to the mixed liquor to the 15 liter level to compensate for evaporation that occurred throughout the 24 hour period.
3. Remove 750 milliliters (5% of the reactor volume) of mixed liquor reactor.
4. Shut down the airflow to the reactors and allow solids to settle for an hour.
5. Remove the clamp on the drain hose located on the back of the reactors and allow supernatant to drain.
6. Reattach the clamp and add 10 milliliters of feed and the appropriate amount of ammonium chloride solution into the reactor.
7. Add tap water into the reactor until the water level reaches the 15 liter mark.
8. Adjust the airflow until 15 SCFH is attained.

3. Bioassay tests

The purpose of the bioassay is to determine the ability of the non-specific and nitrifying cultures to degrade the target chemicals DBCP, EDB, and TCP under anaerobic, aerobic and anoxic conditions. Controls were required for each of the three conditions to quantify the natural disappearance of the chemical substances through breakdown and/or volatilization.

The equipment required for all three bioassay tests consisted of a flask shaker, 500 ml Erlenmeyer flasks which were used as the laboratory-scale reactors, magnetic stirrers and stir plate, reactor feed, 450 ml of mixed liquor, the chemical compound to be degraded, and deionized water. According to Viessman (1985), the typical VSS value used in bioassays at or above 1000 mg/L. This initial concentration was found to be excessive due to the limited volume of mixed liquor available. A reactor volume of 450 ml was determined to be adequate for all the tests to be

performed per day of analyses since 40, 10 and 2 mL were required for the GC analysis, solids tests and COD test, respectively. Thus, the volume allowed for approximately six days of analysis to be performed. Additional tests were performed, but these tests did not require additional sample volumes. These tests include the ammonia nitrogen (NH_4), nitrate (NO^-_3), and pH tests. The performance and frequency of these tests depended on the type of bacterial culture and environmental conditions.

Initially, a stir plate was used for the mixing within the reactors, but it was determined that a shaker would provide increased accuracy and reproducibility. Aeration via diffusers were not acceptable due to the volatile nature of the target chemicals. The shaker used throughout this project was the G24 Environmental Incubator Shaker of New Brunswick Scientific Co. Inc., capable of simultaneously shaking nine 500 ml Erlenmeyer flasks. The shaker was set to 200 r.p.m., and since temperature adjustments were not required, temperature controls were turned off, allowing degradation to take place at room temperature. Room temperature fluctuated between 20 and 25°C.

The seed cultures for all reactors were prepared by placing 450 ml of mixed liquor (ML) into 500 mL graduated cylinders and allowing the ML to settle for 1 hour. After the settling period, the supernatant was removed, and the cells were added to deionized water in the 500 mL Erlenmeyer flasks. Then feed was added which contains vitamins, minerals, buffer. and carbon sources. Each of the conditions: anaerobic, aerobic and anoxic, required different materials and pre-test procedures.

Anaerobic conditions were produced with the stopper assembly (Figure 5) which prevented oxygen from entering the reactor, while allowing samples to be taken. The nitrifying bacterial culture was not tested under anaerobic conditions because nitrifiers depend on oxygen for growth. After adding the deionized water and bacterial culture, the reactor was plugged using the stopper assembly. The solution was then deoxygenated by bubbling nitrogen gas into the mixture for approximately 30 minutes. Finally, the feed, additional buffer solution (Table 20) and the target chemical (1 mg/L) were added, the ports clamped, and reactors placed on the shaker. A table detailing the exact quantity of each component of the anaerobic reactors can be found in Table 21.

Aerobic conditions were easily met by simply covering the mouth of the flask with aluminum foil following to the addition of the target compound. When using the nitrifying bacteria, ammonia nitrogen in the form of ammonium chloride (50 mg/L) was also added to the solution. The aluminum foil prevents unwanted particles from entering the reactor, while allowing oxygen to pass freely into and out of the flasks. Unlike the anaerobic experiment, no special preparation (ie.

deoxygenation) of the solution was required. A table detailing the exact quantity of each component of the aerobic reactors for both non-specific and nitrifying bacterial cultures can be found in Table 22.

Anoxic conditions requires the absence of oxygen and the presence of nitrate (NO_3^-). Nitrate, in the form of potassium nitrate (KNO^-_3) (31 g/L), was used in place of oxygen as the energy source for the bacteria. Again, the nitrifying bacteria will not survive with the absence of oxygen and therefore the culture was not used. Similar to the anaerobic experiment, after combining the DI water, bacterial culture and potassium nitrate solution, the mixture was deoxygenated using nitrogen gas. The feed solution and the target chemical was added and the ports clamped to prevent oxygenation. A table detailing the exact quantity of each component of the anoxic reactors can be found in Table 21.

4. Sample collection and distribution

Sample collection began with switching off the environmental shaker. Then, one at a time, placing each bioreactor onto a magnetic stirrer. Each reactor contained a one inch magnetic stir bar throughout the experiment to allow retrieval of a representative sample. Set the stirrer as to promote sufficient mixing, while being careful to keep turbulence to a minimum.

The aerobic experiment involved simply using 10 ml glass pipettes and removing the required volume from each of the bioreactors. Following the collection procedure, make sure to recap the flasks using aluminum foil. The rubber stopper assembly was needed for both the anaerobic and anoxic experiment to prevent oxygen contamination. Therefore, it was necessary to input nitrogen gas into the reactor via port 2 (Figure 5), thereby increasing the pressure within, and collecting the sample from port 1. Clamps were securely fastened following the collection procedures.

The volumes needed for each test: GC analysis, solids test, and COD test, were approximately 40, 10, and 2 ml, respectively. The 40 ml required for the GC analysis was placed in 50 mL polystyrene graduated centrifuge tubes and capped. These tubes were then centrifuged at 5000 r.p.m. for 15 minutes to separate the bacterial culture from the liquid substrate. The substrate was poured into a graduated cylinder and 35 ml of the substrate was transferred to the Kimax tube for the microextraction process. When required, following the microextraction process, the additional tests, NH_4 or NO^-_3 were performed using the solution remaining in the Kimax tube. Tests were previously performed to check the applicability of analyzing ammonia and nitrate following the

microextraction process. These applicability tests resulted in approximately 95% recoveries for both NH_4 or NO^-_3 tests. The solid phase cell extraction process was performed using the bacterial cells remaining in the centrifuge tube following centrifugation.

Though the 10 ml volume is insufficient according to Standard Methods (1995) for the total solids test, it is all that could be spared in order to have enough sample material for seven days. Other than the small sample volume, the total and volatile suspended solids tests were performed in accordance with Standard Methods (1995).

The 2 ml required for the COD test was taken from the collected filtrate from the TSS test. Since the COD concentrations were as high as 3500 mg/L in the initial stages of each of the experiments, dilutions were required. The COD test was performed in accordance with HACH procedures.

5. Cell Fraction Extraction Methodology

Equipment

The required materials for the cell fraction extraction are as follows: polystyrene graduated centrifuge tubes (50 mL, 30 O.D. x 115 mm with positive seal screw caps), Pasteur pipette (146 mm), the bulb for Pasteur pipette (38 mm), the Eppendorf micropipette (100-1000 µL), centrifuge conical-bottom tube (15 mL), bench top centrifuge (maximum speed 5100 r.p.m.) and clear screw thread vials(4 ml, with open-top cap and septa). Sodium sulfate and methanol were used during the extraction process.

Procedure

1. Add 5 ml of methanol using the micropipette to the centrifuge tube with the bacterial culture.
2. Cap the tube and centrifuge at 5000 rpm for 15 minutes.
3. Remove the cap and carefully transfer the methanol into a glass-stopped centrifuge tube.
4. Add a few grams of sodium sulfate to the extract and shake for a few seconds to remove all water.
5. Transfer the extract into 4 ml tubes for storage, using a Pasteur pipette.

6. Laboratory Cleanup

Reusable materials (glassware, stoppers, etc.) were put through a cleansing process to remove trace chemicals. The glassware was rinsed and placed in an Alconox detergent solution to soak overnight. The glassware was then scrubbed with the same detergent, and rinsed first with tap water, followed by distilled and deionized waters. The final rinsing was with acetone before

drying in a 160°C oven overnight. Following oven drying, the glassware was placed on a cooling rack.

The non-glass equipment such as plastic screwcaps and centrifuge tubes were put through the same soaking and rinsing process as the glassware. However, following the acetone rinse, the equipment was immediately placed on the drying rack.

7. Sample Disposal

Following completion of analysis, contaminated water samples were disposed in a glass waste container located under a laboratory hood. The waste container was capped at the end of each day. Solid waste such as contaminated bacterial cultures were also disposed of in a glass waste container under a laboratory hood, separate from the liquid samples. The waste containers are collected by the University of Hawaii Health and Safety Department. All waste material are stored in compliance with EPA regulations. Ultimate disposal of hazardous waste are performed at mainland sites.

RESULTS AND DISCUSSION

RSSCT/Regeneration

Column Design Criteria.

Assuming proportional diffusivity, a mini-column was sized and the following dimensions determined. All equations for mini-column design can be found in the Appendix.

Table 7 - Comparison of Design Criteria for Mini-Column Vs. Full Scale Column

Design Parameters	Full-scale Column	Mini-column
Carbon Bed Depth	2.1 m	110 mm
Column Diameter	3.66 m	4.6 mm
Carbon characteristics	No. 12 x No. 40 mesh,	No. 80 x No. 100 mesh
Hydraulic Loading Rate	314.8 m/d	60.2 mm/min
EBCT	576.5 sec	111.2 sec
Flow rate	3312 m^3/day	1 cm^3/min
Reynolds Number, Stanton Number, Peclet Number	7.9,4.11x 10^{-5}, 4900	0.42, 1.38 x 10^{-4}, 16000

To size the column, proportional diffusivity was assumed since previous work showed this criteria provided the most promising results and mimicked the full-scale operation more closely. Previous mini-column work conducted at the University of Hawaii applied a much smaller column (Dugan, et al., 1995). The column used in those studies possessed the following characteristics: carbon bed depth = 18 mm, column diameter 2.3 mm, carbon characteristics = No. 200 x No. 325, flow rate = 1 cm^3/min (Dugan, et. al., 1995). That particular mini-column was similar to the one used in a study by Bilello and Beaudet (1983). The column itself was not sized according to the Crittenden, et. al. criteria and was originally intended to predict carbon adsorption capacities for specific compounds (Bilello and Beaudet, 1983). When Dugan, et. al. did apply the design criteria to the chosen column, discrepancies were seen and recommendations for use of a new mini-column were given. Thus, the Crittenden, et. al. design criteria were reviewed and a new, larger column sized.

Column runs with spiked deionized water.

The first RSSCT was conducted with a desorption cycle using 70% acetone. After regeneration, a 24-hr rinse with deionized water was performed to remove any residual desorbent from the carbon

itself and from the influent and effluent lines. Figure 14 in the Appendix, displays the breakthrough curve for EDB, TCP and DBCP. From the breakthrough curves, one can see that TCP breaks through first, followed by DBCP, then EDB. This breakthrough behavior, perhaps, may be attributed to competitive behavior among the compounds. Because competition is exhibited between compounds of similar size, it is possible that this is the case here (Newcombe, et. al., 1997b). When one compares the molecular weights of the three compounds, they are: EDB = 187.88 g/mol, TCP = 147.44 g/mol, and DBCP = 234.45 g/mol. It is important to note that all three pollutants are aliphatic hydrocarbons, so their structures are based on the same "backbone." Perhaps because of the relatively larger DBCP molecule, it cannot compete for the same sites as TCP and EDB, and thus, pore blockage may be the driving factor here. In essence, DBCP may not be able to compete for the same sites, and thus, non-competitive behavior is exhibited. DBCP may occupy all the carbon's sites specific to it and once saturated, breaks through. On the other hand, because TCP and EDB are similar in size, there may be competition for active sites between these two compounds. Since EDB breaks through last, it seems to occupy the sites that TCP may also be able to occupy, thus, causing TCP to break through. Influent concentrations, though not shown here varied from an initial start-up concentration of 200 ng/L for EDB and DBCP and 2000 ng/L for TCP to a final concentration of 5000 times the original concentration near breakthrough. As described in the Materials and Methods section, influent concentrations were increased according to the following increments each day: 5x, 10x, 50x, 200x, 1000x, and 5000x. Carbon adsorption capacity at time of breakthrough for the VOCs are as follows: 19.7 mg/g for EDB, 74.1 mg/g for TCP, and 5.9 mg/g for DBCP.

After the initial loading of the carbon, the column was then regenerated. From Figures 16, 17, and 18, one can see that the 70% solution of acetone seemed to remove a significant portion of the VOCs; however, when one looks at the amount adsorbed compared to the amount removed, acetone did not perform well. Table 8 displays the contrast:

Table 8 - Comparison of Pesticide Adsorbed vs. Pesticide Removed using 70% Acetone

Pesticide	Amount Adsorbed (ng/g)	Amount Removed (ng/g)
EDB	19700	278
TCP	74100	1883
DBCP	5900	114

From Table 8, the percentage removed for each pesticide was calculated to be: 1.4% for EDB, 2.5% for TCP, and 1.9% for DBCP. These percentages are quite discouraging since the amount of bedvolumes of regenerant passed through the column was over 200. Though the results are dismal, they are not surprising because of the mechanism by which acetone removes the contaminant from carbon. As discussed in the literature review portion of this study, acetone is an organic solvent and thus, its molecular weight plays a large role in removing the pesticides (Martin and Ng, 1983). Its molecular weight (58.08 g/mol) is smaller than the three pesticides which allows it to penetrate the pores to remove them. However, because acetone is miscible with water and also possesses an affinity for the carbon, its regeneration capacity is low.

Post-regeneration breakthrough curves were then plotted when the carbon was reloaded in the same manner as in the first loading. Figure 15 shows that the pesticide concentrations remained quite high even after 4.5 L of influent had been treated (2250 bedvolumes). Again, these results were quite dismal; however, were not surprising due to the low removal percentages using acetone. Even though sites were regenerated, the poor performance during the second loading cycle was perhaps attributed to irreversible adsorption and also because acetone itself occupied sites in which the pesticides were eliminated. Even with a deionized water rinse, these results cannot be avoided. The loss in carbon capacity is irreversible and prolonging regeneration does not usually produce improved results. Irreversible adsorption has been attributed to the trapping of molecules in micropores; however, there is speculation on other causes of this phenomenon. Modell et. al. attributed irreversible adsorption to chemical binding of the adsorbate to high-energy sites. These sites correspond to surface oxides on the sorbent itself (i.e., carboxyl, hydroxyl, and carbonyl groups) formed during pretreatment of the carbon (Modell et. al., 1980). These sites have the ability to chemically react with the adsorbates, and thus, produce an irreversible reaction.

Concurrently running with the column set for 70% acetone regeneration, another column was loaded. Breakthrough behavior as seen in Figure 12 exhibit the same pattern seen in Figure 14. TCP breaks through first followed by DBCP and EDB. However, because influent concentrations were increased over a shorter amount of time, carbon capacities at time of breakthrough differ markedly from the previous column: EDB = 5.32 mg/g, TCP = 41.6 mg/g, and DBCP = 2.7 mg/g. It is important to note that EDB never broke through in this run which may account for the low carbon capacity. Due to the time required to load the carbon and reach breakthrough, influent concentrations were then set to increase incrementally according to the scheme outlined in the Materials and Methods section. All runs subsequent to this one followed that scheme, and thus, carbon capacities for subsequent runs are more similar.

When this column was regenerated, an interesting difference can be seen in the regeneration plots (Figures 16, 17, and 18). TCP and EDB followed the same desorption behavior; however, DBCP did not appear in the effluent until roughly 80 bedvolumes of desorbent had passed through the column. It is not clear as to why this occurred. A plausible explanation may be in the characteristics of the compounds themselves. As noted earlier, it seems as if competition is exhibited between TCP and EDB because of their relatively similar size. Because of this, one may be more weakly adsorbing causing it to break through first. In this case, TCP may be the more weakly adsorbing compound and thus, is removed easily. DBCP may be a strongly adsorbing compound, and thus, is not removed as easily. Also, because of the decrease of acetone by volume in solution, it would take much more acetone to handle the amount of pesticide being removed. Subsequent to regeneration, the breakthrough curves show that solute never really adsorbed onto the carbon surface with the exception of EDB. After several days of operation, solute continued to leach out in concentrations exceeding the designated breakthrough concentrations. Though these results were disappointing, there may have been a plausible, non-technical reason for the premature breakthrough of the pesticides. Influent and effluent lines may have had a build-up of pesticide which could have possibly contributed to the high concentrations seen in the effluent. Rinsing procedures were not practiced during the regeneration process and may have led to an accumulation of pesticide within influent and/or effluent lines. To test this theory, the influent line was detached from the column and 35 mL collected. Via GC, pesticides were found in the line even after a 24 hour rinse of deionized water. Because of this, all subsequent runs were rinsed with a solvent mixture followed by a 24 rinse of deionized water to eliminate contamination or residual build-up as a reason for the abnormal breakthrough behavior. When compared to the removal percentages for 70% acetone regeneration, 50% acetone performed just as poorly. Figures 16,17, and 18 also show that pesticide removal does not vary a great deal when the acetone is reduced in concentration. Table 9 displays the contrast in removal efficiencies:

Table 9 - Comparison of Pesticide Removal for 50% and 70% Acetone

Pesticide	Amt. Adsorbed (µg/g)	Amt. Removed with 50% acetone (µg/g)	% Removal in 50% acetone	% Removal in 70% acetone
EDB	5320	333	6%	1.4%
TCP	41600	3140	7.5%	2.5%
DBCP	2700	262	9.7%	1.9%

When one compares the amount of pesticide removed between the two column runs, the quantities are similar regardless of amount of pesticide adsorbed onto the carbon. Still, the removal

percentages are low and acetone's poor regeneration is once again reflected in the breakthrough curves displayed in Figure 13 for the second loading cycle.

Along with 50% and 70% acetone, one column run was conducted using 100% acetone. For this portion of the study, two regeneration cycles were performed on the carbon. Thus, the carbon was loaded three times according to the influent scheme described in the Materials and Methods section. This experiment was conducted to determine if the same carbon adsorption capacity can be regained after each regeneration. If it is observed that adsorption capacity remains the same for each loading after regeneration, the carbon may be kept in place and reused for an indefinite amount of time. For this portion, two regeneration cycles were performed. Adsorption capacity (i.e., regeneration efficiency) was then calculated as stated in the literature review: subsequent adsorption capacity/original adsorption capacity or A_1/A_o (Martin and Ng, 1983). Figures 19 - 21 display the breakthrough behaviors for the pesticides. From these figures, it can be seen that the full adsorption capacity is not regained. Figures 22 - 24 display the regeneration data for these runs. Again, very little difference can be seen between the two. It is interesting to note that the second regeneration cycle removed more pesticide than the first. This may have been attributed to pesticide that was never removed in the first cycle, thus, resulting in higher pesticide concentrations leaching out in the regenerant stream. Interestingly, regeneration efficiencies differ quite a bit between the two cycles. Table 10 shows the data for the two regeneration runs:

Table 10 - Comparison of Regeneration Efficiencies for Two Cycles using 100% Acetone

Pesticide	Amt. Adsorbed in Run1 (A_o) (ug/g)	Amt. Adsorbed in Run 2 (A_1) (ug/g)	Amt. Adsorbed in Run 3 (A_2) (ug/g)	Regeneration Efficiency Run 2 (A_1/A_o)	Regeneration Efficiency Run 3 (A_2/A_o)
EDB	26890	26880	8392	99%	31 %
TCP	112484	112417	32708	99%	29%
DBCP	15453	15421	3616	99%	23%

The first regeneration cycle restored almost all of the carbon's adsorption capacity while the second regeneration restored only 30% of the original adsorption capacity. Such a sharp drop in adsorption capacity may indicate that the carbon's capacity decreases with each succeeding regeneration. The sharp drop in adsorption capacity may be attributed to adsorbed acetone that replaces the desorbed pesticide, and perhaps over time, subsequent regenerations may produce

even lower adsorption capacities than 30%. These results may not be very promising; however, the fact that nearly 99% of the carbon's capacity is restored in one regeneration is quite good. Theses results may just point to the fact that the carbon may only last one reusable loading cycle and would need to be disposed of after that cycle. Still, the cost of using nearly 200 bedvolumes of solvent would need to be weighed against the savings to reuse the carbon. Because of the amount of time necessary to complete this portion of the study and the dismal results, a short-term series of tests were added to test several solvent/acid/base combinations. This seemed to be a necessity since the conventional solvents were not performing well on their own.

Short-term regeneration experiments.

As stated in the Materials and Methods section, a short-term matrix was developed to evaluate the regeneration ability of several acid/base combinations. Experiments were conducted in roughly 2 days time. The incorporation of the acids/bases and solvents in the matrix was dependent on several factors. First of all, previous work by Walton-Green (1996) showed that several of the compounds in the matrix performed well. These include 2-propanol, acetic acid, and formic acid. Also, previously-published work served as the basis for the matrix. Last of all, it was desired that some practicality be incorporated in this study which eliminated any extremely hazardous/carcinogenic solvents or any solvent that possessed certain use restrictions. These chemicals include benzene and ethanol. Also based on practicality, acetone was included because all three pesticides are soluble in it and acetone is readily available. This portion of the study is not complete yet; however, finished experiments will be discussed here. Below is a table displaying the removal percentages for the acids/bases in combination with deionized water. Removal percentage is calculated as the (amount adsorbed - amount remaining on the carbon)/amount adsorbed. It is important to note that this differs from adsorption capacity. Carbon was not reloaded because it would take too much time using the natural well water. Still, these results are far better than the removal percentages for acetone alone.

Table 11 - Comparison of Removal Percentages for Acid/Base Desorbents Used in Combination with Deionized Water

Pesticide	Formic Acid	Acetic Acid	Hydrochloric Acid	Sodium Hydroxide	Sodium Hydroxide Salt
EDB	99%	81%	74%	30%	3%
TCP	98%	71%	53%	37%	0%
DBCP	14%	48%	76%	45%	0%

**volume of acid/base = 10 bedvolumes (20 mL), volume of water = 10 bedvolumes*

From the above table, it can be seen that formic acid performs the best followed closely by acetic acid and hydrochloric acid. It is also not surprising that formic and acetic acid performed poorly in removing DBCP because they are both carboxylic acids and undergo the same mechanism to remove the pesticides. Why both exhibit good removal percentages in removing EDB and TCP is not clear. Perhaps it is because both have only one halogen attached to its backbone while DBCP has two. Also, formic acid performs slightly better than acetic acid. Both being carboxylic acids, they form solutions in water, so their removal mechanism is the same; however, formic acid is a smaller molecule and perhaps penetrates the pores more readily (Martin and Ng, 1983). In contrast, hydrochloric acid (HCl) tends to change the surface charge of the carbon, thus causing a contaminant to be removed (Martin and Ng, 1983). This may be the case here. HCl is thought to produce a very positive charge on the carbon surface, thus causing the neutral species to be repelled from the carbon surface and washed out in the effluent stream.

Sodium hydroxide (NaOH) was anticipated to produce better results, but the removal percentages calculated are lower than the aforementioned desorbents. It is not certain why these results are not good. NaOH at molar concentrations $\leq$ 3M are thought to remain in tact and form soluble species with the contaminants. The soluble species is then carried out of the column in the effluent stream. Typically, at concentrations greater than 3M, NaOH ionizes into Na^+ and OH^- which is thought to then occupy sites on the carbon and fail to remove the contaminants. It is not known for sure which phenomenon occurred here. Further study would be necessary to determine the following: 1) what reaction products are produced when the pesticides are contacted with NaOH, if any and 2) if NaOH does remain in tact or ionizes at a concentration of 3M. Because previous work indicated that improved regeneration is seen when NaOH was heated, one experiment was conducted with NaOH heated to 50°C, also followed by the deionized water rinse. The results, as shown in Table 11 above, are poor. It only removed 3% of EDB and none of TCP or DBCP. This result seems puzzling and there is only speculation as to why this occurred. One explanation may be that NaOH ionized at the elevated temperature and instead of removing the pesticides, it occupied sites on the carbon. Because these results for NaOH at the elevated temperature seemed incorrect, the experiment was repeated and the results were the same.

Along with the acids/bases used in conjunction with water, they were also tested in conjunction with acetone and 2-propanol. Tables 12 and 13 display the results for this portion of the study:

Table 12 - Comparison of Removal Percentages for Formic Acid/Acetone Combinations

Pesticide	Formic Acid	Acetone	Formic Acid	Acetone
EDB	99%	1%	99%	1%
TCP	95%	5%	98%	2%
DBCP	90%	10%	92%	8%

**1 = SAS combination (solvent/acid/solvent); 2 = ASAS combination (acid/solvent/acid/solvent)*

Table 13 - Comparison of Removal Percentages for Formic Acid/2-Propanol Combinations

Pesticide	Formic Acid	2-Propanol	Formic Acid	2-Propanol
EDB	99%	1%	85%	15%
TCP	95%	5%	81%	18%
DBCP	92%	8%	80%	20%

**1 = SAS combination (solvent/acid/solvent); 2 = ASAS combination (acid/solvent/acid/solvent)*

In both tables above, it can be seen that formic acid certainly performs better than the organic solvents. The discrepancy between 2-propanol and acetone is difficult to explain since both have very similar molecular weights (2-propanol = 60 g/mol). Referring to previous work, both performed quite similarly in removing phenol (Martin and Ng, 1983). Their removal mechanisms are also the same, so the difference in removal percentage may be attributed to the solubility of the pesticides in each solvent. In both tables, it is interesting to note that running two acid cycles does not necessarily result in better removals. As stated above the short-term experiments are not complete, however, one last run has been included here to serve as a contrast to the above regenerations. Table 14 displays the data for two cycles of acetone with one cycle of HCl:

Table 14 - Removal Percentages for Hydrochloric Acid/Acetone Combination

Pesticide	Hydrochloric Acid	Acetone
EDB	28%	84%
TCP	5%	31%
DBCP	0%	100%

**SAS=two cycles solvent, 1 cycle acid*

These results serve as an interesting contrast to Tables 12 and 13 above. HCl does not seem to remove the pesticide. Instead, it seems to "prepare" the carbon surface for the acetone, thus, increasing acetone removal. Perhaps in this column run, HCl did alter the carbon surface which repelled the pesticides, thereby facilitating their removal in the acetone cycle.

The results listed here are only about half of the entire matrix. Work is ongoing and it is anticipated that promising results will continue to be obtained. Once the matrix has been successfully completed, two or three of the most successful combinations will undergo more testing to see if decreasing the solvent and/or acid volume still produces good results.

Column runs with natural well water vs. spiked deionized water.

Two columns were set up for this section of the research. One column was set up with natural well water from Mililani while another was set up to be run with spiked deionized water only. It was anticipated that the well water column would break through first indicating that the three pesticides are indeed competing with NOM and possibly silica. Figures 25 - 26 display the breakthrough curve for the Mililani well water. Breakthrough of TCP occurred after 18000 bedvolumes of water had been treated. DBCP did not breakthrough in this time period. In contrast, the column with spiked deionized water broke through after 25000 bedvolumes had passed (Figures 27 - 28). The fact that TCP broke through first is a good sign since this also occurs in the full-scale column; however, breakthrough in the field occurs after about 50000 bedvolumes (Dugan, et. al., 1995). This discrepancy may be attributed to the column design criteria. The column sized as it was did mimic the carbon's affinity for the two pesticides even though the bedvolumes treated were not the same. Like the previously-published work states, the mini-column shows promise in mimicking full-scale behavior but is not in any way, intended to replace pilot-scale studies (Crittenden, et. al., 1985). Along with the GC analyses performed each day, TOC samples were collected and analyzed to see if the carbon was in fact removing NOM

(measured as non-purgeable organic carbon (NPOC)). Equipment problems were encountered for this test and reliable data could not be obtained; however, one portion of the TOC samples was analyzed correctly. Data indicated that effluent concentrations were lower than influent concentrations (influent concentrations vary in the range 0.1 - 0.9 ppm). This result, perhaps, shows that NOM is being removed; however, some data points show that effluent concentrations exceeded the influent concentration. High effluent NOM readings may also indicate that an adsorption/desorption phenomena is occurring. Adsorbed NOM may desorb with time which produces free sites that would again be occupied by molecules in the influent. This may be a plausible explanation for the fluctuations in NPOC readings. Silica data are also not presented here, but will be analyzed to determine if it too is being removed by the carbon.

The columns with natural well water and deionized water were then regenerated with a combination of NaOH and acetone - 2 cycles each. The following table displays the results:

Table 15 - Removal Percentages for Regeneration of Columns 1 and 2 using NaOH and Acetone**

Pesticide	Col 1 - NaOH	Col 1 - Acetone	Col 2 - NaOH	Col 2 - Acetone
TCP	98.9%	1.14%	99%	1%
DBCP	100%	0%	100%	0%

*** Column 1 = Mililani Well Water, Column 2 = Spiked Deionized Water*

Table 15 shows that NaOH clearly removes most of the pesticide for both columns. These results are quite different from that shown in Table 11. NaOH seems to perform better when used in conjunction with another desorbent. Short-term experiments with NaOH are not yet complete and thus, it is difficult to settle on this conclusion. It is also premature to state definitively that NOM competes with the pesticides. To determine whether this competitive behavior is indeed being exhibited further study is necessary. Further study would be necessary to: 1) determine the nature of the competition - whether the NOM compounds are as small as the pesticides themselves causing site competition or if the compounds are large, thereby causing pore blockage and 2) identification of these compounds.

Biodegradation

The biodegradation - GC analysis requires calculation of the recovery efficiency of the DBCP, EDB and TCP extracted by the microextraction method. Using the equation listed in the Appendix,

the concentrations of target chemicals were calculated for four known, spiked concentrations (0.05, 0.2, 0.5 and 1.0 mg/L). The average of duplicates was used to determine the linear regression equation which provided for the calculation of the recovery efficiency factor and R^2 accuracy factor for each of the chemicals (Figures 31-33 in appendix)(Table 16).

TABLE 16 - Microextraction Recovery Efficiency for DBCP, EDB, and TCP

Analyte	Recovery Efficiency Factor	R^2 Accuracy Factor
DBCP	0.498	0.9993
EDB	0.611	0.9980
TCP	0.385	0.9916

Each recovery efficiency factor is divided into the microextraction concentrations to determine the actual concentrations, as shown in the following equation:

Actual concentration = Microextraction recovery / Recovery Efficiency Factor

The minimum detectable levels for the GC of DBCP and EDB, are 20 ng/L and for TCP 100-200 ng/L. Therefore, in a typical experiment of approximately 500 ml, 10 ng of DBCP and EDB, and 100 ng of TCP may not appear as a peak on the chromatogram plot. However, these levels of analyte are insignificant compared to the typical levels of interest.

To date, the non-specific bacterial culture has been tested for degradability of the target chemicals under three conditions: aerobic, anaerobic, and anoxic. The nitrifying bacteria have been tested solely under aerobic conditions since nitrifiers require oxygen for growth. Additional tests on the bioassays were pH, TSS and VSS, ammonia and nitrate-nitrogen (if required) and COD tests.

The bioassay experiments were set-up as described in the Material and Method - Bioassay section. All tests can be simplified by separating each into two stages. Stage 1 involved a seven day acclimation period in which the cells were to degrade the feed and organic chemical and hopefully grow and reproduce into agents capable of greater degradation of the chemical. Following the first seven days, the cell culture was isolated, resuspended, and used in Stage 2 of the bioassay to analyze its performance for an additional seven days.

Tables 23-25 (in appendix) are the TSS and VSS results for the non-specific and nitrifying bacterial cultures under aerobic conditions. Both bacterial cultures increased between 19-40% (of initial conc.) after third day of acclimation. The bacterial populations (VSS) displayed a significant

decrease ranging from 50-61% following the first seven days of experimentation. The population was expected to increase as it consumed the feed solution and its components. Following the consumption of the feed, the population would ideally acclimate itself, and consume the additional substrate (pesticides). A steady increase in solids concentration was anticipated, thus developing a population which would thrive on the substrate. This does not seem to be the case. After the consumption of the feed, the solids concentration had increased, but eventually dropped below the initial concentrations. The decrease may be due to inadequate quantities of vitamins and minerals within the reactors throughout the duration of each stage. Approximately half (39-52% of initial conc.) of the bacterial culture population remained for resuspension of the culture for the second stage of experimentation (days 7-14). As in first stage, the second stage displayed the same rise and fall pattern. An error made during the first series of aerobic experiments was the addition of feed to the control reactors in an attempt to simulate the bioassay reactors with the exception of the bacterial culture. Even through careful autoclaving of the reactor and their components, the feed provided the means for bacteria to grow within the control reactors, possibly contributing to the chemical disappearance. This growth within the controls is reported as increase in TSS and VSS values during the aerobic experiments. Therefore, future control reactors were composed of deionized water and the target chemical, which resulted in no growth within the reactors. The controls for the aerobic experiment were repeated and these results have been reported in the same tables.

The anaerobic and anoxic TSS and VSS results are in Tables 26-28. Unlike the aerobic results, the bacterial population under these conditions decreased throughout the duration of the experiment (with a few minor exceptions). This seems to indicate that the bacterial culture cannot easily adapt to the new (deoxygenated) environment.

The COD test is a recommended method for chemical characterization of biodegradation (Gibson, 1984). The soluble COD concentrations of the aerobic experiment are located in Tables 29-31. As expected, the soluble COD concentrations decreased considerably down to 4-5% (remaining) when tested on the third day and remained the same when tested on the seventh day. This suggests that the contaminants were disappearing and the soluble COD was at its lowest level by the third day. During the second stage of testing, the COD again bottomed by the third day. This decrease implies the occurrence of biodegradation, but to what extent is unknown.

Tables 29-31 (in appendix) also display the control COD concentrations which decreased considerably throughout the experiment. Since no biodegradation was expected to occur, the COD concentrations should have remained constant. This decrease was attributed to the bacterial growth

within the control reactors. The control components were changed (feed eliminated) and growth was no longer detected. Since no competition was assumed within the control reactor, all the target chemicals were injected into one reactor to test for volatilization and/or natural breakdown. In Table 32 (in appendix), the COD concentrations of the repeated control experiment remained constant, implying no degradation. Unfortunately, significant disappearance still persisted.

The COD results of the anaerobic and anoxic experiments are located in Table 33 (in appendix). The COD concentrations of the controls remained relatively constant. In contrast to the aerobic experiment, the COD concentrations of the anaerobic degradation flasks decreased only 8-20%, while the anoxic decrease was slightly greater at 30-41%. As in the aerobic experiment, the decrease in COD concentrations implies the occurrence of biodegradation, but to what extent is unknown.

The pH, ammonia-nitrogen, and nitrate-nitrogen test were performed to ensure a proper environment suitable for the efficient degradation of the substrate by the bacterial culture. The addition of the buffer solution ensured that the pH remained at approximately 7.0, which can be seen in Figure 34-36 (in appendix) of the aerobic experiments and in Table 34 (in appendix) of the anaerobic and anoxic experiments. A pH range between 6.5 and 7.5 maintains a healthy bacterial population, though pHs of as low as 4.0 can be tolerated by most bacteria (Tchobanoglous & Schroeder, 1987). The data show that tests which required ammonia-nitrogen (Table 35) and nitrate-nitrogen (Table 36) were supplied with sufficient concentrations throughout the duration of the experiments.

Figures 37-42 are plots of analyte concentration versus time of the control flasks, and the biodegradation flasks under aerobic conditions. In the anaerobic and anoxic experiments, the cell fraction was included, but due to their consistently low concentrations (~0.01-3% of initial conc.), the aerobic plots do not include these values. Volatilization and/or natural disappearance in the control flasks accounted for 82, 60, and 26% reduction in analyte concentration for EDB, TCP, and DBCP, respectively. Figures 43-54 are plots of analyte concentration versus time of the control flask experiments, and biodegradation flasks under anaerobic and anoxic conditions. The disappearances of EDB, TCP, and DBCP from the control flasks for the anaerobic experiment were 59, 50, and 61%, respectively. For the anoxic experiment, these values were 59, 41, and 64%, respectively. The percent reduction (of the control conc.) ranged from 84% for the EDB test under anaerobic conditions to 8% for the TCP test under anaerobic conditions. Unfortunately, due to the excessive disappearance in the controls, it is unclear how much of the reduction is attributed to biodegradation. The disappearance within the control flasks was the major problem of these

experiments, caused by volatilization into the head-space within the flasks. Though the highly volatile nature of the target chemicals was known, the biodegradability of the target chemicals was not. It was hoped that considerable (>99% of control conc.) reduction of analyte concentration would occur prior to the seven day testing period. Unfortunately, this was not the case under any of the three conditions. Due to the excessive volatilization, it is uncertain if significant biodegradation had occurred.

CONCLUSIONS AND RECOMMENDATIONS

RSSCT/Regeneration

Though there is still some work left in this study, results to date do show promise and offer a little more insight to the competitive behavior among compounds on GAC. One can safely conclude that organic solvents alone do not effectively regenerate the carbon. Even with nearly 100% adsorption capacity regained, it does not seem economical to regenerate the column with over 200 bedvolumes of solvent. Therefore, the data in the short-term matrix is quite valuable. Solvents in conjunction with an acid or a base show a marked improvement in regeneration of the carbon. Not only is the increased pesticide removal an advantage but also the decrease in solvent bedvolumes. Removal percentages were high with a regeneration cycle of 10 bedvolumes of acid/base and 88 bedvolumes of solvent. The solvent volume is still high; however, optimizing the matrix will proceed shortly in which 10 bedvolumes of solvent are recycled. If this proves to be successful, carbon regeneration using conventional solvents may become more practical and economical.

This study has also shown that the desorbents in the short-term matrix can be used to regenerate spent carbon containing the pesticides and NOM. This eliminates the need for additives to the solution to remove the NOM. However, this is not definite and any future work in this area should include NOM characterization. The natural well water run does show that the pesticides seem to be competing with something else other than themselves (column1 - bedvolumes treated = 18000, column 2 - bedvolumes treated = 25000). It does not, however, serve as the means to identifying the nature of the competition or the types of NOM compounds found in the well water.

Biodegradation Studies

In an attempt to determine an economical and efficient method to remove pesticides from the effluent waste stream created by the GAC regeneration process, bacterial cultures were developed and tested. The bacterial cultures would ideally metabolize the substrate completely and the regenerant would be recycled. The contaminants were found to be extremely volatile in nature; as high as 82% reduction in chemical (EDB) control concentration after seven days under aerobic conditions. With the reactors sealed (under anaerobic and anoxic conditions), the reduction of the chemicals still ranged from 41-64%. In some cases, biodegradation seemed to occur, but to what extent was uncertain. The supposed biodegradation is supported by the significant decrease in COD concentrations of the aerobic experiment. The behavior of the VSS implies difficulty by the bacterial culture to acclimate itself to the new environmental conditions. Though the results of this

study are inconclusive, it seems to indicate that biodegradation is possible. But conclusive results rest on attaining quantifiable data which can be repeated. For this to happen, volatilization must be controlled. Testing methodology must be improved to increase the likelihood of greater and quantifiable biodegradation. Most important is the elimination of volatilization, which is recommended for any further experiments. The inadequate concentration of bacterial culture may have led to the lack of significant biodegradation. Therefore, since the typical VSS value used in bioassays is at or above 1000 mg/L (Viessman, 1985), further experiments should abide by this range.

The non-specific bacterial culture should also be re-tested under anaerobic and anoxic conditions, with modifications that will eliminate any head space, thus eliminating volatilization. According to previous studies, testing under sulfate reducing conditions appear promising because it led to high percent removals with relatively short acclimation periods.

Recommendations

In conclusion, future work can be built around this study and is recommended to incorporate the following: 1) NOM characterization to provide a firm understanding of the nature of site competition, 2) NaOH experiments with the pesticides to determine its exact mechanism of removal, and 3) characterization of the GAC to provide a better understanding of the carbon surface itself, 4) further biodegradation tests that can produce accurate, repeatable results which incorporate some mechanism to control volatilization, and 5) biodegradation tests that apply the use of sulfate-reducing conditions. It is hoped that with further work in this area, the possibility does exist that an effective, bioregeneration process can be developed.

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REFERENCES

1. Aiken G. and Cotsaris E. (1995). Soil and hydrology: their effect on NOM. *J. Amer. Water Works Assoc.* Vol. 87, 36-45.
2. American Water Works Association (1995). Standard Methods 19th Edition. Washington, DC.
3. American Water Works Association (1990). Water Quality and Treatment. 4th Edition. McGraw-Hill, Inc., New York, NY.
4. Babcock, R.W. (1996). Investigation of sorption, desorption, and bioregeneration of natural organic matter and pesticides on granular activated carbon used to treat contaminated drinking water. Research proposal, University of Hawaii at Manoa.
5. Baugh, P.J. (editor) (1993). Gas Chromatography. New York, USA: Oxford University Press Inc.
6. Beccari, M., Paolini, A. E., and Variali, G. (1977). Chemical regeneration of granular-activated carbon. *Effl. Wat. Treat. J.* No. 17, 287-294.
7. Bercic, Gorazd and Pintar, Albin. (1996). Desorption of Phenol from Activated Carbon by Hot Water Regeneration. Desorption Isotherms. *Ind. Eng. Chem. Res.* Vol 35., No. 12, 4619-4625.
8. Bilello L.J. and Beaudet, B.A. (1983). "Evaluation of Activated Carbon by the Dynamic Mini-column Adsorption Technique." In Treatment of Water by Granular-Activated Carbon. Irwin R. Suffet, M.J. McGuire (Eds.) American Chemical Society.
9. Bouwer, E.J., and Wright, J.P. (1988). Transformation of trace halogenated aliphatics in anoxic biofilm columns. *J. Contam. Hydrol.* 2:155-69.
10. Bouwer, E. J.; McCarty, P. L. (1985). *Appl. Environ. Microbiol.* 50, 527-528.
11. Brennan B., "Agricultural Chemical Use in Hawaii" In Toxic Organic Chemicals In Hawaii's Water Resources. P. S. C. Rao and R. E. Green (Eds). University of Hawaii at Manoa. 1987.
12. Burch, T.A., Kawaguchi, P., and Oyama N. (1982). Health assessment of a community with pesticide contaminated drinking water: Part I. Household health interview survey. Hawaii Dept. of Health, R and S. Rpt. 42.
13. Burlinson, N.E., Lee, L.A., and Rosenblatt, D.H. (1982). Kinetics and Products of Hydrolysis of 1,2-Dibromo-3-chloropropane. *Environ. Sci. Technol.* 16: 627-632.
14. Castro, C.E., and N.O. Belser. (1968). Biodehalogenation. Reductive dehalogenation of the biocides ethylene dibromide, 1,2-dibromo 3-chloropropane, and 2,3-dibromobutane in soil. *Environ. Sci. Technol.* 2:779-783.
15. Choudry, G. G. (1984). Humic Substances - Structural, Photophysical, Photochemical, and Free Radical Aspects of Interactions with Environmental Chemicals. Gordon and Breach, New York, NY.
16. Cooney, David O., Nagere, Andrew, and Hines, Anthony L. (1983). Solvent Regeneration of Activated Carbon. *Water Res.* Vol. 17, No. 4, 403-410.
17. Crittenden, John. C., et. al. (1987). Design of Rapid Fixed-Bed Adsorption Tests for Non-Constant Diffusivities. *Journal of Environmental Engineering.* Vol. 113, No. 2., 243-259.

18. Crittenden, John. C., Berrigan, John K., Hand, David. W. (1986). Design of rapid small-scale adsorption tests for a constant diffusivity. *Journal WPCF.* Vol. 58, No. 4, 312-319.
19. Crittenden, John. C., et. al. (1991). Predicting GAC Performance With Rapid Small-Scale Column Tests. *Journal AWWA.* Vol. 81, No. 1, 77-87.
20. Cummings, Laura and Summers, R. Scott. Using RSSCTs to predict field-scale GAC control of DBP formation. *Journal AWWA.* Vol. 86, No. 6, 88-97.
21. Davis, Stanley N. (1969). Silica in Streams and Groundwater of Hawaii. Tech. Rpt. No. 29. Water Resources Research Center, University of Hawaii at Manoa.
22. Dugan, Gordon. L., Fugioka R., Lau, L.S., Takei, G., Gee, H., McParland, T., and Chu, H. (1995) Extending the Effective Life of the GAC Used to Treat Well Water: Phase II of Evaluative Study at Mililani. Project Report No. PR-95-07. Water Resources Research Center, University of Hawaii at Manoa.
23. Ephraim, J., Alegrat, S., Mathuthu, A. Bicking, M., Malcolm, R.L., and Marinsky, J.A. (1986). A united phsicochemical description of the protonation and metal ion complexation equilibria of natural organic acids (humic and fulvic acids): 2. Influence of polyelectrolyte properties and functional group heterogeneity on the protonation equilibria of fulvic acid. *Environ. Sci. Technol.* Vol. 20, 354-366.
24. Eto, M.A., Burbank, N.C., Klemmer, H.W., and Lau, L.S. (1967). Behavior of selected pesticides with percolating water in Oahu soils. Tech. Rep. No. 9, Water Resources Research Center, University of Hawaii at Manoa.
25. Fischer, C., Green, R.E., and Burbank, N.C. (1977). Refractory organic compounds in treated effluent and their removal in soil, Mililani, Oahu, Hawaii. Tech. Rep. No. 115, Water Resources Research Center, University of Hawaii at Manoa.
26. Fox, R.D., Keller, R.T., Pinamount, C.J., and Severson J.L. (1970). Purification of a waste brine by carbon adsorption with emphasis on wastewater reuse. *Proc. 25th Ind. Waste Conf. Engng. Bull., Purdue Univ. Indiana.* 322-330.
27. GMP Associates (1984) Treatment Study for Groundwater Supply Final Report. Prepared for Board of Water Supply, City and County of Honolulu.
28. Himmelstein K.J., Fox, R.D. and Winter, T.H. (1973). In-place regeneration of activated carbon. *Chem. Eng Progress.* No. 11, 65-69.
29. Howard, P.H. (Editor) (1991). Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Lewis Publishers, Chelsea, Michigan.
30. Huang J.C. and Garrett, J.T. (1975). Effects of colloidal materials and polyelectrolytes on carbon adsorption in aqueous solution. *Proc. Ind. Waste. Conf.* Vol. 30, 1111-1121.
31. Hyman M.R., Wood P.M. (1983). Methane oxidation by *Nitrosomonas europaea. Biochem. Journal* 212: 31-37.
32. Hyman M.R., Wood P.M. (1984). Ethylene oxidation by *Nitrosomonas europaea. Archives of Microbiology* 137: 155-158.
33. Hyman M.R., Murton, I.B., and Arp, D.J. (1988). Interaction of Ammonia Monooxygenase from Nitrosomonas europaea with Alkanes, Alkenes, and Alkynes. *Applied and Environmental Microbiology* 54: 3187-3190.
34. Isaacson, D.J.; Hankin, L.; Fink, C.R. (1984). *Science* (Washington D.C.), 225:672.

35. Jain, J.S. and Snoeyink, V.L. (1973). Adsorption from bisolute systems on active carbon. *J. WPCF.* Vol. 45, No. 12, 2463 - 2479.
36. Kawata, E. (1996) Personal communication. Board of Water Supply, City and County of Honolulu.
37. Lam, T., and V.L. Vilker. (1987). Biodehalogenation of bromotrichloromethane and 1,2-dibromo-3-chloropropane by *Pseudomonas putida* PpG-786. *Biotechnol. Bioeng.* 29:151-159.
38. Lau, L.S. (1987). Organic Chemical Contamination of O'ahu Groundwater. Technical Report No. 181. Water Resources Research Center, University of Hawaii at Manoa.
39. Leng, Chi-Cheng and Pinto, Neville G. (1996). An Investigation of the Mechanisms of Chemical Regeneration of Activated Carbon. *Ind. Eng. Chem. Res.* No. 35, 2024-2031.
40. Leon-Guerrero, E.D., Loague, K., and Green, R.E. (1994). Wellhead treatment costs for groundwater contaminated with pesticides: a preliminary analysis for pineapple in Hawaii. *Environmental Management*, No. 18, Vol. 1, 93-104.
41. Long, W.C. and Babcock, R.W. (1997). Enhancement of the Biodegradability of Wastestreams Containing Polynuclear Aromatic Hydrocarbons through Ozonation. Water Resources Research Center, University of Hawaii at Manoa.
42. Martin, R.J. and Ng, W.J. (1984). Chemical Regeneration of Exhausted Activated Carbon-I. *Water Res.* Vol. 18., No. 1, 59-73.
43. Martin, R.J. and Ng, W.J. (1985). Chemical Regeneration of Exhausted Activated Carbon-II. *Water Res.* Vol. 19., No. 12, 1527-1535.
44. Modell, M., deFilippi, R., and Krukonis, V. "Regeneration of Activated Carbon With Supercritical Carbon Dioxide" In Activated Carbon Adsorption of Organics from the Aqueous Phase - Volume 1. Irwin H. Suffet and Michael J. McGuire (Eds). Ann Arbor Science Publishers, Inc., 1980.
45. Najm, I.N., Snoeyink, V.L., Suidan M.T., Lee, C.H., and Richard, Y. (1990). Effect of particle size and background natural organics on the adsorption efficiency of PAC. *J. Amer. Water Works Assoc.* Vol. 82, No. 1, 65-73.
46. Narbaitz, R.M. and Benedek, A. (1994). Adsorption of 1,1,2 - trichloroethane from river water. *J. Environmental Engineering.* Vol. 120, No. 6, 1400-1615.
47. National Cancer Institute/National Toxicology Program. (1980) Bioassay of DBCP (Inhalation) for possible carcinogenicity, Carcinogen Testing Program (NCI), Bethesda, MD, and National Toxicology Program, Research Triangle Park, NC.
48. Nelson, S. J., et. al. (1981). *Studies Environmental Science*. Volume 17, pg. 169-74.
49. Newcombe, Gayle, Drikas, Assemi, Shoeleh, and Beckett, Ronald. (1997). Influence of Characterized Natural Organic·Material on Activated Carbon Adsorption: I. Characterization of Concentrated Reservoir Water. *Water Res.*, Vol. 31, No. 5, 965-972.
50. Newcombe, Gayle, Drikas, Mary, and Hayes, Rob. (1997b). Influence of Characterized Natural Organic Material on Activated Carbon Adsorption: II. Effect on Pore Volume Distribution and Adsorption of 2-methylisoborneol. *Water Res.*, Vol. 31, No. 5, 1065-1073.
51. NIH Carcinogenicity Testing Program. (1978). Bioassay of DBCP for Carcinogenicity. Dept. Health, Education and Welfare Publication No. NIH-78-828.

52. Oki, D.S., G.L. Dugan, R.S. Fujioka, H.K. Gee, L.S. Lau, and G.S. Takei. (1994). Extending the effective life of the GAC used to treat Mililani well water: Phase I of evaluative study at Mililani. Proj. Rep. PR-95-02, Water Resources Research Center, University of Hawaii at Manoa.
53. Oshiro, K.M. (1986) Treatment of groundwater contaminated by EDB and DBCP by volatilization. Master's thesis (Civil Engineering), University of Hawaii at Manoa.
54. Pahl, R.H., Mayhan, K.G., and Bertrand, G.L. Organic Desorption from Carbon-II. The Effect of Solvent in the Desorption of Phenol from Wet Carbon. (1973) *Water Research,* Vol 7, 1309-22.
55. Rosene, M.R., Deithun, R. T., Lutchko, J.R., Wayner, W.J. (1979). "High Pressure Technique for Rapid Screening on Activated Carbons for Use in Potable Water." Calgon Corporation.
56. Rovel, J.M. (1972). Chemical regeneration of activated carbon. *Prog. Wat.Technol.* No. 1, 187-197.
57. Rylander P. N. (1979). Catalytic Hydrogenation in Organic Synthesis. Academic Press, New York.
58. Sebastiani, Enio G., Snoeyink, Vernon L., and Angelotti, Robert W. Thermal regeneration of spent and acid-washed GAC from the Upper Occoquan Sewage Authority. (1994). *Water Environ. Res.* Vol. 66, No.3, 199-205.
59. Smith, E.H. and Weber, Jr., W. T. (1985). The effect of dissolved organic matter on the adsorption capacity of organic compounds on activated carbon. *Proc. Amer. Water Works Assoc., Ann Conf.,* 553-574.
60. Srivastava, S. K. and Tyagi, Renu. Organic Desorption and Chemical Regeneration of Spent Carbon Developed from Fertilizer Waste Slurry. (1995). *Journal of Envir. Engr.* Vol. 121, No. 2, 186-193.
61. Summers, R.S., Haist, B., Koehler, J. Ritz, J., Zimmer, G., and Sontheimer, H. (1989). The influence of background organic matter on GAC adsorption. *J. Amer. Water Works Assoc.,* Vol. 81, No. 5, 66-72.
62. Sutikno, and Himmelstein, K.J. (1979). Solvent regeneration of activated carbon used for the adsorption of phenolics. Paper presented at the *72nd Annual AIChE Meeting*, San Francisco, CA.
63. Taylor, P. H., et al. (1990) Development of a thermal stability based ranking of hazardous organic compound incinerability. *Environ. Sci. Technol.*, 24, 316-328.
64. Torkelson, T.R. et al. (1961) *Toxicol. Appl. Pharmacol.*, 3: 545-559.
65. Tchobanoglous, G., & E.D. Schroeder. (1987). Water Quality. Addison-Wesley Publishing Company.
66. Thacker, William, Snoeyink, Vernon, and Crittenden, John C. (1983). Desorption of compounds during operation of GAC adsorption systems. *Journal AWWA.* Vol. 76 No. 3, 144-149.
67. US EPA (1980). 1,2,3-Trichloropropane: Health and environmental effects. No. 169 in Carcinogen Assessment Group List of Carcinogens, Carcinogen Assessment Group, Office of Health and Environmental Assessment, Office of Research and Development, Washington, DC.

68. US EPA (1979). Fed. Regist, Vol. 44: 65135-65179.
69. US EPA (1981). Fed. Regist, Vol. 46: 19592-19599.
70. US EPA (1989). Federal Register, 22 May 1989. Vol. 54, No. 97, 22062-22160.
71. Uyema, A.K. and Babcock, R.W., 1996. Development of analytical methods for extraction concentration, and quantification of ethylene-dibromide, 1,2-dibromo-3-chloropropane, and 1,2,3-trichloropropane. Water Resources Research Center, University of Hawaii at Manoa, Honolulu.
72. Verschueren, Karel (Editor) (1996). Handbook of Environmental Data on Organic Chemicals. 3rd Edition. Van Nostrand Reinhold, New York, NY.
73. Viessman, W. Jr., & M.J. Hammer. (1985). Water supply and pollution control, 4th ed. Harper Collins, New York, NY.
74. Vogel, T.M. and Reinhard, M. (1986). Reaction Products and Rates Disappearance of Simple Bromalkanes, 1,2-Dibromopropane, and 1,2-Dibromoethane in Water. *Environ. Sci. Technol.* 20, 992-997.
75. Vogel T. M., Criddle C.S. and McCarty P.M. (1987). *Environmental Science and Technology*. **21**, 722-736.
76. Walton-Green. A., (1997) Regeneration of Granular-Actived Carbon (GAC) Using Solvent-Desorption of DBCP, EDB, and TCP. Master's Thesis. University of Hawaii at Manoa.
77. Weast R. C. (Editor), 1983-1984. CRC Handbook of Chemistry and Physics, 64th edn. CRC Press, Inc., Boca Raton, RL.
78. Wilson, J. T., et. al. (1981) *Environmental Quality*. Volume 10, pg. 501-6.
79. Wilson, B.H., G.B. Smith, and J. F. Rees. (1986). Biotransformations of Selected Alkylbenzenes and Halogenated Aliphatic Hydrocarbons in Methanogenic Aquifer Material: A Microcosm Study. *Environ. Sci. Technol.*, 20, 997-1002.
80. Wong, Lyle. "Analysis of Ethylene Dibromide Distribution in the Soil Profile Following Shank Injection for Nematode Control in Pineapple Culture" In Toxic Organic Chemicals In Hawaii's Water Resources. P. S. C. Rao and R. E. Green (Eds). University of Hawaii at Manoa. 1987.
81. Zaidi, S.I.R. (1976). Determination of organic contamination in Oahu's groundwaters through carbon chloroform extraction. Master's Thesis. University of Hawaii at Manoa.
82. Zimmer, G., Brauch, H. J., and Sontheimer, H. (1989). Activated carbon adsorption of organic pollutants. *Adv. Chem. Ser.* Vol. 219 (Aquat. Humic Sub.), 579-596.

APPENDIX

TABLE 17. Original Feed Solution of Babcock et al. (1992)

Compound	Concentration (mg/L)
Bacto Peptone	189
Yeast Extract	38
K_2HPO_4	95
KH_2PO_4	150
$(NH_4)_2SO_4$	38
$CaCl_2 \cdot H_2O$	12.5
$MgCl_2 \cdot 6H_2O$	19.4
$FeCl_3$	3.0×10^{-1}
$MnCl_2 \cdot 4H_2O$	7.2×10^{-2}
$ZnCl_2$	5.0×10^{-2}
$CuCl_2 \cdot 2H_20$	3.1×10^{-2}
$CoCl_2 \cdot 6H_2O$	4.4×10^{-2}
$(NH_4)Mo_7O_{24} \cdot 4H_2O$	3.2×10^{-2}
$Na_2B_4O_7 \cdot 10H_2O$	1.9×10^{-2}
Pyridoxamine Dihydrochloride	5.7×10^{-4}
Nicotinic Acid	3.8×10^{-4}
Thaimine Hydrochloride	3.8×10^{-4}
D-pantothenate	1.9×10^{-4}
p-aminobenzoic acid	1.5×10^{-4}
d-botin	3.8×10^{-5}

TABLE 18. Modified Reactor Feed Solution for Non Specific Bacterial Culture

Compound	Quantity
Bacto Peptone	160 g
Yeast Extract	35 g
K_2HPO_4	50 g
KH_2PO_4	124 g
$(NH_4)_2SO_4$	20 g
Trace Mineral Solution	4 mL
Vitamin Solution	10 mL
Ca^{2+}/Mg^{2+} Solution	50 mL
Tap Water	Dilute to 2000 mL
Ca^{2+}/Mg^{2+} Solution	
Compound	**Quantity**
$CaCl_2 * 2H_2O$	10.52 g
$MgCl_2 * 6H_2O$	16.40 g
Distilled Water	Dilute to 400 mL
Trace Mineral Solution	
Compound	**Quantity**
$FeCl_3$	19.5 g
$MnCl_2 * 4H_2O$	4.75 g
$ZnCl_2$	3.30 g
$CuCl_2 * 2H_20$	2.05 g
$CoCl_2 * 6H_2O$	2.90 g
$(NH_4)Mo_7O_{24} * 4H_2O$	2.10 g
$Na_2B_4O_7 * 10H_2O$	1.20 g
Distilled Water	Dilute to 500 mL
Vitamin Solution	
Compound	**Quantity**
Pyridoxamine Dihydrochloride	0.030 g
Nicotinic Acid	0.020 g
Thaimine Hydrochloride	0.020 g
D-pantothenate	0.010 g
p-aminobenzoic acid	0.008 g
d-botin	0.002 g
Distilled Water	Dilute to 1000 mL

TABLE 19. Modified Reactor Feed Solution for Nitrifying Bacterial Culture

Compound	Quantity
Bacto Peptone	500 g
Yeast Extract	100 g
K_2HPO_4	50 g
KH_2PO_4	124 g
$(NH_4)_2SO_4$	100 g
Trace Mineral Solution	4 mL
Vitamin Solution	10 mL
Ca^{2+}/Mg^{2+} Solution	50 mL
Tap Water	Dilute to 2000 mL
Ca^{2+}/Mg^{2+} Solution	
Compound	**Quantity**
$CaCl_2 \cdot 2H_2O$	10.52 g
$MgCl_2 \cdot 6H_2O$	16.40 g
Distilled Water	Dilute to 400 mL
Trace Mineral Solution	
Compound	**Quantity**
$FeCl_3$	19.5 g
$MnCl_2 \cdot 4H_2O$	4.75 g
$ZnCl_2$	3.30 g
$CuCl_2 \cdot 2H_20$	2.05 g
$CoCl_2 \cdot 6H_2O$	2.90 g
$(NH_4)Mo_7O_{24} \cdot 4H_2O$	2.10 g
$Na_2B_4O_7 \cdot 10H_2O$	1.20 g
Distilled Water	Dilute to 500 mL
Vitamin Solution	
Compound	**Quantity**
Pyridoxamine Dihydrochloride	0.030 g
Nicotinic Acid	0.020 g
Thaimine Hydrochloride	0.020 g
D-pantothenate	0.010 g
p-aminobenzoic acid	0.008 g
d-botin	0.002 g
Distilled Water	Dilute to 1000 mL

Table 20. Buffer solution components and quantity required to maintain a pH of approximately 7.0

Components	Quantity (g)
KH_2PO_4 powder	16
K_2HPO_4 crystals	31
Deionized water	500

TABLE 21. Anaerobic and Anoxic Biodegradation Reactor Components

Components (mL)	Anaerobic Control	Anoxic Control	Anaerobic Bioassay	Anoxic Bioassay
DI Water	448.65	448.65	298.5	288.5
Feed Solution	NR	NR	1.05	1.05
KNO_3 Solution	NR	NR	NR	10
Buffer Solution	NR	NR	50	50
Bacterial Culture	NR	NR	100	100
Target Chemical (TC)	0.45 of each TC	0.45 of each TC	0.45 of one TC	0.45 of each TC
Total Volume	450	450	450	450

NR=Not required

TABLE 22. Aerobic Biodegradation Reactor Components

Components (mL)	Non-Specific Bacterial Culture		Nitrifying Bacterial Culture	
	Control	Bioassay	Control	Bioassay
DI Water	448.65	298.95	448.65	289.25
NS Culture Feed Solution	NR	1.05	NR	NR
Nitrifying Cult. Feed Solution	NR	NR	NR	0.3
NH_4Cl Solution	NR	NR	NR	10
Buffer Solution	NR	50	NR	50
Bacterial Culture	NR	100	NR	100
Target Chemical (TC)	0.45 of each TC	0.45 of one TC	0.45 of each TC	0.45 of one TC
Total Volume	450	450	450	450

NR= Not required

Table 23. TSS and VSS concentrations under aerobic conditions of EDB biodegradation experiment utilizing non-specific and nitrifying bacterial cultures.

Days	Total and Volatile Suspended Solids Concentration (mg/L)							
	Initial Test Control		Revised Control		Non-Specific Bacterial Culture		Nitrifying Bacterial Culture	
	TSS	VSS	TSS	VSS	TSS	VSS	TSS	VSS
0	0	0	0	0	730	610	680	480
3	80	70	0	0	940	850	830	620
7	190	150	0	0	620	540	750	480
Following Resuspension								
7	0	0	0	0	290	240	640	240
10	190	140	0	0	430	390	900	480
14	160	140	0	0	250	190	630	260

Table 24. TSS and VSS concentrations under aerobic conditions of TCP biodegradation experiment utilizing non-specific and nitrifying bacterial cultures.

Days	Total and Volatile Suspended Solids Concentration (mg/L)							
	Control		Revised Control		Non-Specific Bacterial Culture		Nitrifying Bacterial Culture	
	TSS	VSS	TSS	VSS	TSS	VSS	TSS	VSS
0	0	0	0	0	780	680	710	500
3	60	50	0	0	920	810	930	720
7	130	90	0	0	680	590	730	480
Following Resuspension								
7	0	0	0	0	290	240	610	240
10	110	70	0	0	540	500	910	490
14	110	60	0	0	350	290	800	340

Table 25. TSS and VSS concentrations under aerobic conditions of DBCP biodegradation experiment utilizing non-specific and nitrifying bacterial cultures.

Days	Total and Volatile Suspended Solids Concentration (mg/L)							
	Control		Revised Control		Non-Specific Bacterial Culture		Nitrifying Bacterial Culture	
	TSS	VSS	TSS	VSS	TSS	VSS	TSS	VSS
0	0	0	0	0	720	610	680	490
3	3	40	0	0	890	820	870	680
7	7	230	0	0	650	570	750	500
Following Resuspension								
7	0	0	0	0	290	240	580	230
10	210	170	0	0	590	520	940	500
14	100	70	0	0	350	290	810	360

Table 26. TSS and VSS concentrations under anaerobic and anoxic conditions of EDB biodegradation experiment utilizing non-specific bacterial culture.

Days	Total and Volatile Suspended Solids Concentration (mg/L)			
	Anaerobic Condition		Anoxic Condition	
	TSS	VSS	TSS	VSS
0	1350	660	1120	590
3	940	510	970	520
7	960	410	920	430
Following Resuspension				
7	660	200	660	180
10	410	160	590	260
14	450	150	570	220

Table 27. TSS and VSS concentrations under anaerobic and anoxic conditions of TCP biodegradation experiment utilizing non-specific bacterial culture.

Days	Total and Volatile Suspended Solids Concentration (mg/L)			
	Anaerobic Condition		Anoxic Condition	
	TSS	VSS	TSS	VSS
0	1000	540	1180	660
3	970	530	940	530
7	880	430	980	480
Following Resuspension				
	620	180	700	200
10	450	170	510	240
14	650	340	560	250

Table 28. TSS and VSS concentrations under anaerobic and anoxic conditions of DBCP biodegradation experiment utilizing non-specific bacterial culture.

Days	Total and Volatile Suspended Solids Concentration (mg/L)			
	Anaerobic Conditions		Anoxic Conditions	
	TSS	VSS	TSS	VSS
0	1000	580	1340	750
3	970	560	970	510
7	800	370	980	470
Following Resuspension				
7	770	210	660	210
10	430	150	540	270
14	440	150	590	250

Table 29. Soluble COD concentration under aerobic conditions of EDB biodegradation experiment.

Day	Chemical Oxygen Demand Concentration (mg/L)		
	Initial Control Test	Non-Specific Bacterial Culture	Nitrifying Bacterial Cult
0	1098	1204	1068
3	590	49.3	56.3
7	38.2	49.3	56.3
Following Resuspension			
7	971	1242	1113
10	67	78	49
14	69	74.4	41

Table 30. Soluble COD concentration under aerobic conditions of TCP biodegradation experiment.

Day	Chemical Oxygen Demand Concentration (mg/L)		
	Initial Control Test	Non-Specific Bacterial Culture	Nitrifying Bacterial Cult
0	1096	1246	1052
3	908	49.5	54.5
7	165	49.5	54.5
Following Resuspension			
7	1050	1276	1115
10	280	61.5	49
14	188	61.5	43.5

Table 31. Soluble COD concentration under aerobic conditions of DBCP biodegradation experiment.

Day	Chemical Oxygen Demand Concentration (mg/L)		
	Initial Control Test	Non-Specific Bacterial Culture	Nitrifying Bacterial Cult
0	1058	1260	1052
3	960	56.5	61
7	87.8	56.5	61
Following Resuspension			
7	1055	1275	1138
10	304	67.4	57
14	167	67.4	40.7

Table 32. Soluble COD concentration of combined DBCP, EDB, and TCP reactor for revised control experiment under aerobic conditions

Day	Chemical Oxygen Demand Concentration (mg/L)
0	3324
3	3544
7	3256
Following Resuspension	
7	3480
10	3456
14	3348

Table 33. Soluble COD concentration under anaerobic and anoxic conditions of DBCP, EDB, and TCP biodegradation experiment including controls.

Day	Chemical Oxygen Demand Concentration (mg/L)							
	Anaer Cntl	Anaer DBCP	Anaer EDB	Anaer TCP	Anoxic Cntl	Anoxic DBCP	Anoxic EDB	Anoxic TCP
0	3252	1376	1306	1430	3192	1498	1338	1380
3	3440	1134	1104	1184	3212	983	974	1010
7	3184	1180	1202	1126	3076	918	932	812
Following Resuspension								
7	3504	1428	1422	1462	3648	1532	1590	1526
10	3416	1366	1452	1386	3492	948	970	930
14	3516	1323	1399	600	3468	933	950	785

Table 34. Final pH values for DBCP, EDB, and TCP experiments under anaerobic and anoxic conditions, including control flasks.

Experiment	pH Value	
	Anaerobic	Anoxic
Control*	5.59	5.27
DBCP	7.12	7.26
EDB	7.16	7.26
TCP	7.02	7.23

*buffer not added to controls

Table 35. Ammonia-nitrogen concentration under aerobic conditions of EDB, TCP, and DBCP biodegradation experiment utilizing nitrifying bacterial culture.

Day	Ammonia-nitrogen Concentration (mg/L)		
	DBCP	EDB	TCP
0	92.16	113.94	100.08
1	99.9	113.58	104.22
2	89.64	112.86	103.86
3	43.2	66.6	61.2
7	10.944	9.378	0.7362
Following Resuspension			
7	119.88	121.32	119.88
8	118.8	116.64	119.88
9	84.6	80.46	81
11	79.38	51.66	67.68
14	58	50	33.3

Table 36. Nitrate-nitrogen concentration under anoxic conditions of EDB, TCP, and DBCP biodegradation experiment utilizing non-specific bacterial culture.

Day	Ammonia-nitrogen Concentration (mg/L)		
	DBCP	EDB	TCP
0	162	173	173
1	126	124	132
3	69	62	70
6	4	4	10
7	3	5	3
Following Resuspension			
7	143	150	160
10	6	13	6
12	6	4.5	6.5
14	1.7	1.9	1.2

Figure 1. GAC Treatment Facilities on Oahu, Hawaii

(Dugan et al., 1995)

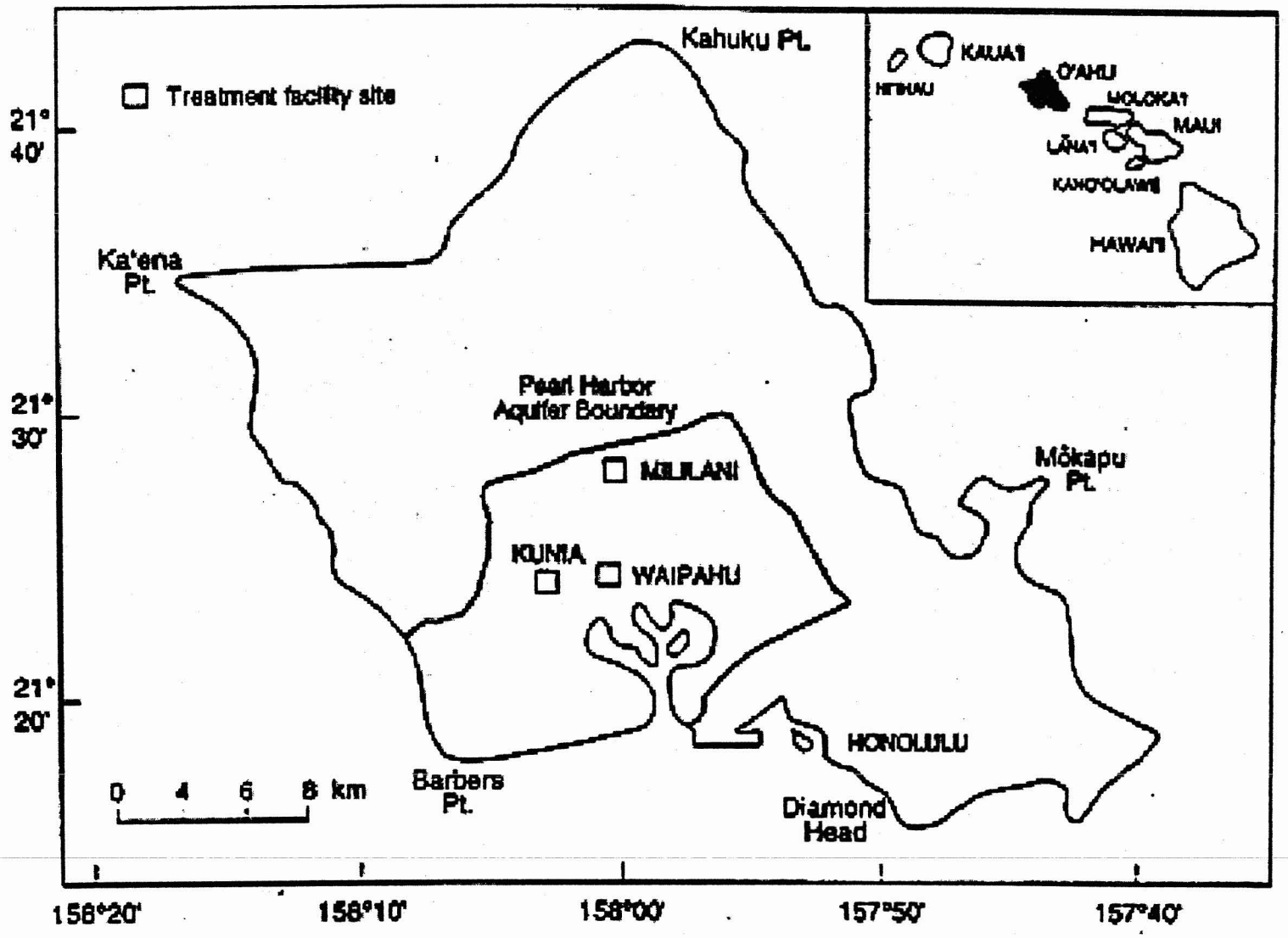


Figure 2 - Column Set-up and Dimensions

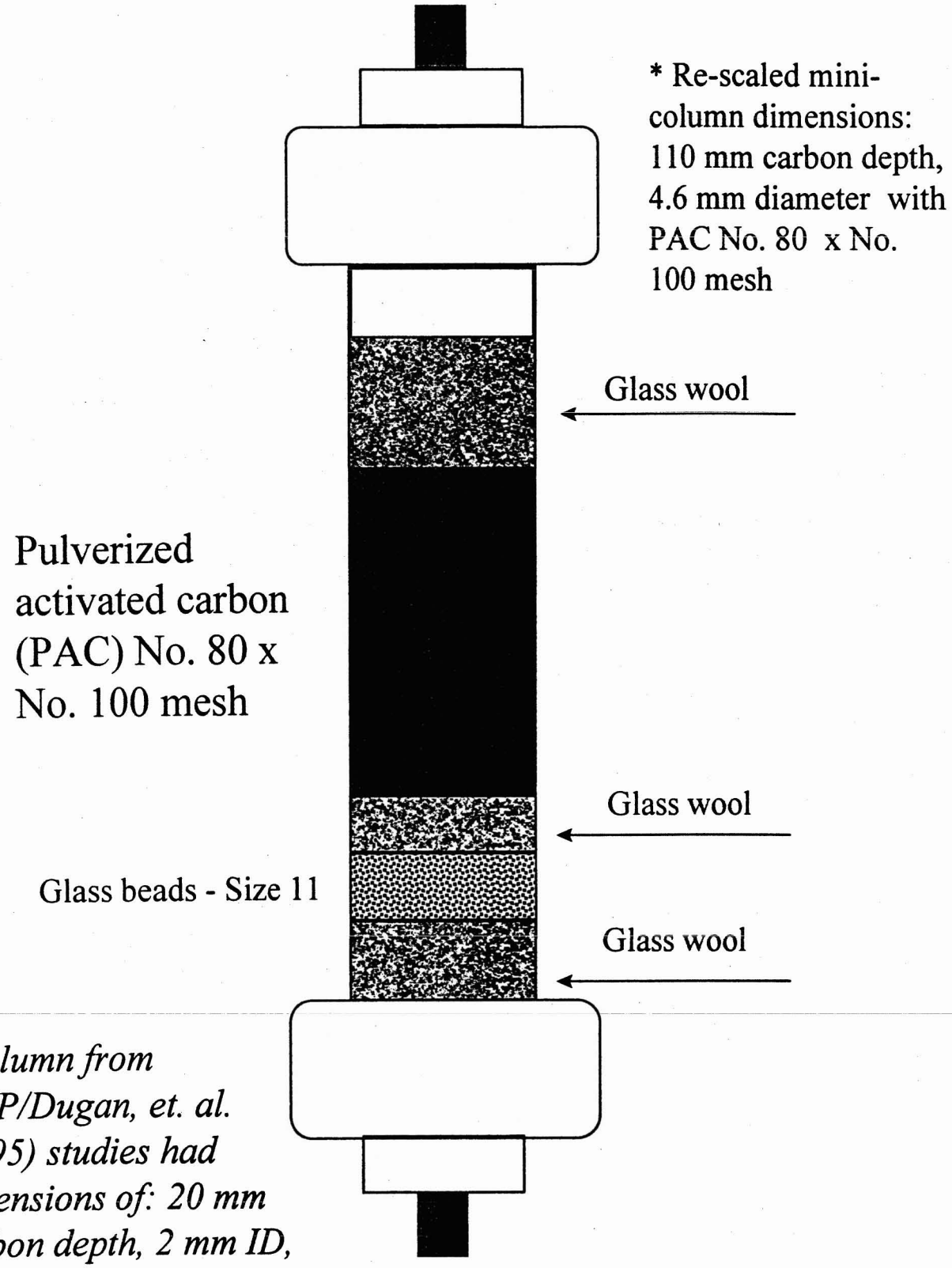
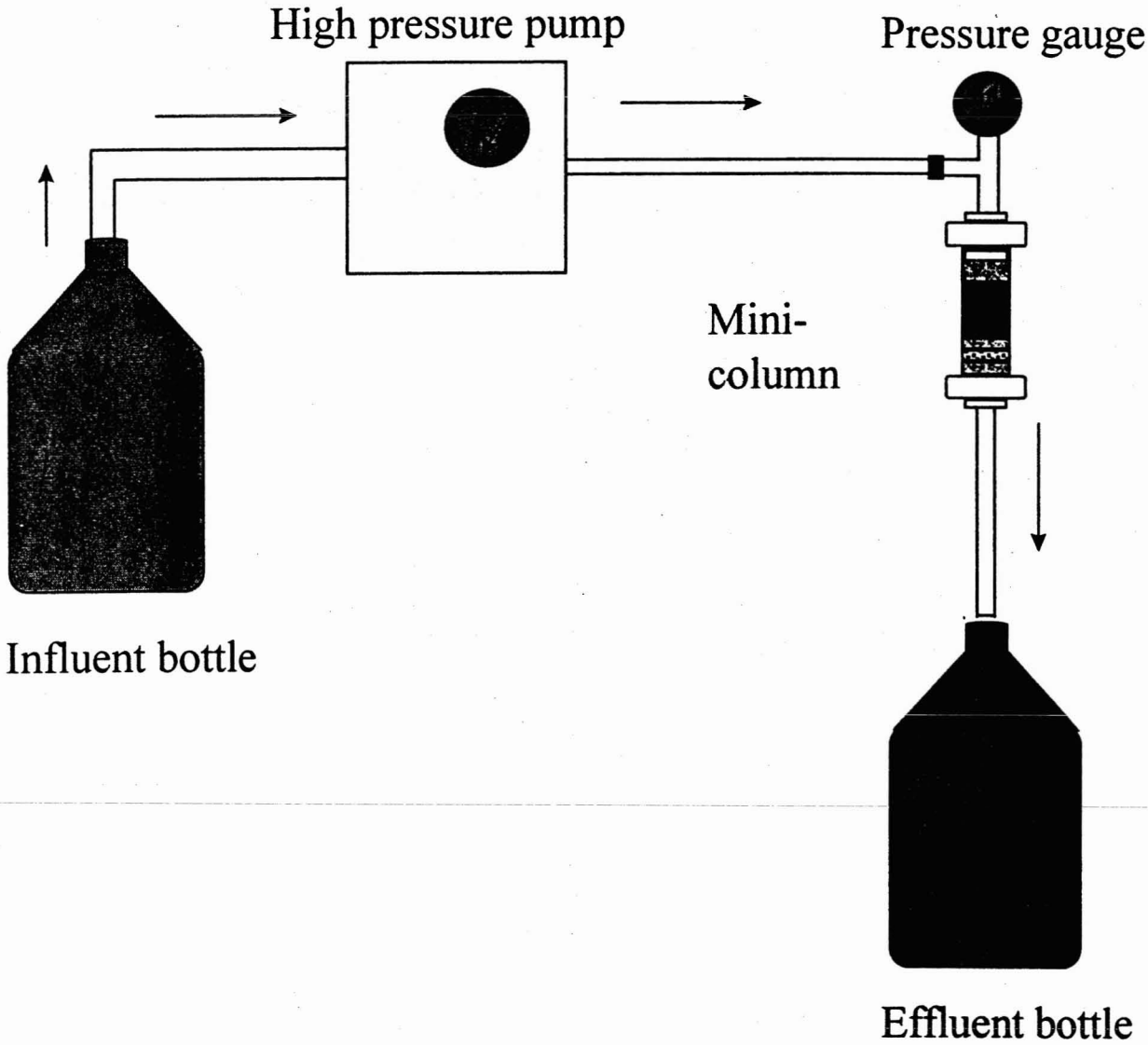


Figure 3 - Schematic of mini-column set-up

(From Dugan, et. al., 1995)



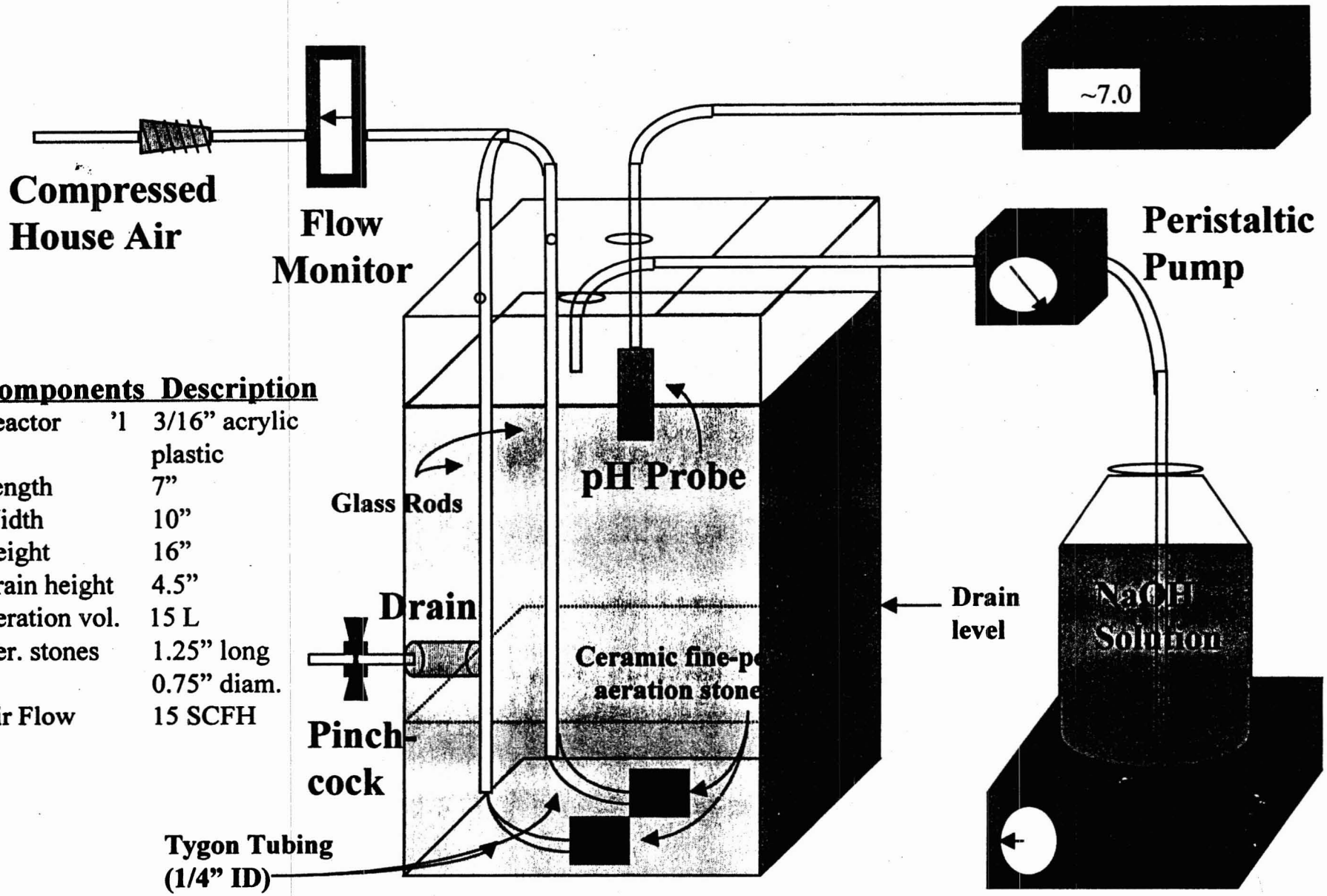
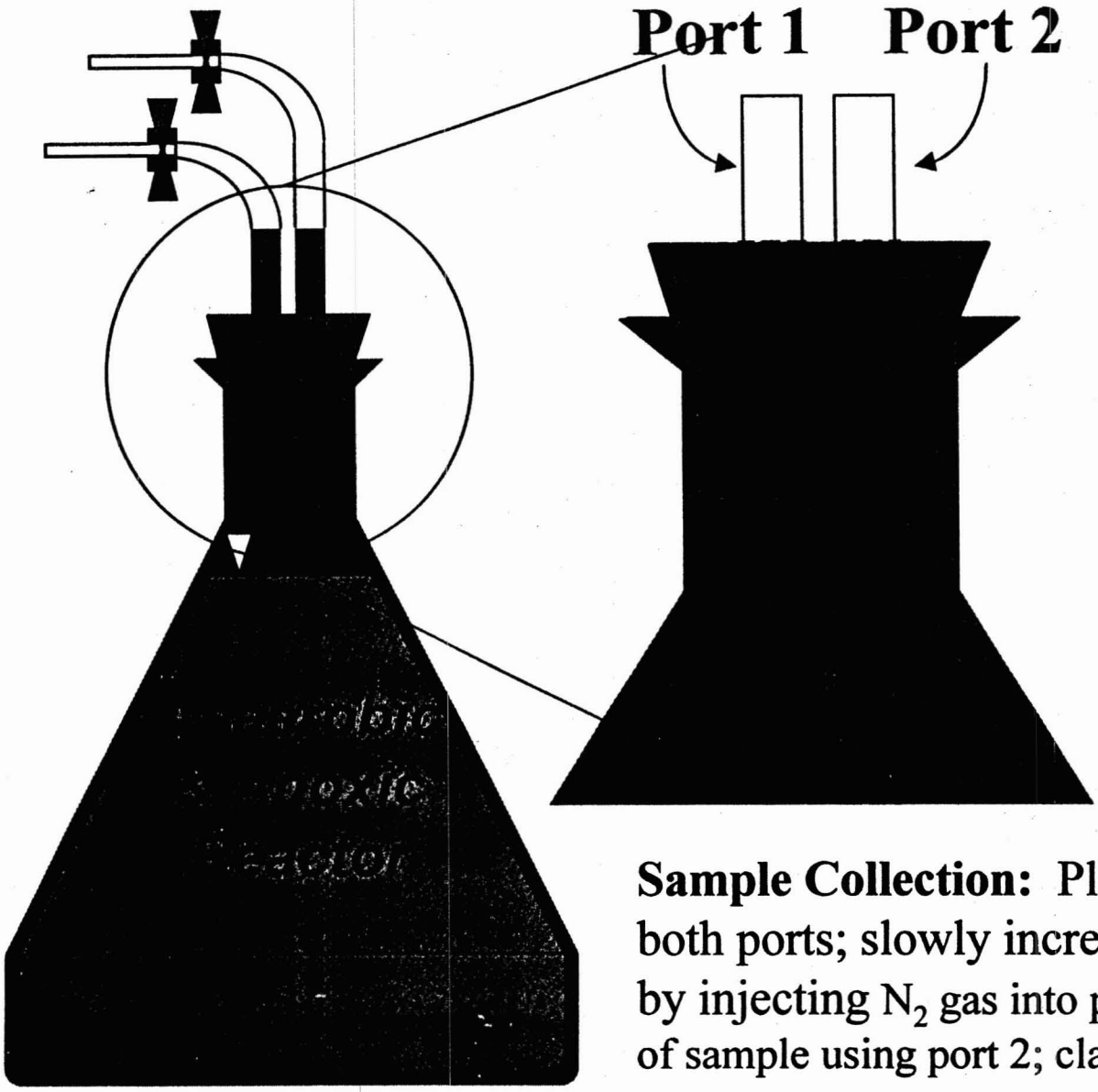


Figure 4. Nitrifying Bacterial Culture Reactor Diagram



Deoxygenation:
Open port 1; use port 2 to bubble N_2 gas for 30 min; clamp both ports.

Chemical Injection:
Open port 1; inject chemical into port 2; purge port 2 using N_2 gas; reclamp ports.

Sample Collection: Place reactor on mixer; open both ports; slowly increase pressure within flask by injecting N_2 gas into port 1; collect required volume of sample using port 2; clamp ports.

Figure 5. Stopper assembly for anaerobic/anoxic experiments and port use instructions

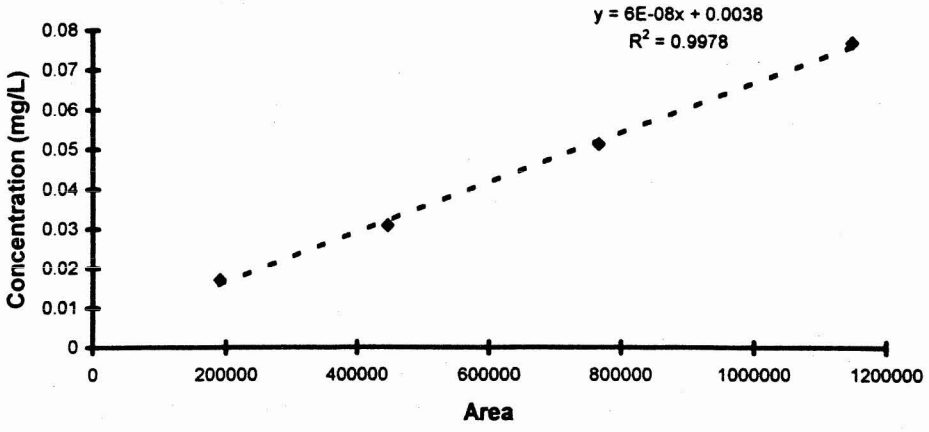


Figure 6: Standard Curve A for EDB. Area limits are 200000 to 1200000. Concentration Limits are 0.015 mg/L to 0.0758 mg/L.

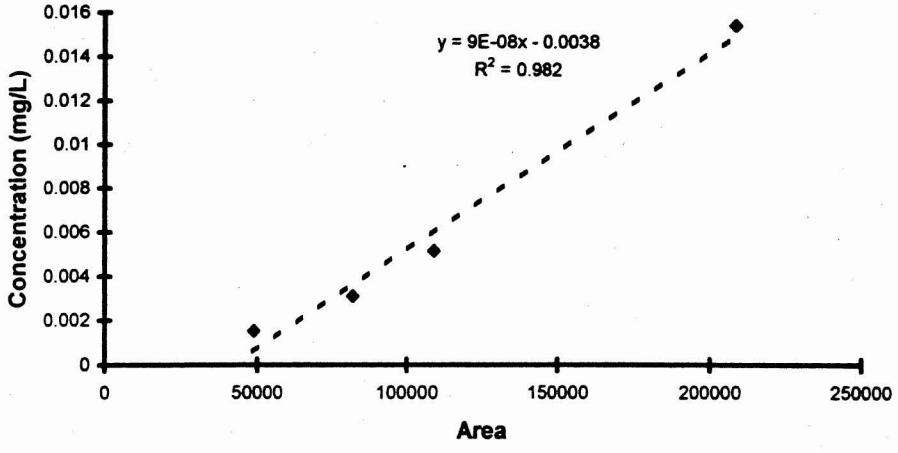


Figure 7: Standard Curve B for EDB. Area Limits are 50000 to 250000. Concentration Limits are 0.0007 mg/L to 0.0187 mg/L.

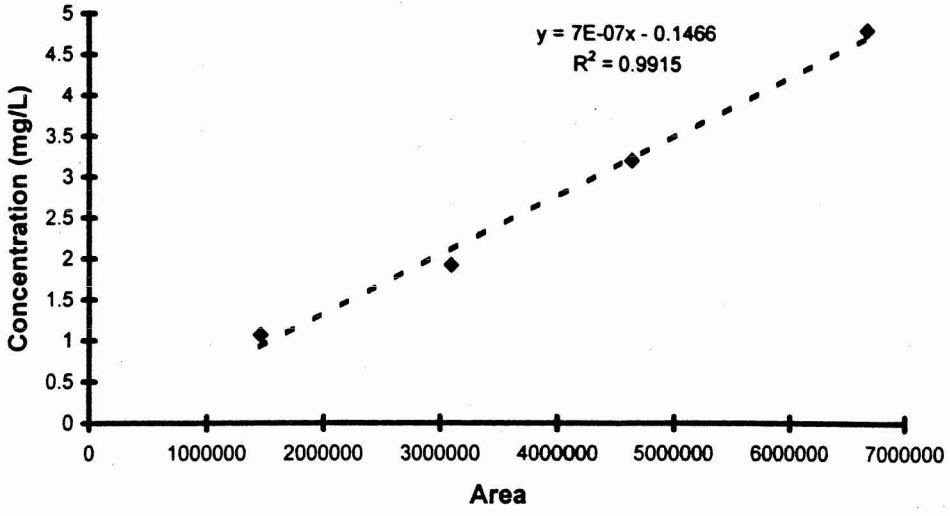


Figure 8: Standard Curve A for TCP. Area Limits are 1500000 to 7000000.
Concentration Limits are 0.9034 mg/L to 4.75 mg/L.

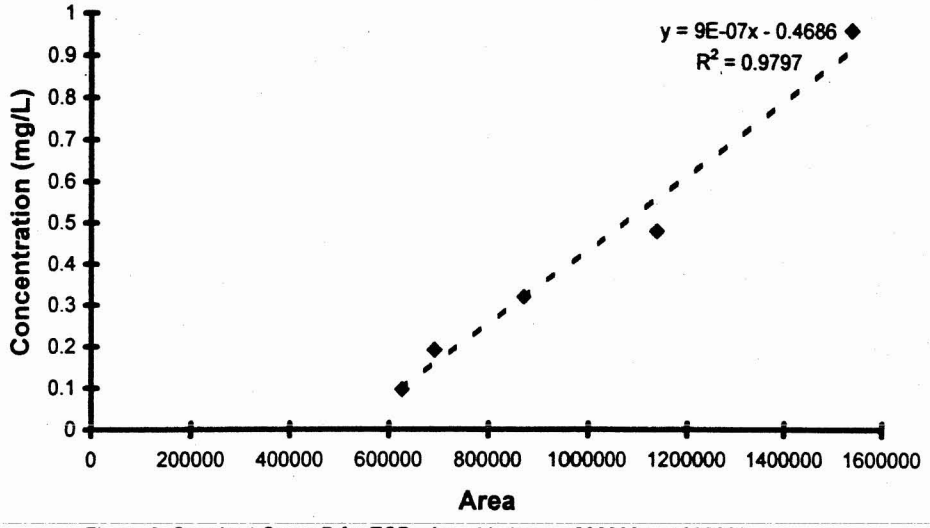


Figure 9: Standard Curve B for TCP. Area Limits are 600000 to 1600000.
Concentration Limits are 0.0714 mg/L to 0.9714 mg/L.

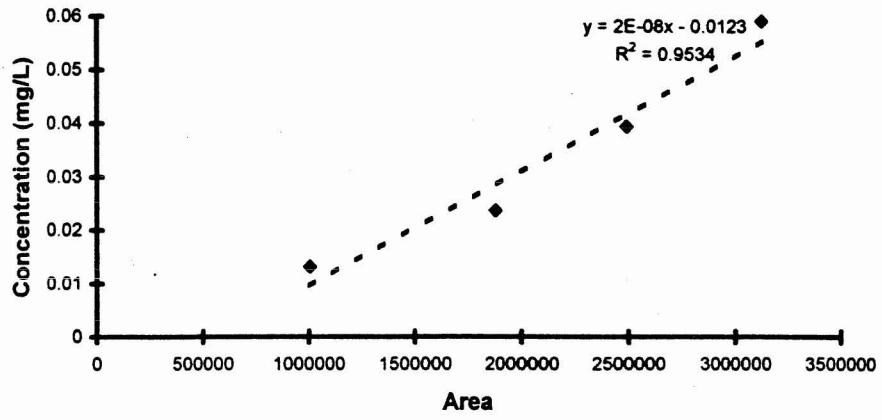


Figure 10: Standard Curve A for DBCP. Area Limits are 1000000 to 3500000. Concentration Limits are 0.0077 mg/L to 0.0577 mg/L.

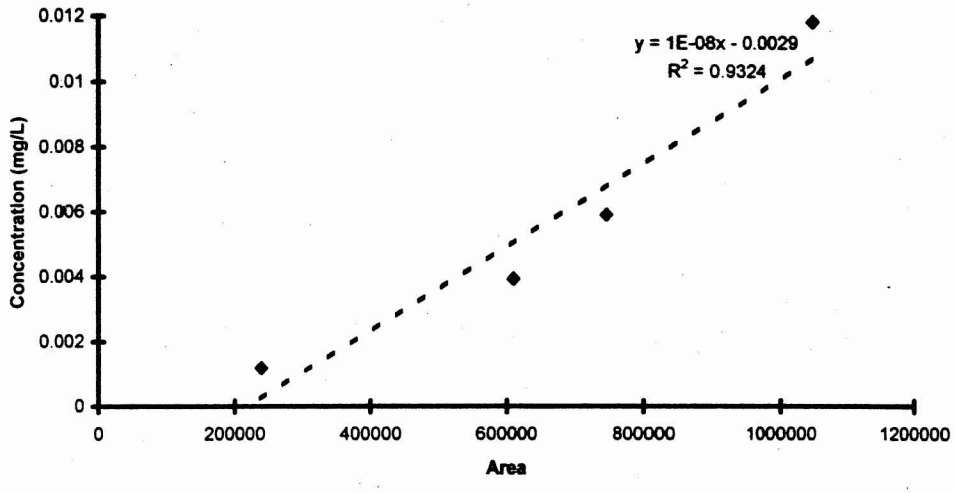


Figure 11: Standard Curve B for DBCP. Area Limits are 200000 to 1200000. Concentration Limits are 0.0001 mg/L to 0.0091 mg/L.

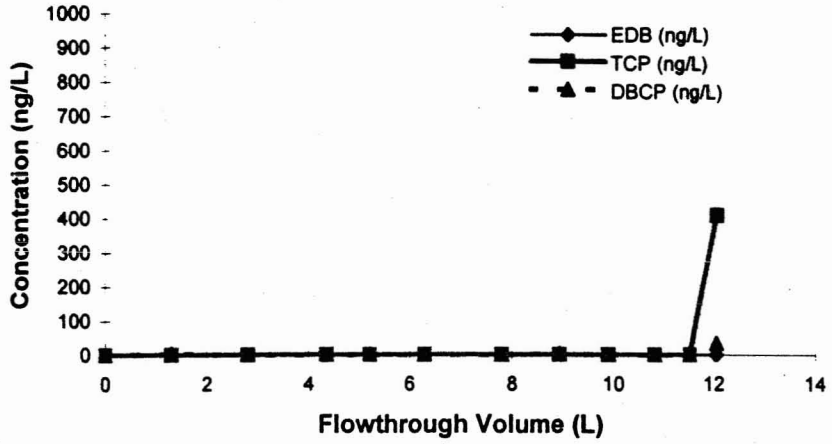


Figure 12: Breakthrough Behavior of EDB, TCP, and DBCP Prior to Regeneration with 50% acetone. Influent concentrations were increased each day from starting concentrations of 200 ng/L, 2000 ng/L, and 200 ng/L, respectively to final concentrations 5000x original to obtain breakthrough.

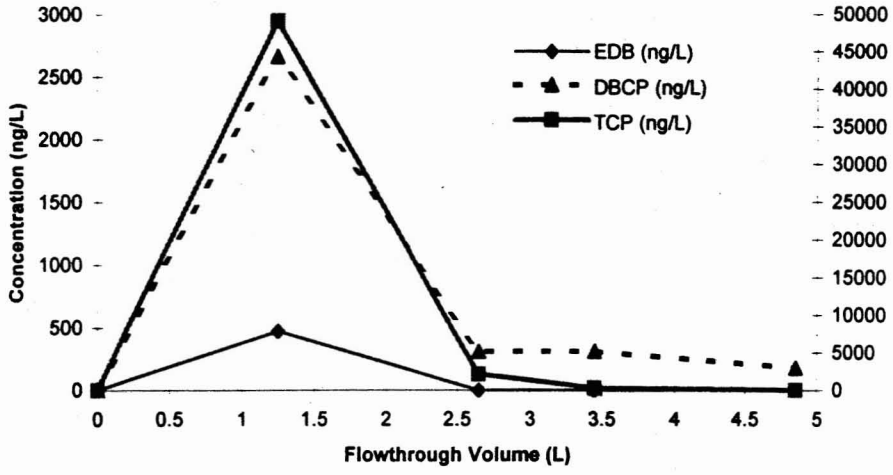


Figure 13: Breakthrough Behavior of EDB, TCP, and DBCP Post-regeneration with 50% acetone. TCP plotted on secondary axis.

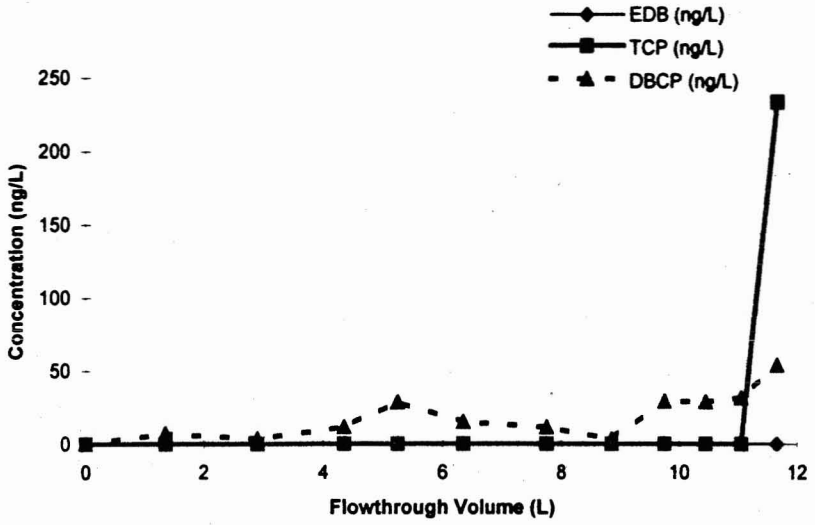


Figure 14: Breakthrough Behavior of EDB, TCP, and DBCP Prior to Regeneration with 70% acetone.

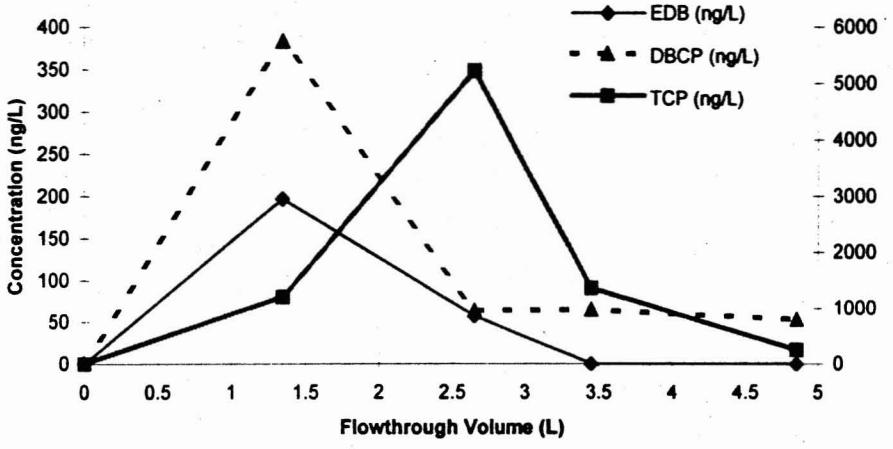


Figure 15: Breakthrough Behavior of EDB, TCP, and DBCP Post-regeneration with 70% acetone. TCP plotted on secondary axis.

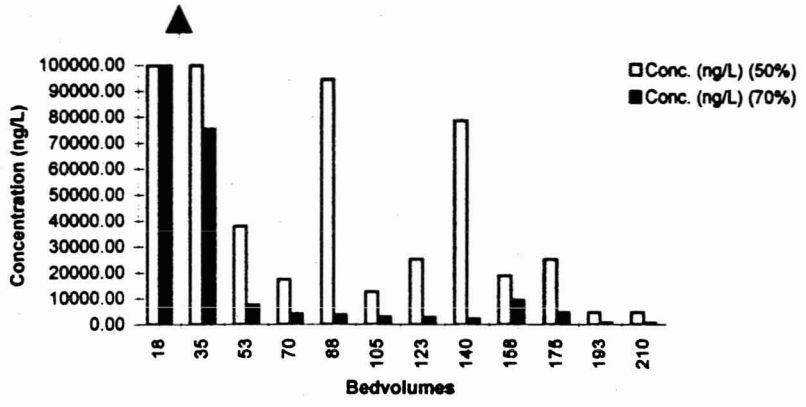


Figure 16: Comparison of Regeneration Cycles for EDB Removal (50 and 70% acetone). In first 35 bedvolumes treated, EDB concentrations exceed scale and reach 7 mg/L (indicated by arrow). Scale has been decreased in order to see lower concentrations.

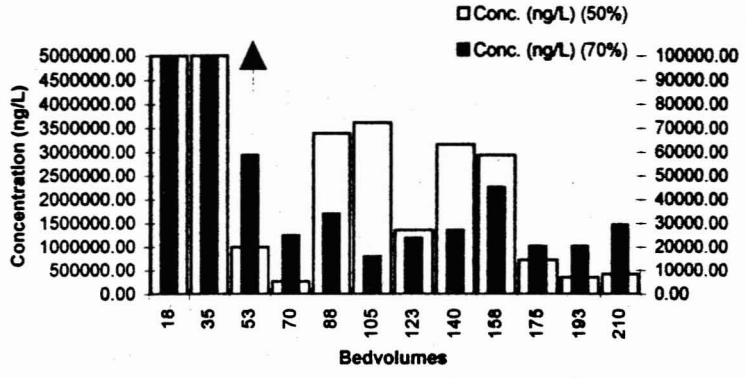


Figure 17: Comparison of Regeneration Cycles for TCP Removal (50 and 70% acetone). Data for 70% concentrations plotted on secondary axis because of lower concentrations when compared to regeneration with 50% acetone. Because concentrations for both regenerants exceed scale, arrow indicates that TCP concentrations initially reached 48 mg/L.

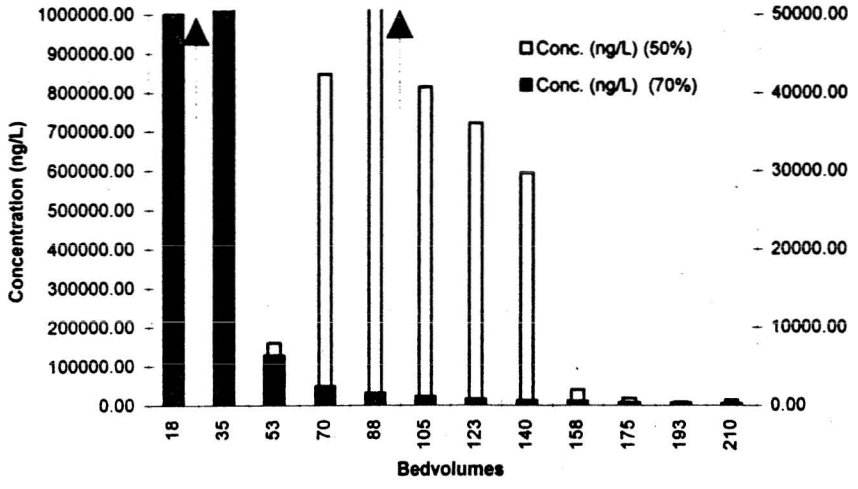


Figure 18: Comparison of Regeneration Cycles for DBCP Removal (50 and 70% acetone). Data for 70% acetone plotted on secondary axis to show DBCP being removed even after 70 bedvolumes. For 50% acetone, bulk of removal does not occur until 70 bedvolumes have been treated. Arrow indicates that concentrations exceed 1 mg/L. For 70% acetone, DBCP conc. in first 18 bedvolumes collected reached 2 mg/L, at 35 bedvolumes, DBCP conc. decreased to 0.2 mg/L.

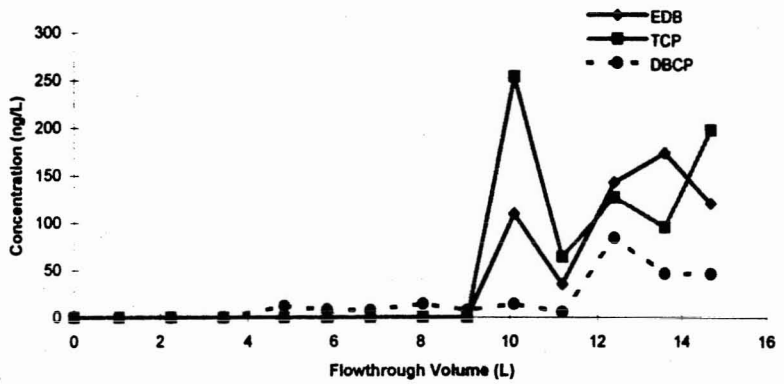


Figure 19: Breakthrough Behavior of EDB, TCP, and DBCP Prior to Regeneration with 100% acetone. This run includes rinsing post-regeneration with deionized water. 1st loading cycle.

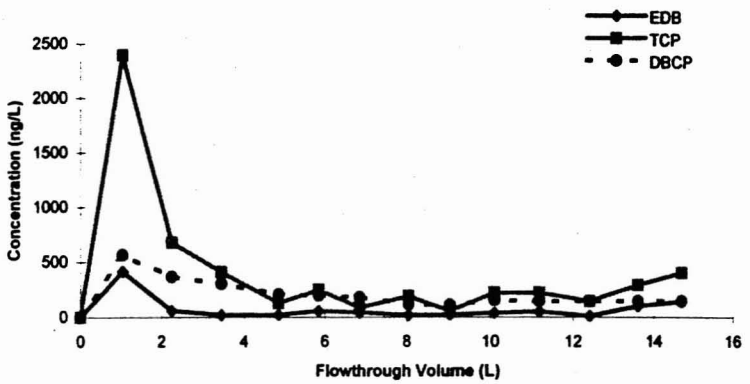


Figure 20: Breakthrough Behavior of EDB, TCP, and DBCP Post-regeneration with 100% acetone. 2nd Loading Cycle. Concentrations do not drop below MCL.

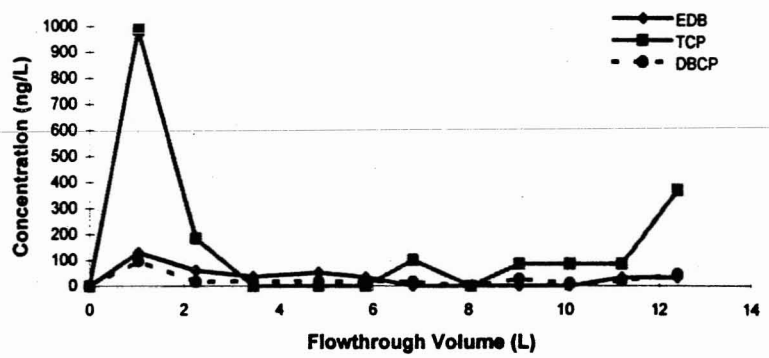


Figure 21: Breakthrough Behavior of EDB, TCP, and DBCP Post-regeneration (2nd regeneration) with 100% acetone. 3rd Loading Cycle.

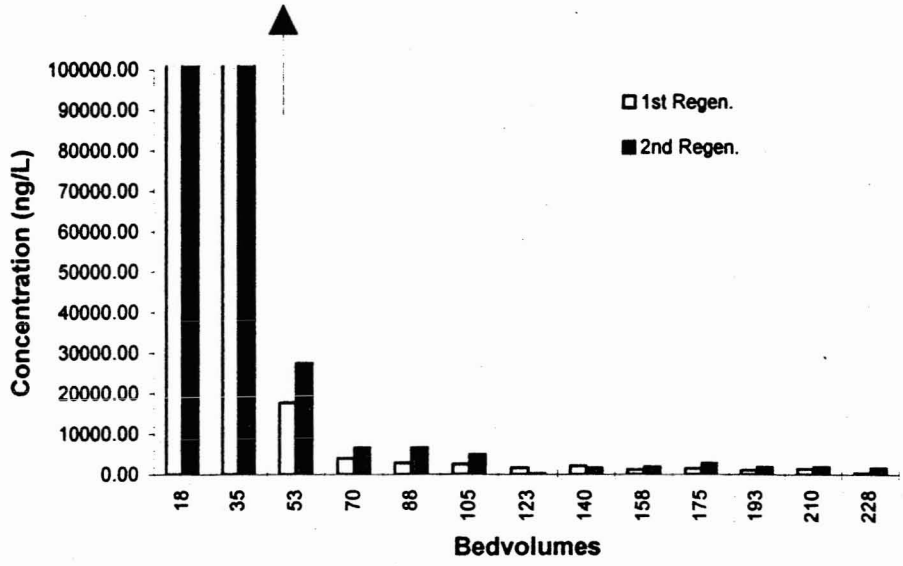


Figure 22: Comparison of 1st and 2nd regeneration cycles for 100% acetone to remove EDB. Arrow indicates concentration exceed 100000 ng/L. For 1st regeneration, concentration reaches 1 and 5 mg/L respectively, and for the 2nd regeneration concentration reaches 0.18 mg/L and 0.2 mg/L respectively. Axis was adjusted to show lingering EDB concentrations had not dropped to zero even after 200 bedvolumes treated.

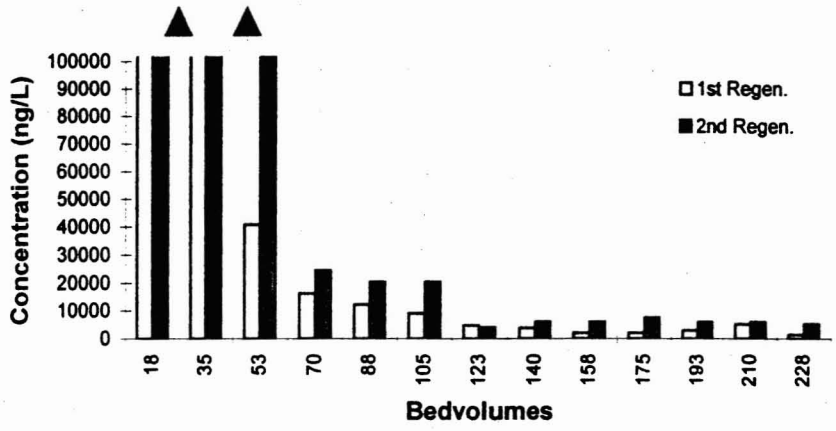


Figure 23: Comparison of 1st and 2nd regeneration cycles for 100% acetone to remove TCP. Arrow indicates that in 1st regeneration cycle, concentrations in the first 18 bedvolumes reached 4 mg/L, then dropped to 0.6 mg/L in subsequent samples. In contrast, for 2nd regeneration, concentrations in first 18 bedvolumes reached 40 mg/L, then subsequent samples show concentrations drop to 1 mg/L. Axis was adjusted to show lingering TCP concentrations had not dropped to zero even after 200 bedvolumes treated.

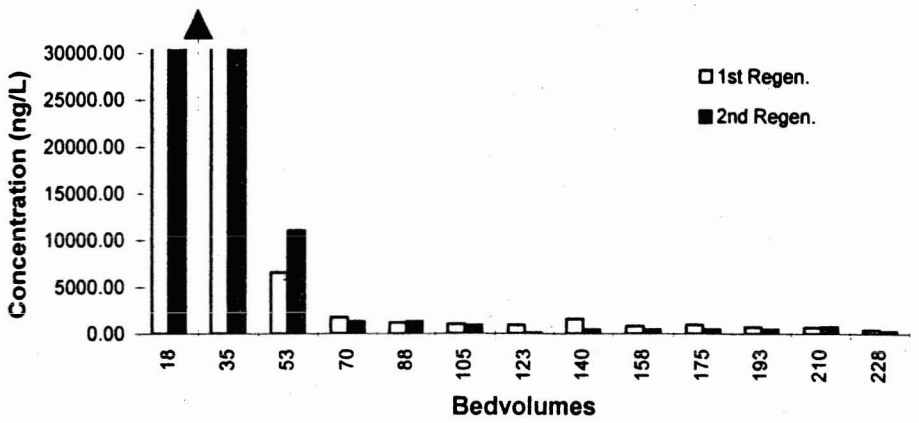


Figure 24: Comparison of 1st and 2nd regeneration cycles for 100% acetone to remove DBCP. Arrow indicates that 1st and 2nd regeneration cycles had DBCP concentrations in first 35 bedvolumes that exceeded maximum value on axis. For 1st cycle, concentrations for 18 bedvolumes reached .6 mg/L then dropped to 0.06 in subsequent sample. In contrast, for 2nd regeneration cycle, concentrations for 18 bedvolumes reached 2 mg/L, then dropped to 0.07 in subsequent sample. Axis was adjusted to show lingering DBCP concentrations had not dropped to zero and residual was present in effluent.

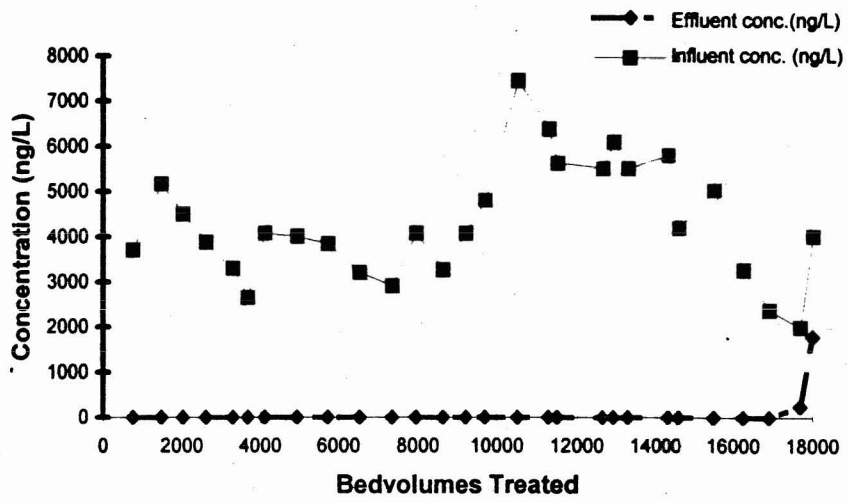


Figure 25: Breakthrough Behavior for TCP in Mililani Well Water. Influent concentrations varied from 2000 ng/L to 7500 ng/L. Average influent concentration = 3500 ng/L.

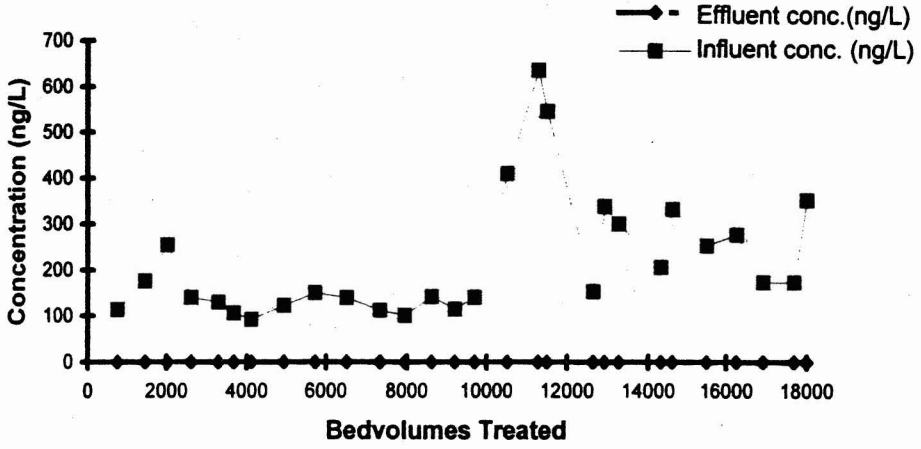


Figure 26: Breakthrough Behavior for DBCP in Mililani Well Water (None occurred). TCP broke through first. DBCP concentrations varied from 100 ng/L to almost 650 ng/L. On average, concentrations remained low (average - 150 ng/L).

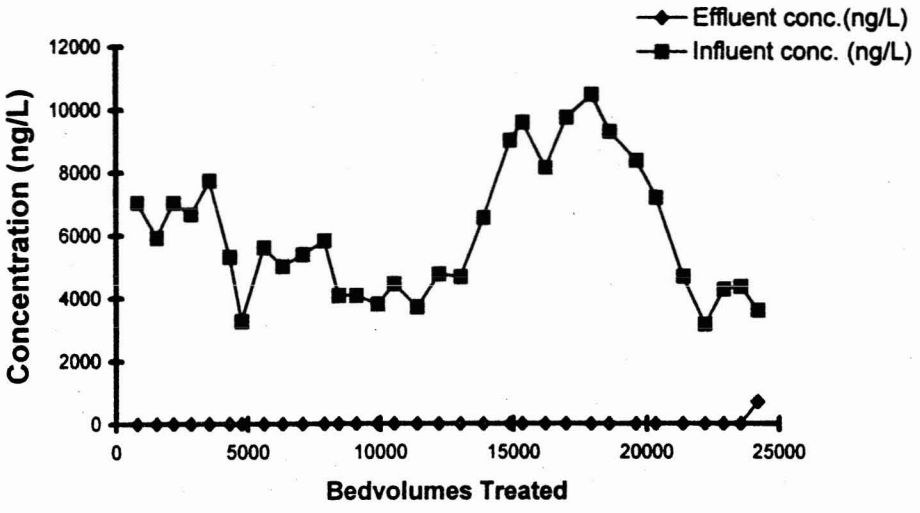


Figure 27: Breakthrough Behavior for TCP in spiked deionized water. Influent concentrations varied from 2500 ng/L to 10000 ng/L.

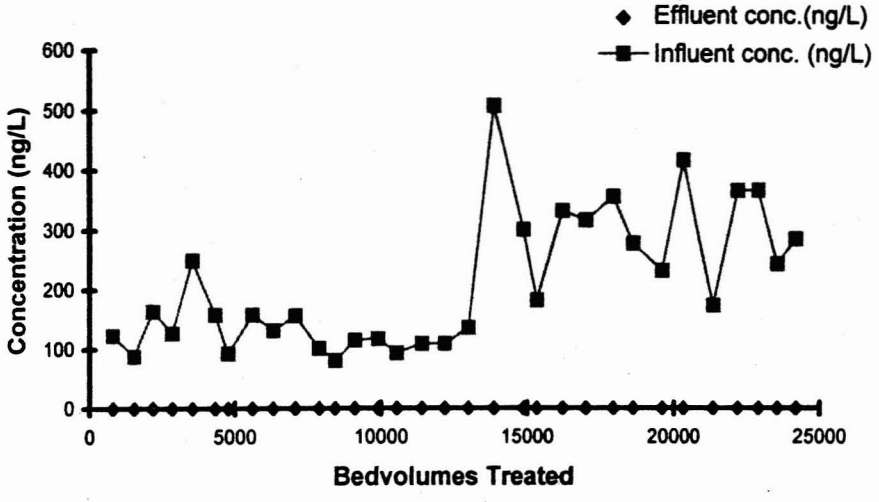


Figure 28: Breakthrough Behavior for DBCP in spiked deionized water. (None occurred). Influent concentrations varied from 90 ng/L to 500 ng/L.

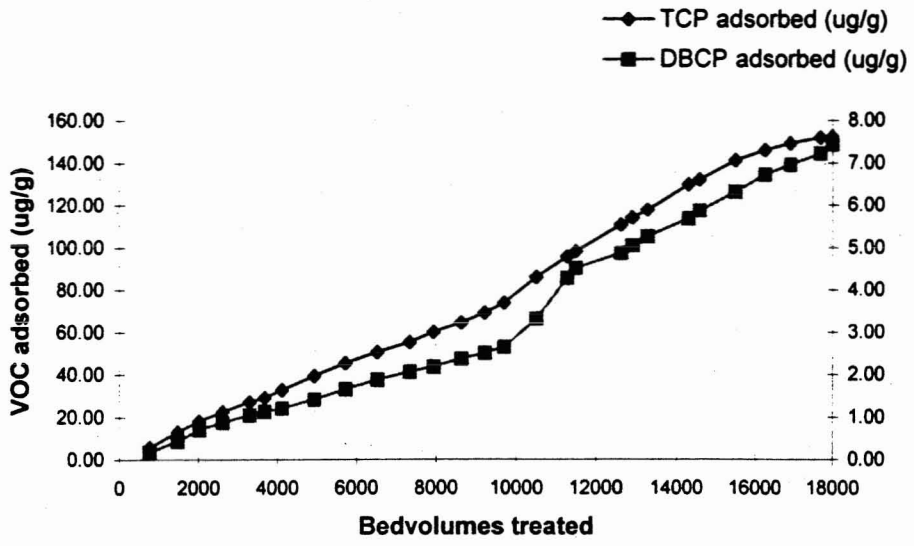


Figure 29: Adsorption Behavior for TCP and DBCP in Mililani Well Water. DBCP plotted on secondary axis. When compared to adsorption for VOCs in spiked deionized water, amounts of both pesticides adsorbed are lower for Miliani Well Water.

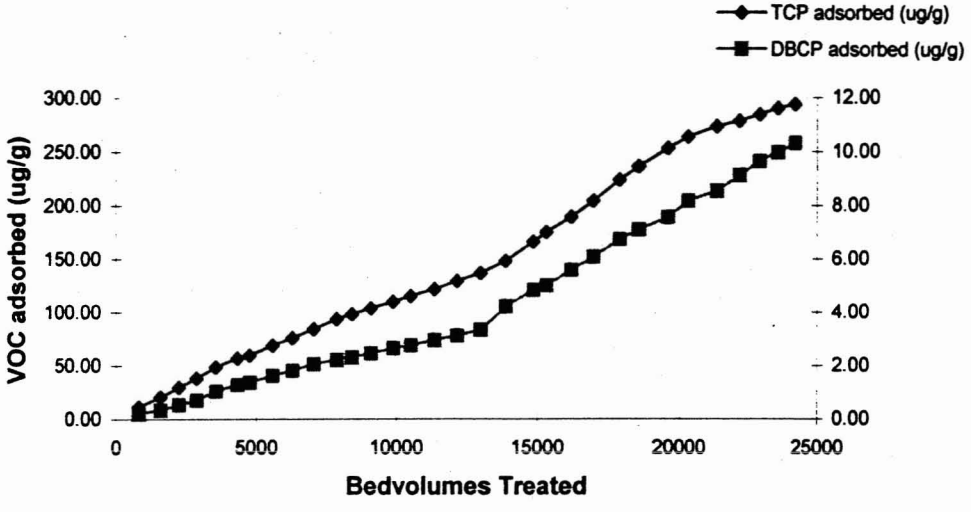


Figure 30: Adsorption Behavior for TCP and DBCP in spiked deionized water. DBCP plotted on secondary axis.

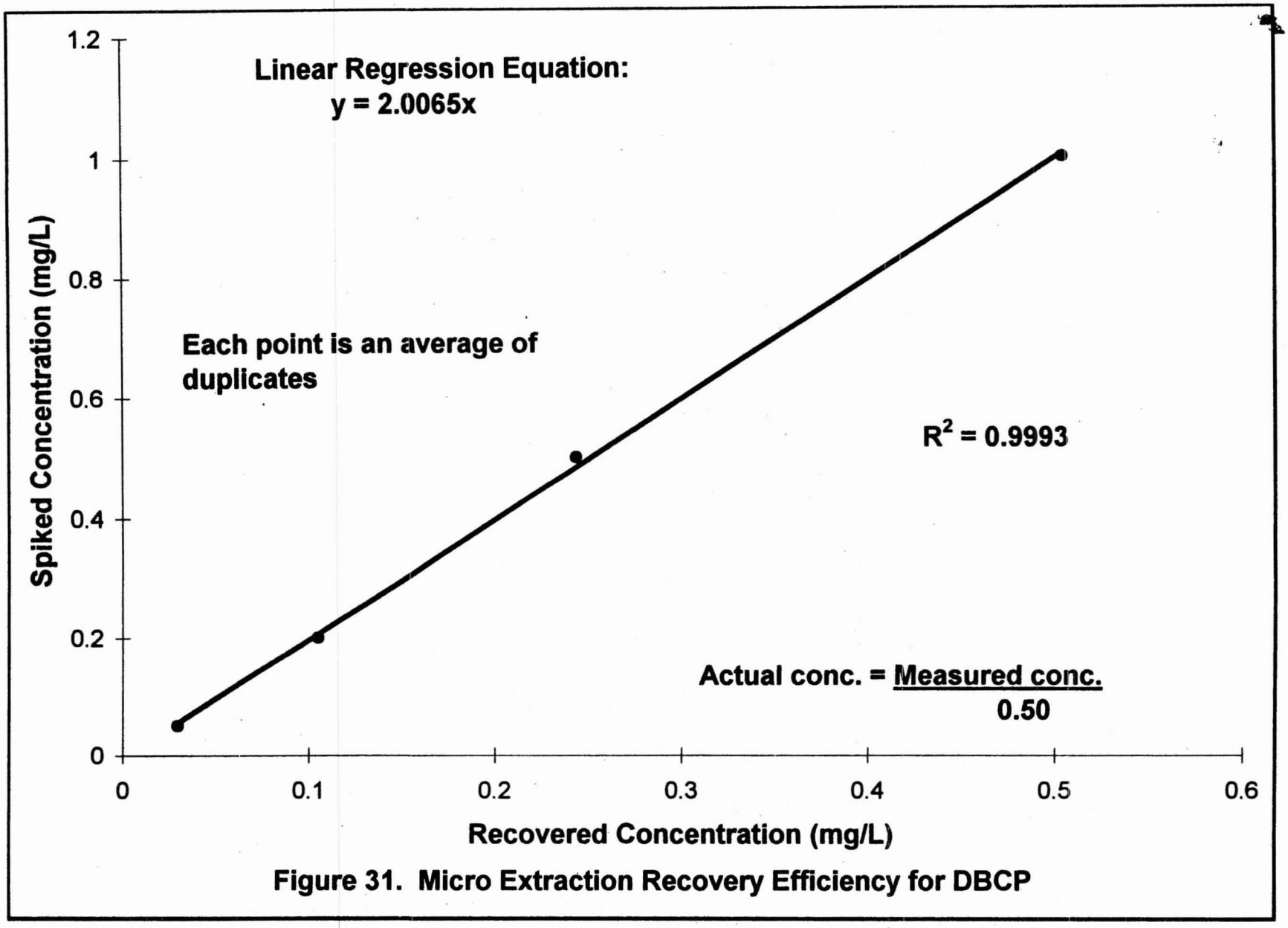


Figure 31. Micro Extraction Recovery Efficiency for DBCP

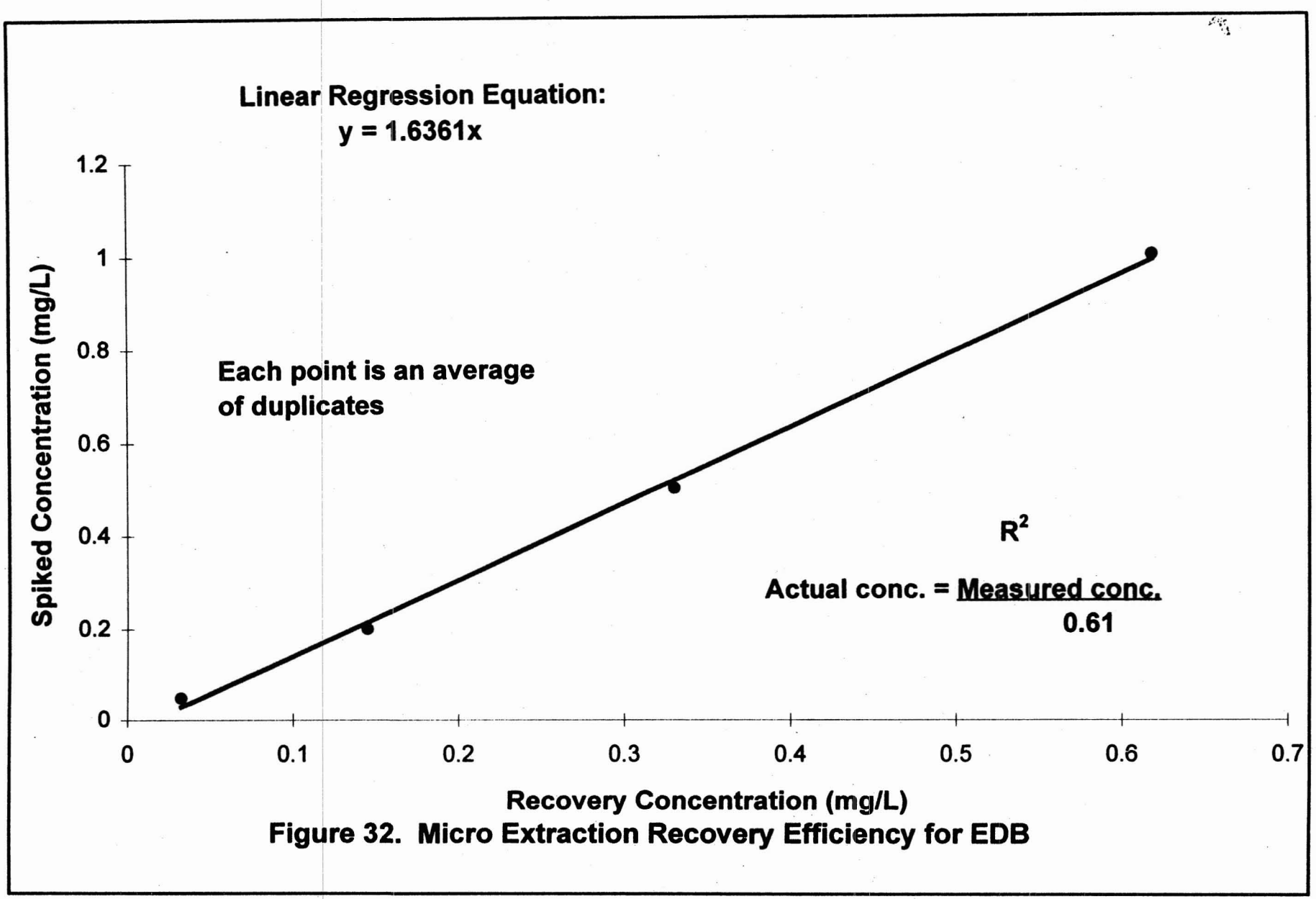


Figure 32. Micro Extraction Recovery Efficiency for EDB

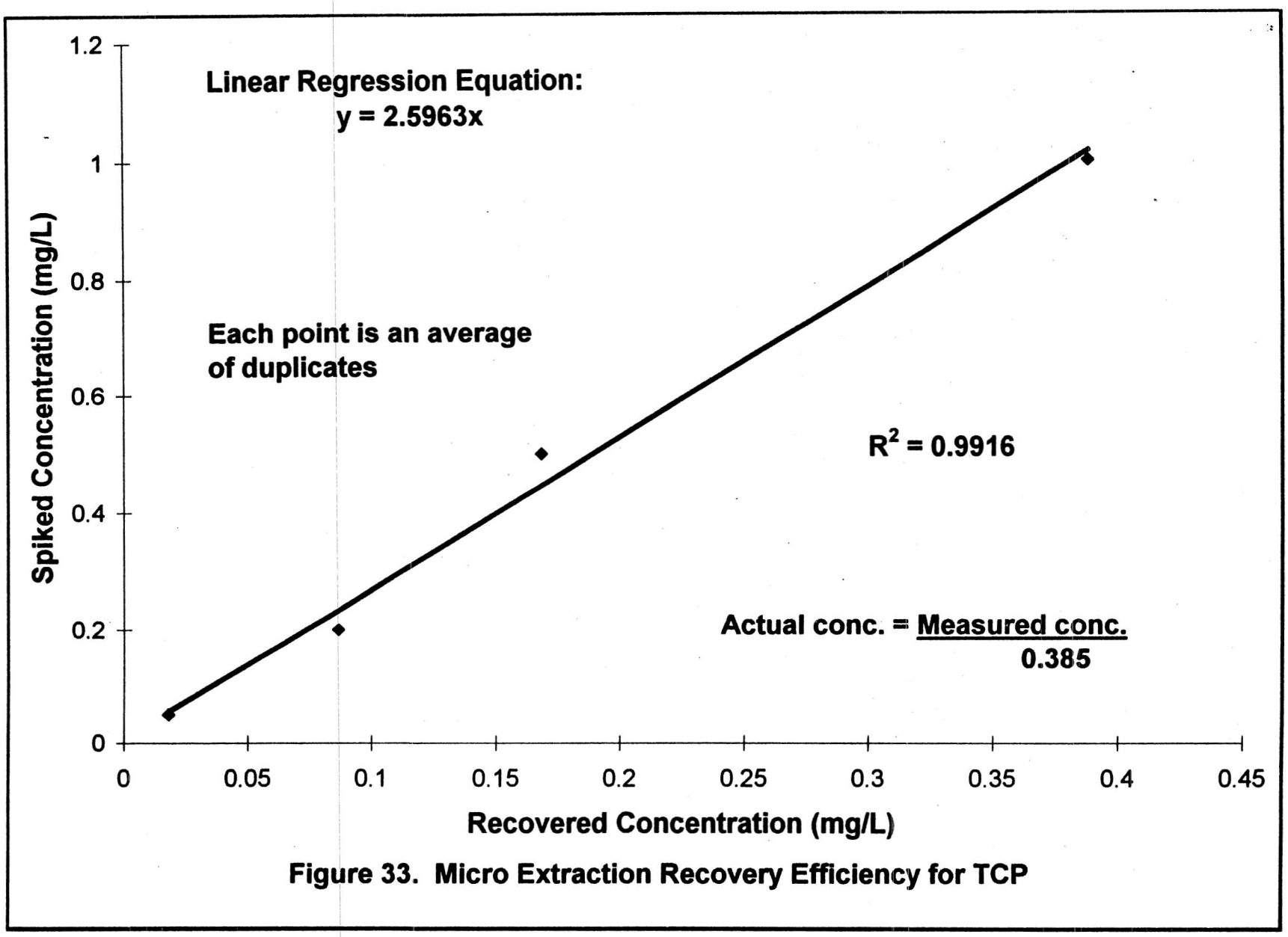


Figure 33. Micro Extraction Recovery Efficiency for TCP

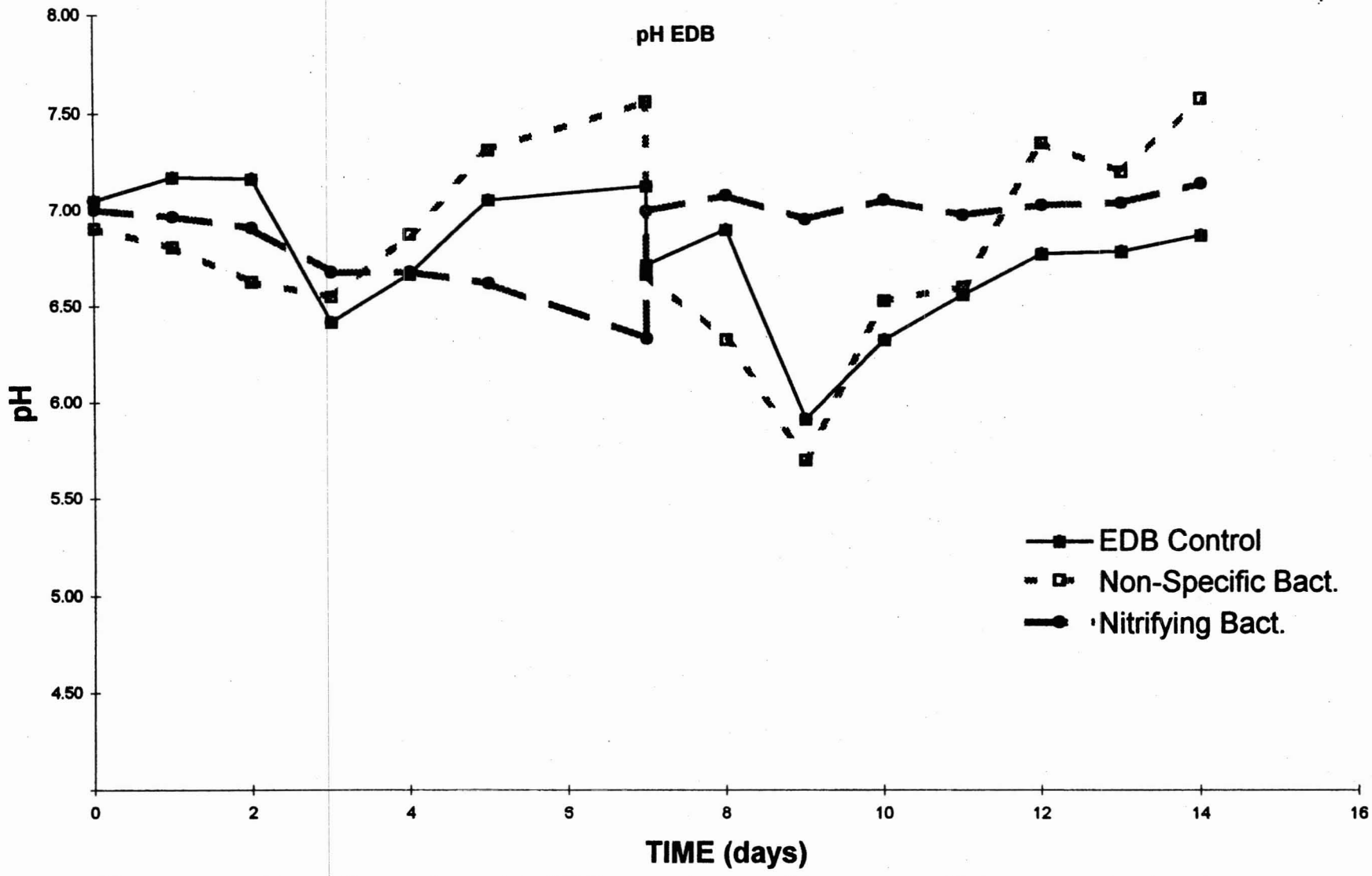


Figure 34. pH readings of aerobic EDB experiment. Bioassays utilizing bacteria deficient (control) flask, non-specific and nitrifying bacterial cultures [Stages 1&2].

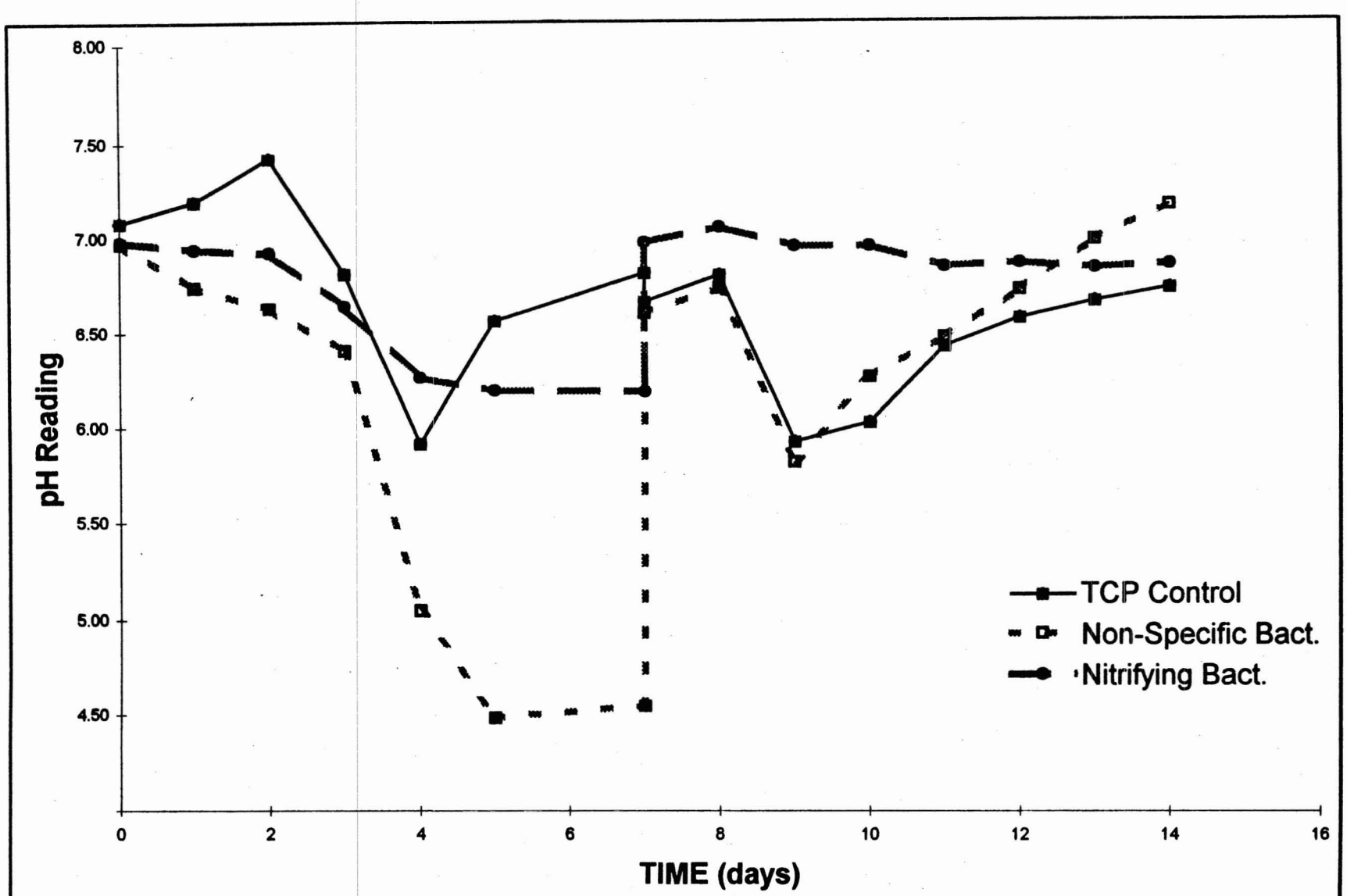


Figure 35. pH readings of aerobic TCP experiment. Bioassays utilizing bacteria deficient (control) flask, non-specific and nitrifying bacterial cultures [Stages 1&2].

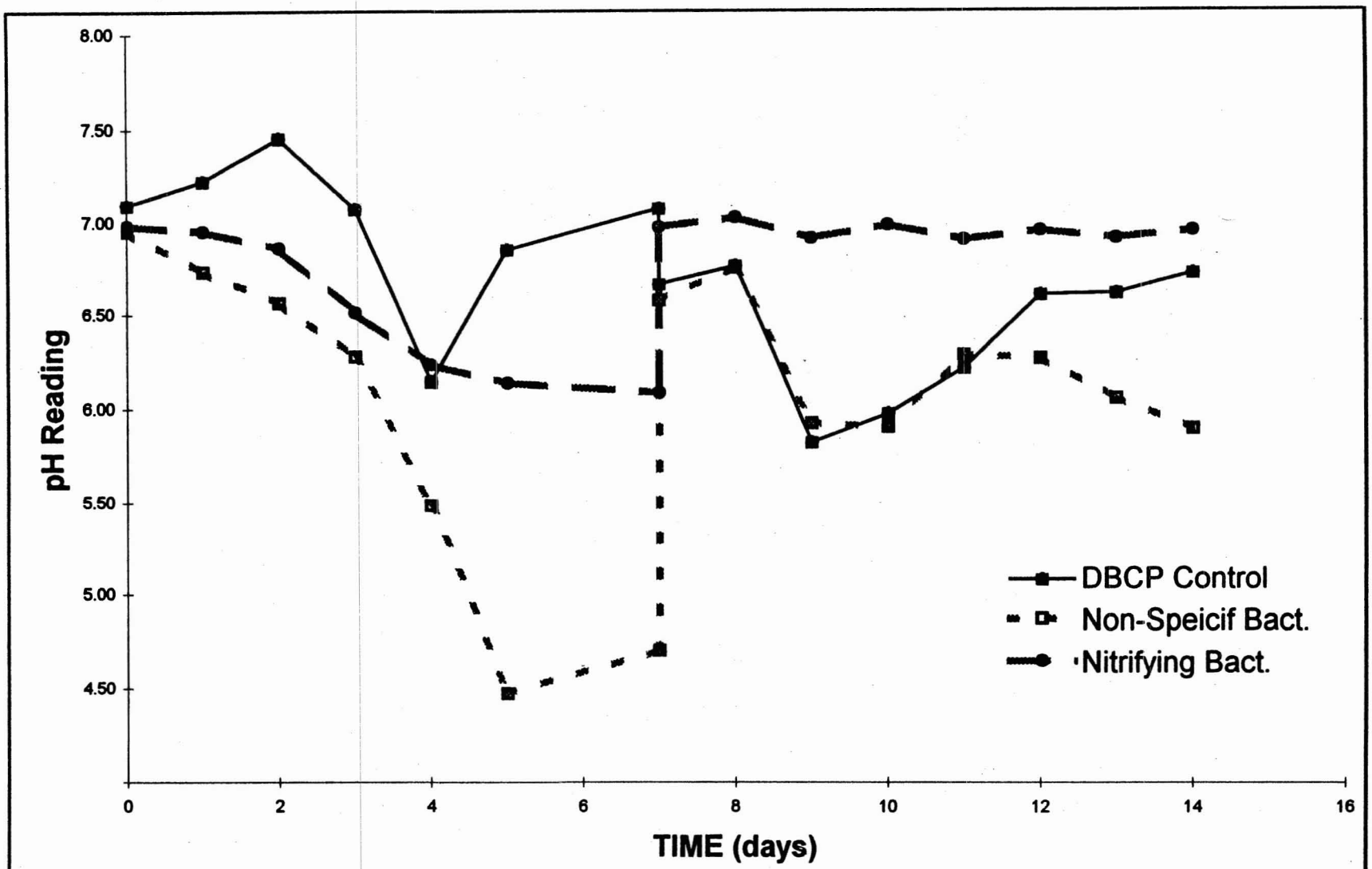


Figure 36. pH readings of aerobic DBCP experiment. Bioassays utilizing bacteria deficient (control) flask, non-specific and nitrifying bacterial cultures [Stages 1&2].

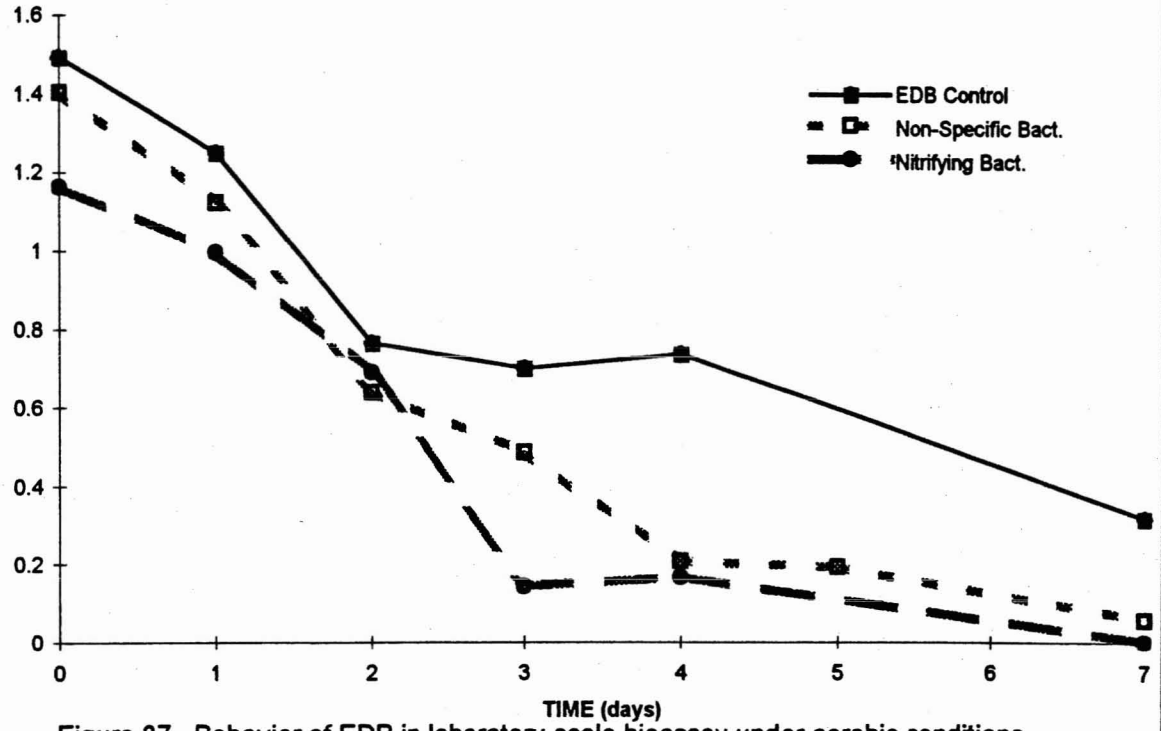


Figure 37. Behavior of EDB in laboratory-scale bioassay under aerobic conditions [Stage 1]. Utilizing bacterial deficient (control) flask, non-specific and nitrifying bacterial cultures.

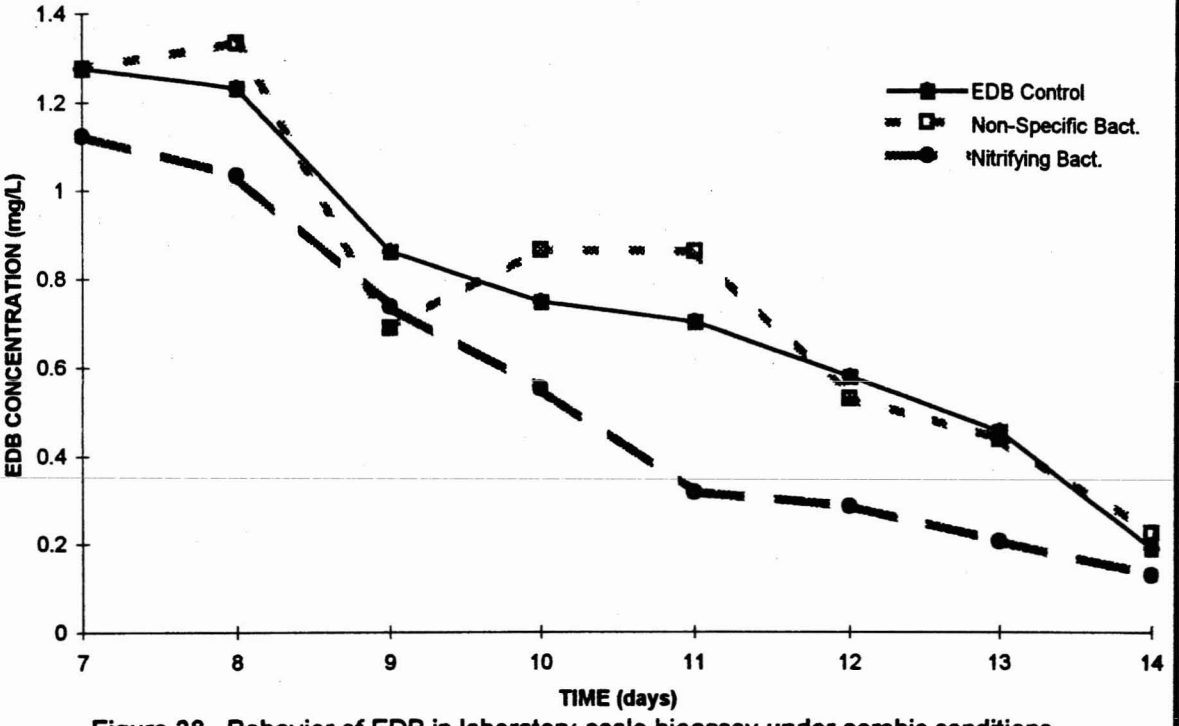


Figure 38. Behavior of EDB in laboratory-scale bioassay under aerobic conditions [Stage 2]. Utilizing bacterial deficient (control) flask, non-specific and nitrifying bacterial cultures.

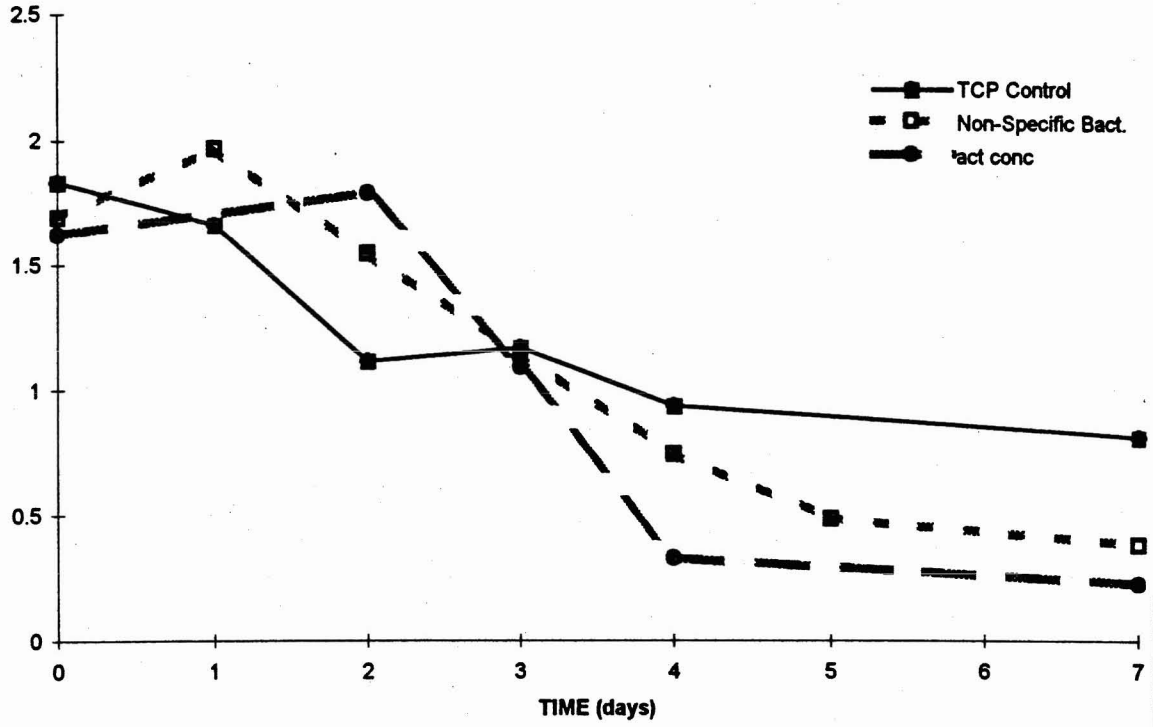


Figure 39. Behavior of TCP in laboratory-scale bioassay under aerobic conditions [Stage 1]. Utilizing bacterial deficient (control) flask, non-specific and nitrifying bacterial cultures.

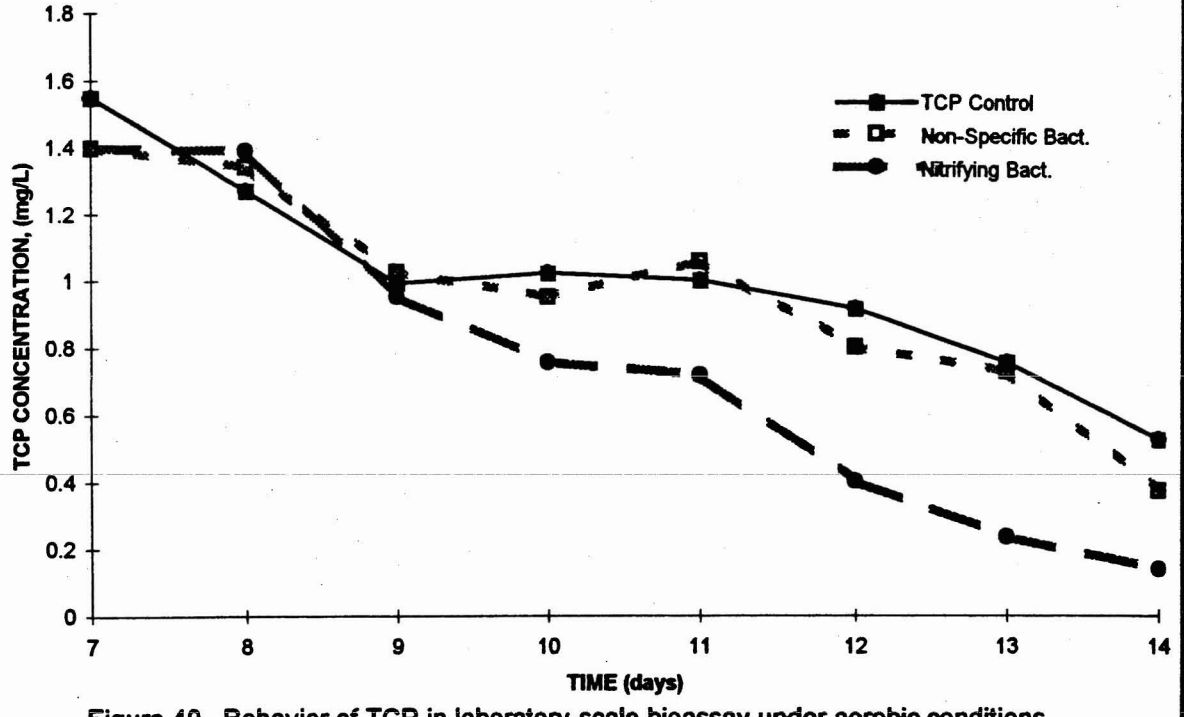


Figure 40. Behavior of TCP in laboratory-scale bioassay under aerobic conditions [Stage 2]. Utilizing bacterial deficient (control) flask, non-specific and nitrifying bacterial cultures.

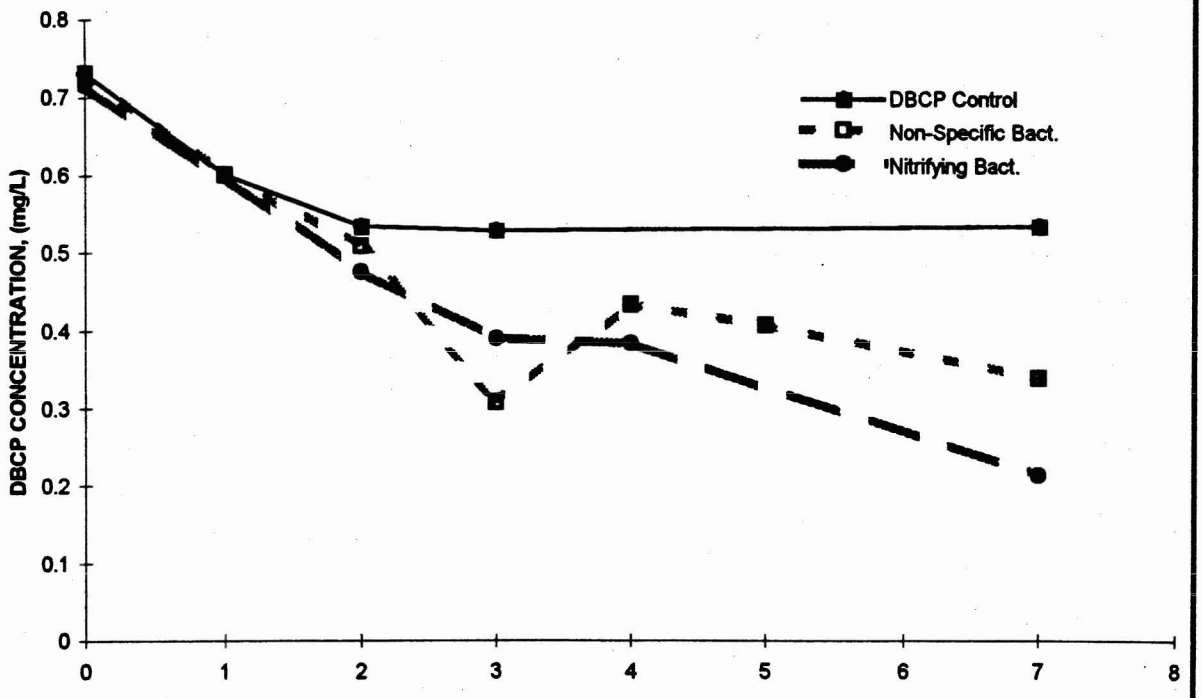


Figure 41. Behavior of DBCP in laboratory-scale bioassay under aerobic conditions [Stage 1]. Utilizing bacterial deficient (control) flask, non-specific and nitrifying bacterial cultures.

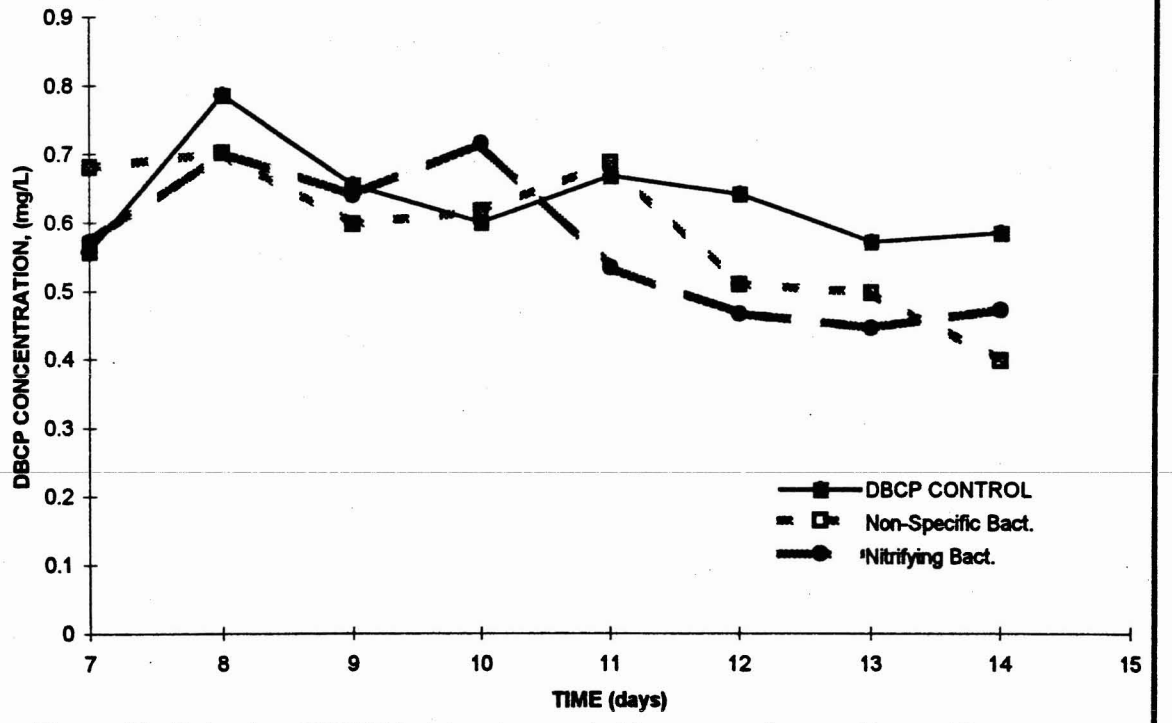


Figure 42. Behavior of DBCP in laboratory-scale bioassay under aerobic conditions [Stage 2]. Utilizing bacterial deficient (control) flask, non-specific and nitrifying bacterial cultures.

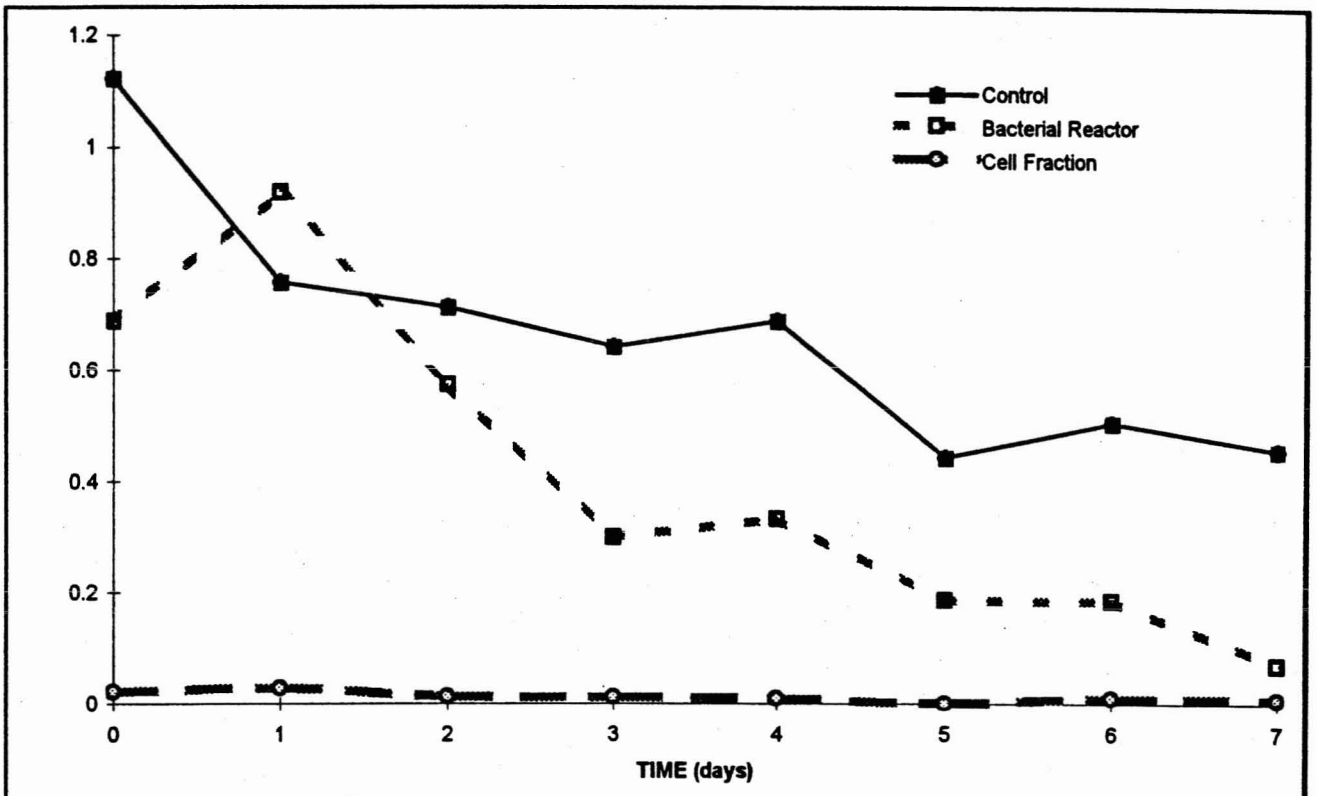


Figure 43. Behavior of EDB in laboratory-scale bioassay under anaerobic conditions [Stage 1]. Utilizing bacteria deficient flask (control) and non-specific bacterial culture.

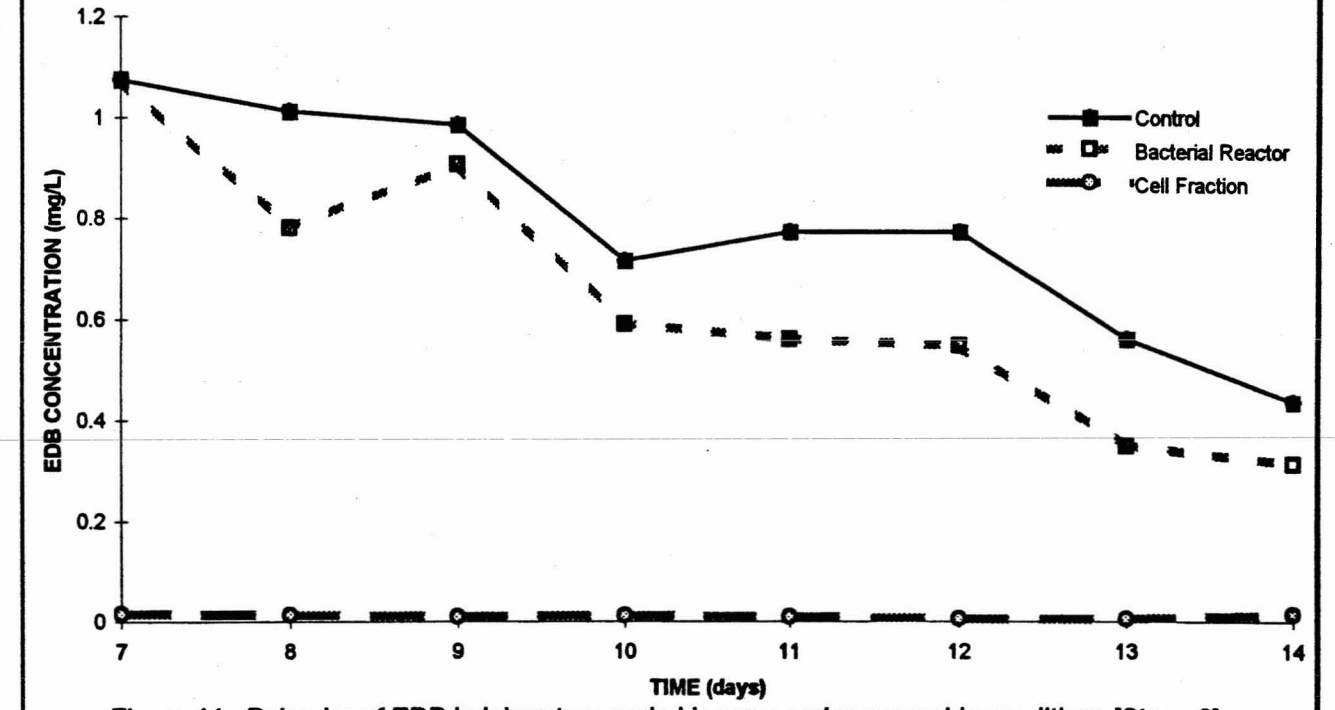


Figure 44. Behavior of EDB in laboratory-scale bioassay under anaerobic conditions [Stage 2]. Utilizing bacteria deficient flask (control) and non-specific bacterial culture.

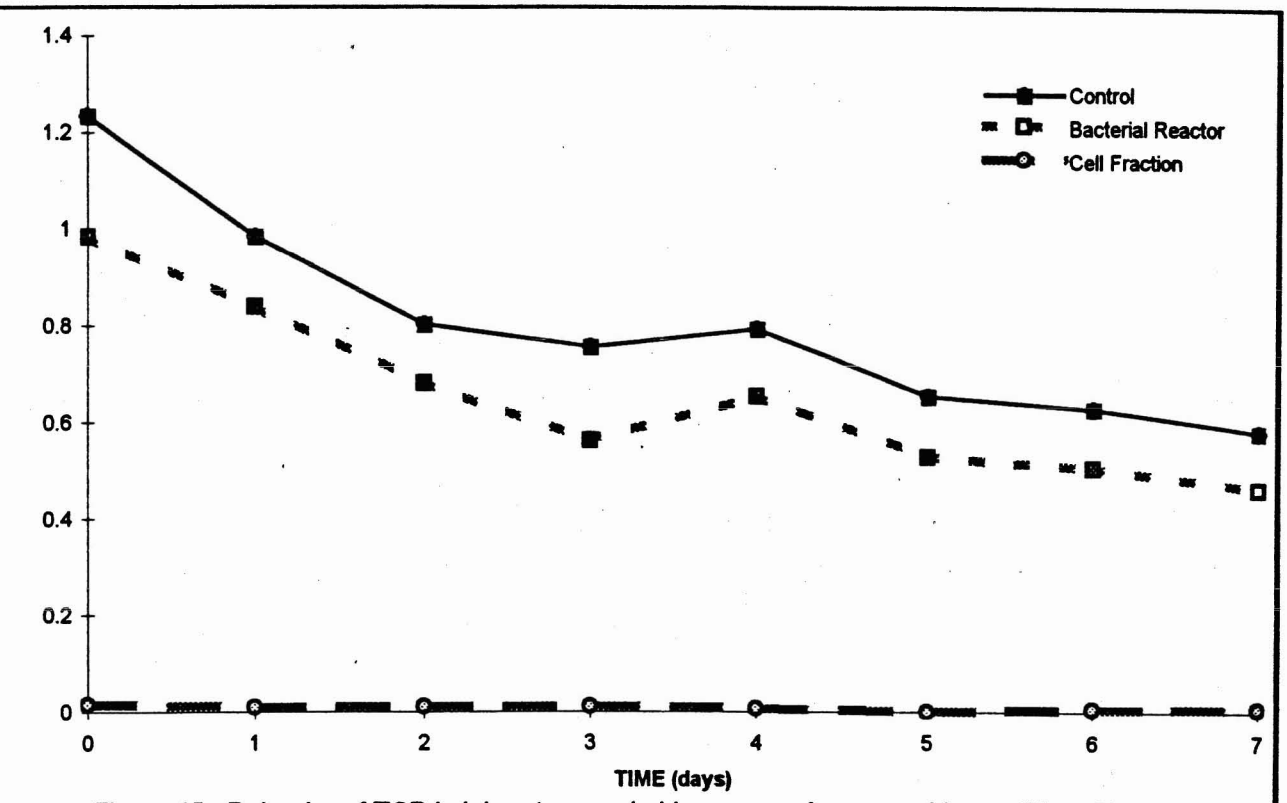


Figure 45. Behavior of TCP in laboratory-scale bioassay under anaerobic conditions [Stage 1]. Utilizing bacteria deficient flask (control) and non-specific bacterial culture.

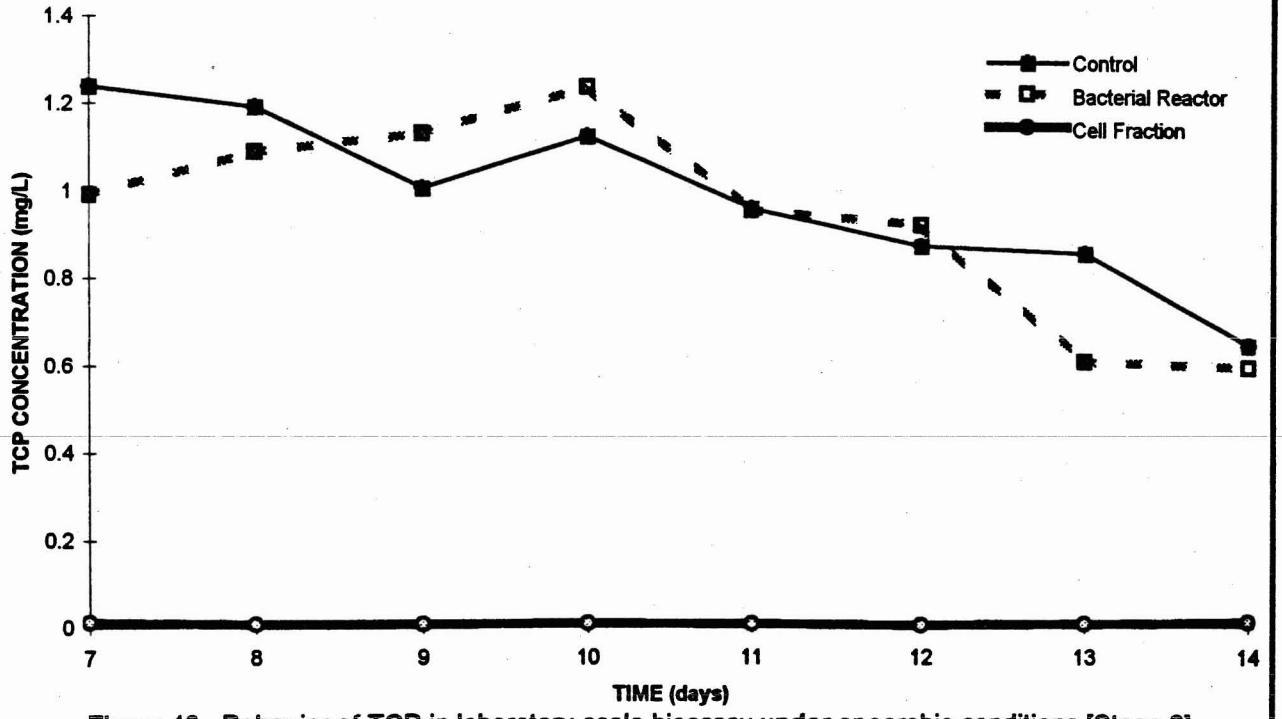


Figure 46. Behavior of TCP in laboratory-scale bioassay under anaerobic conditions [Stage 2]. Utilizing bacteria deficient flask (control) and non-specific bacterial culture.

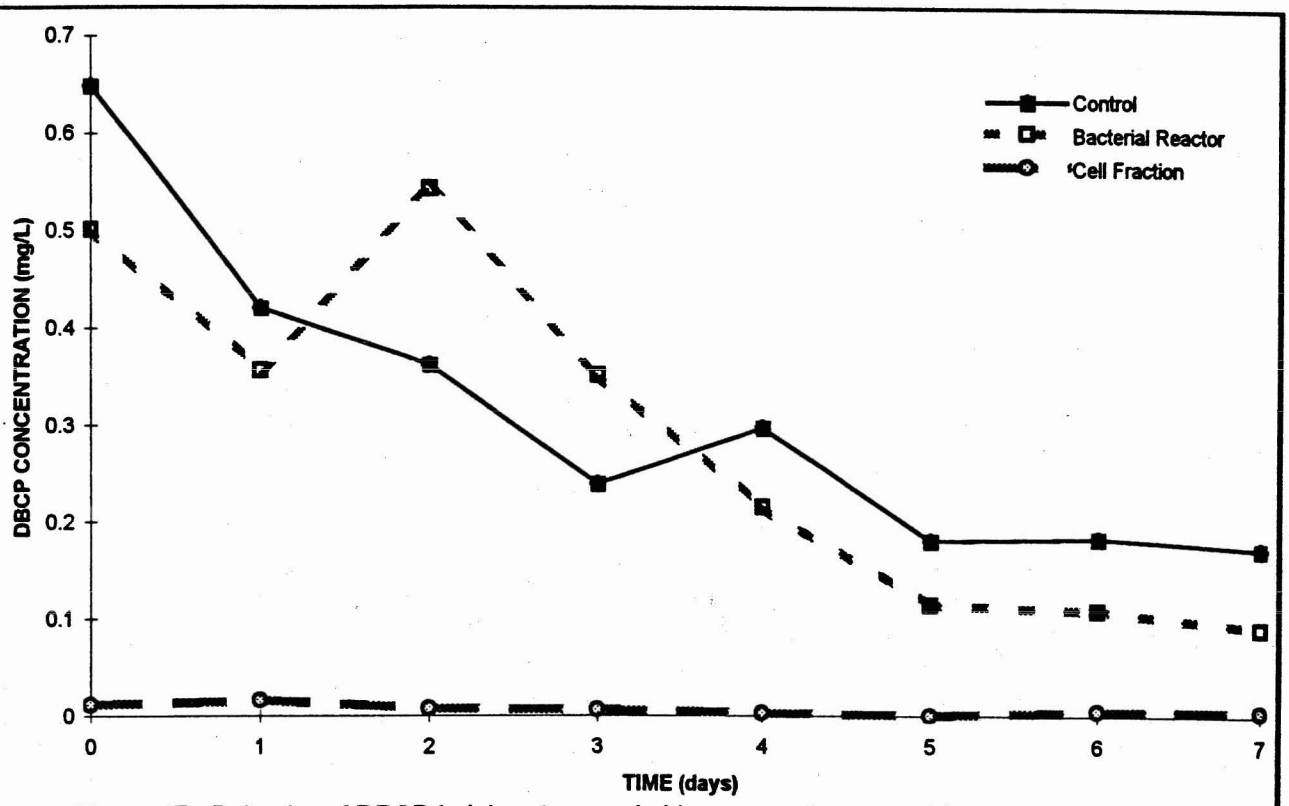


Figure 47. Behavior of DBCP in laboratory-scale bioassay under anaerobic conditions [Stage 1].

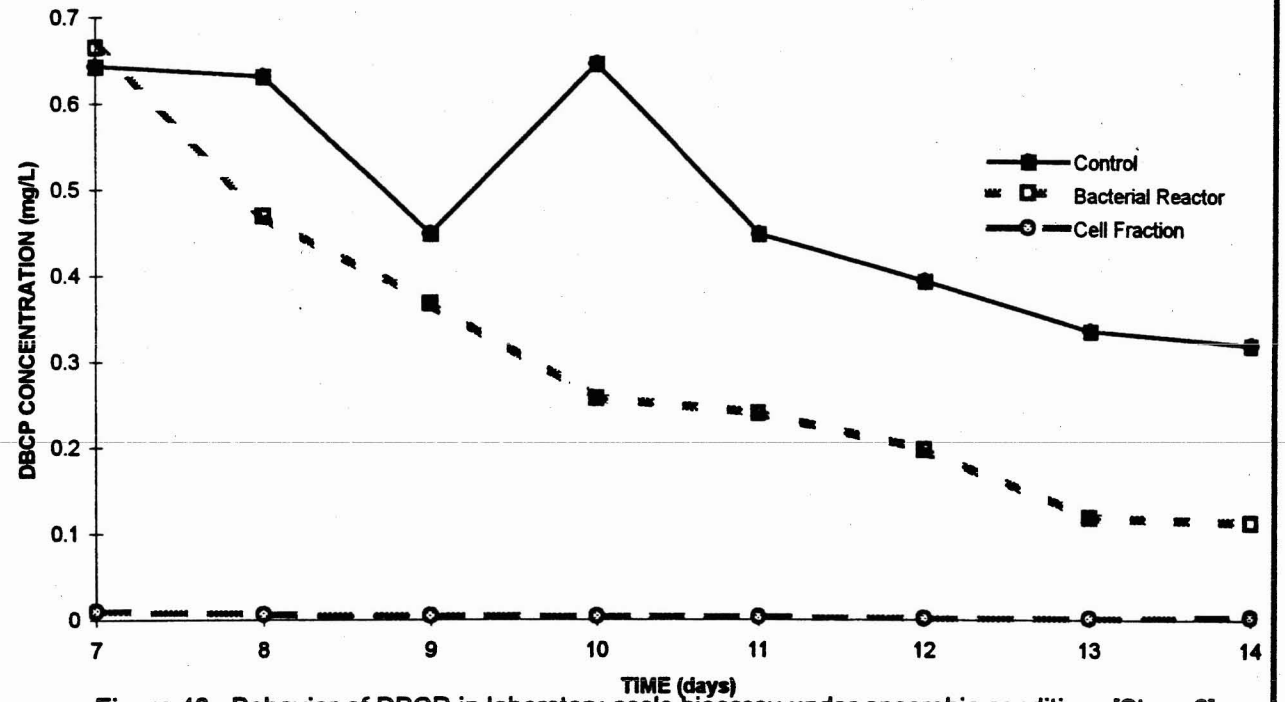


Figure 48. Behavior of DBCP in laboratory-scale bioassay under anaerobic conditions [Stage 2]. Utilizing bacteria deficient flask (control) and non-specific bacterial culture.

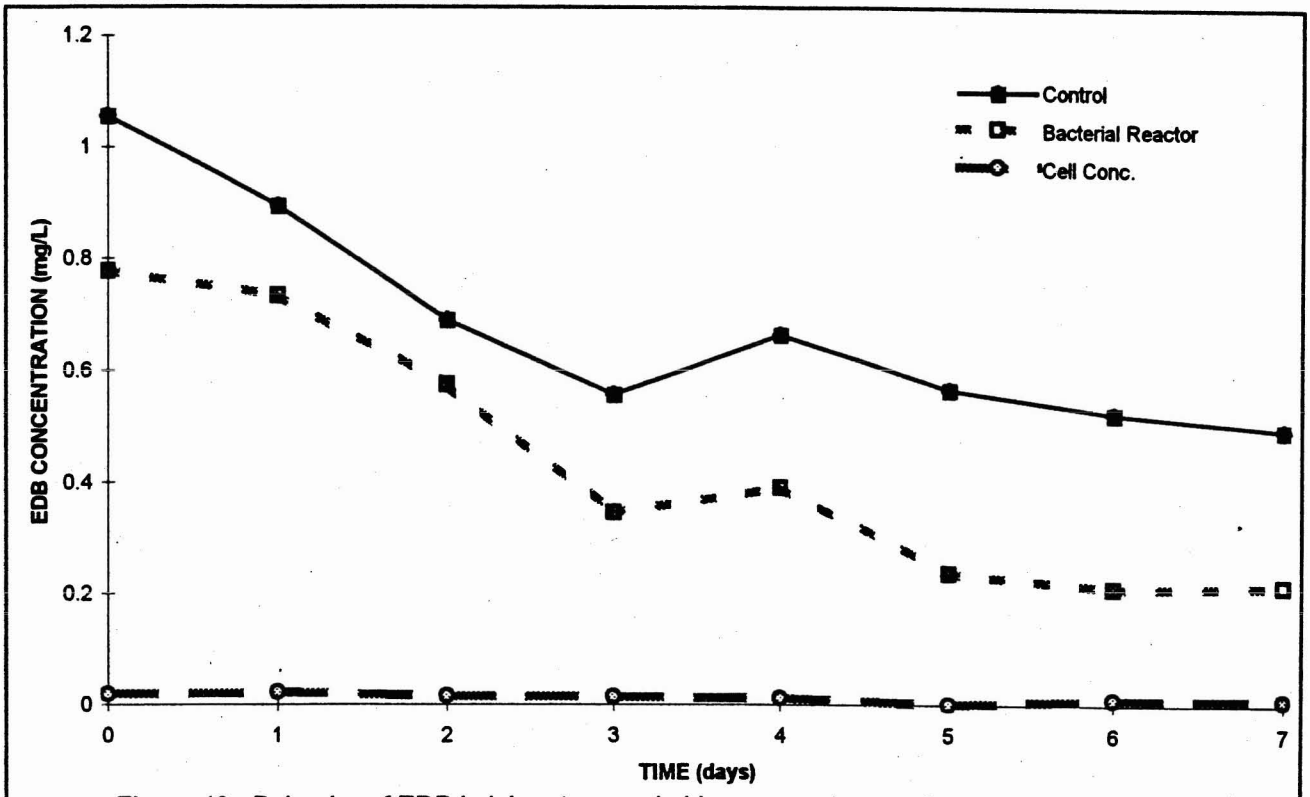


Figure 49. Behavior of EDB in laboratory-scale bioassay under anoxic conditions [Stage 1]. Utilizing bacteria deficient flask (control) and non-specific bacterial culture.

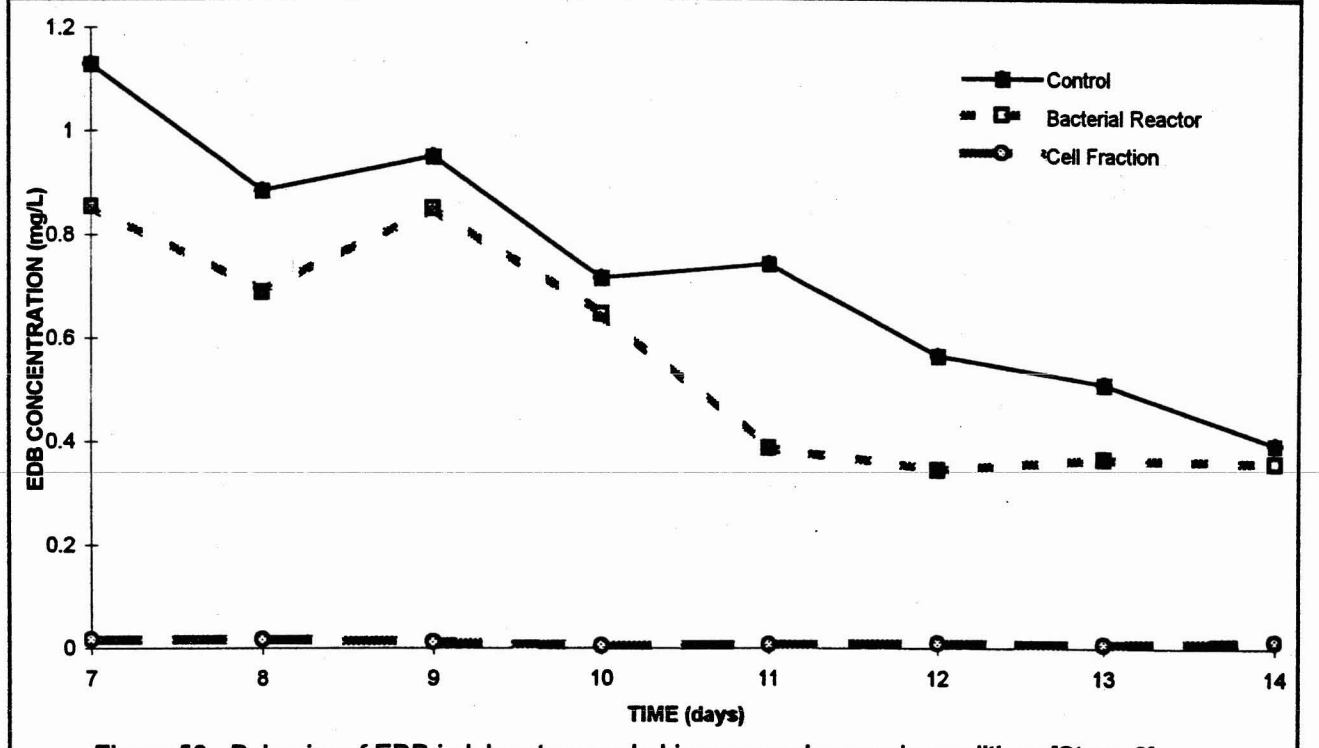


Figure 50. Behavior of EDB in laboratory-scale bioassay under anoxic conditions [Stage 2]. Utilizing bacteria deficient flask (control) and non-specific bacterial culture.

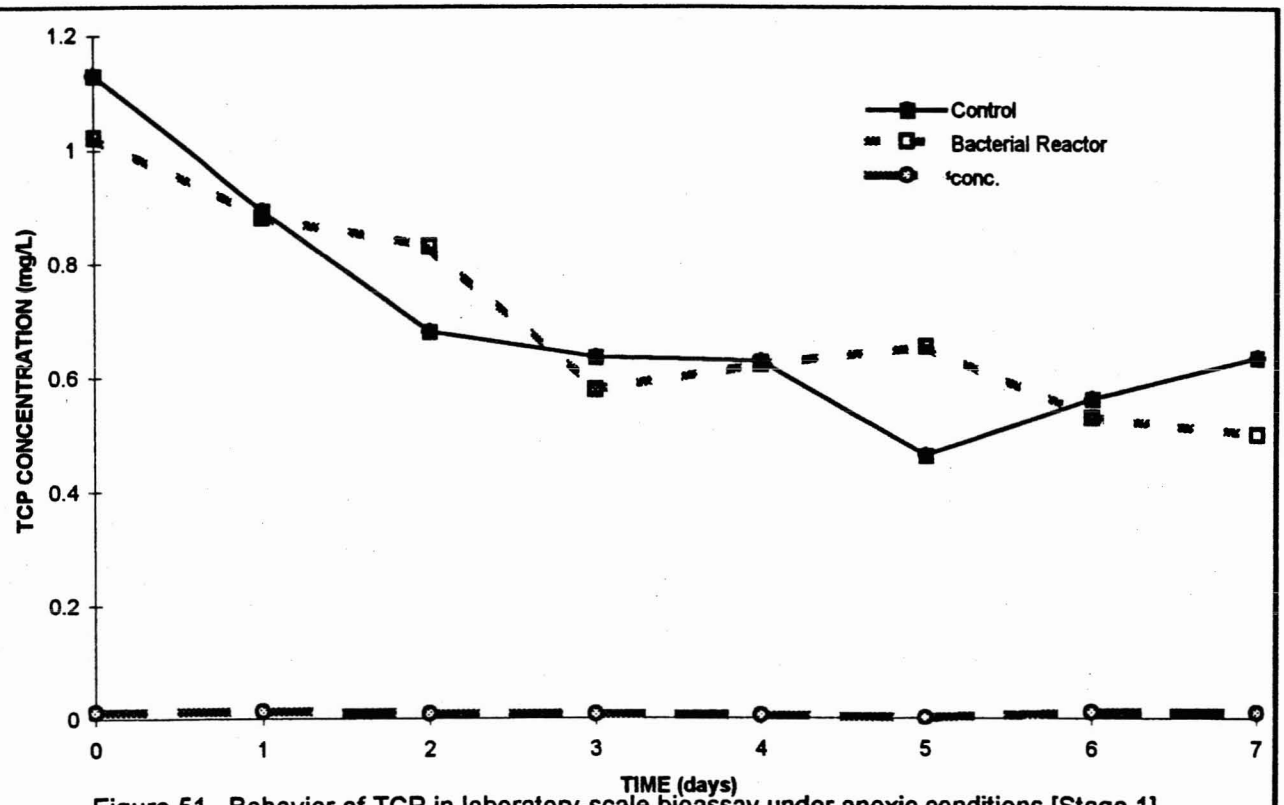


Figure 51. Behavior of TCP in laboratory-scale bioassay under anoxic conditions [Stage 1]. Utilizing bacteria deficient flask (control) and non-specific bacterial culture.

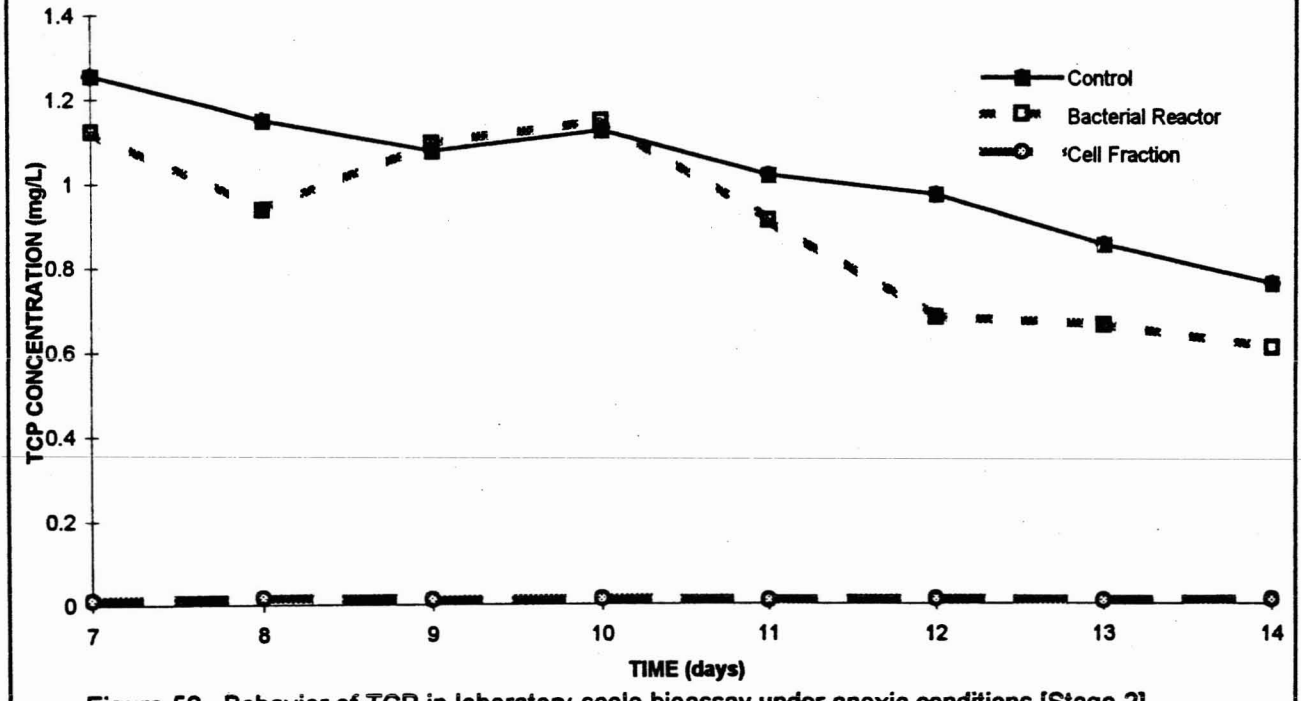


Figure 52. Behavior of TCP in laboratory-scale bioassay under anoxic conditions [Stage 2]. Utilizing bacteria deficient flask (control) and non-specific bacterial culture.

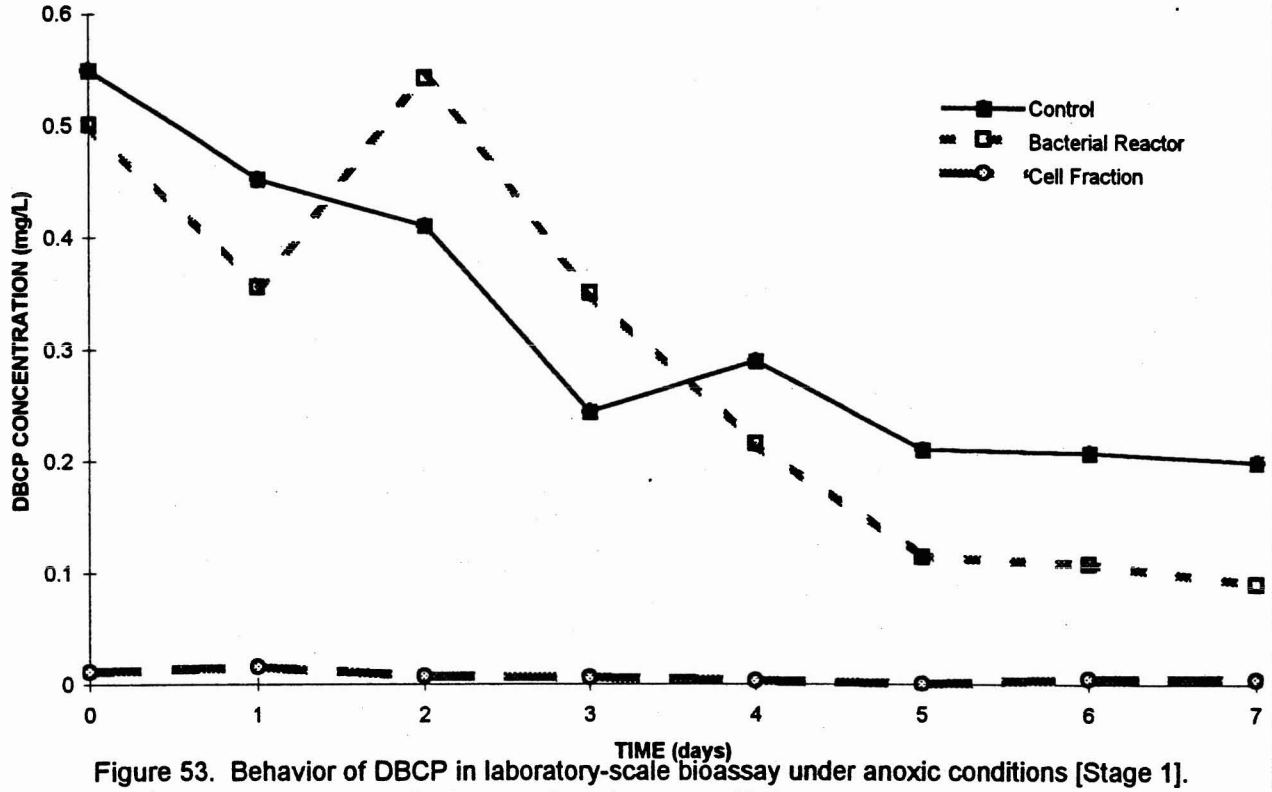


Figure 53. Behavior of DBCP in laboratory-scale bioassay under anoxic conditions [Stage 1]. Utilizing bacteria deficient flask (control) and non-specific bacterial culture.

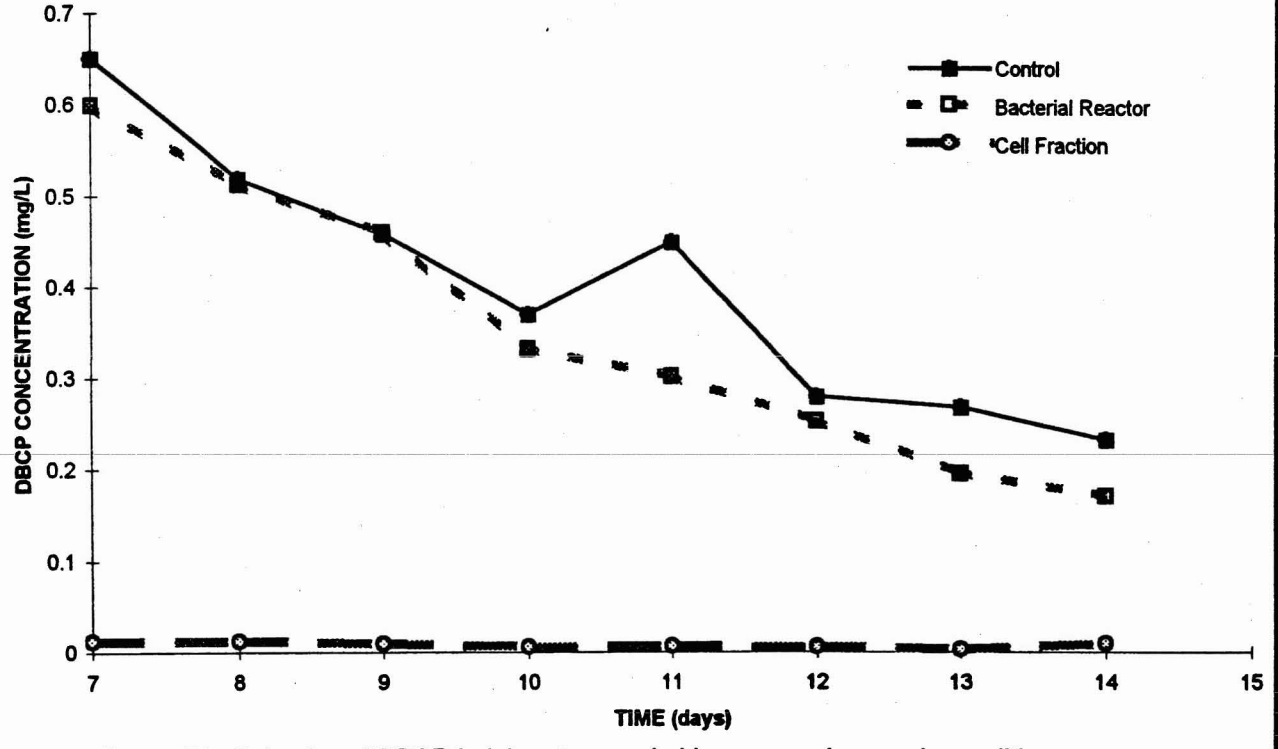


Figure 54. Behavior of DBCP in laboratory-scale bioassay under anoxic conditions [Stage 2]. Utilizing bacteria deficient flask (control) and non-specific bacterial culture.

Equations Used

VOC concentration determination (for microextraction)

$$VOCconc. = \left(\frac{Peakht.sample}{Peakht.std}\right)(Conc.std)(2mL)\left(\frac{1000uL}{mL}\right)\left(\frac{1}{35mL}\right)\left(\frac{1000mL}{L}\right)(Dil.factor)$$

VOC concentration determination (for ultrasonic extraction)

$$VOCconc.(massVOC / carbonmass = \left(\frac{Peakht.sample}{Peakht.std}\right)(Conc.std)(volumemethanol) / carbonmass$$

Column sizing

$$R = 0.5\sqrt{d1d2}$$

$$V = \frac{Q}{An}$$

$$\mathrm{Re} = \frac{vd\rho}{\mu}$$

Ratio of column diameter to particle size ≤ 50

$$EBCTsc = EDCTlc\left(\frac{dp,sc}{dp,lc}\right)$$

$$\mathrm{Re}\,sc,\min = \frac{Vsc}{Vlc}(\mathrm{Re}\,lc)\left(\frac{dp,sc}{dp,lc}\right)$$

$L_{sc} = Vol_{sc}/A_{sc}$

$$PACmass = EBCTlc\left[\left(\frac{dp,sc}{dp,lc}\right)\right]\text{^}(2-x)Qsc\rho_{(b,lc)}$$

$$Sc = \left(\frac{\mu}{\rho D}\right)$$

$$D = (1.173x10^{-16}(\varphi M)^{1/2}T) / \mu V^{0.6}$$

$$Kf = \frac{Dl}{2R}\left(2 + 1.1\mathrm{Re}^{0.6}Sc^{1/3}\right)$$

$$St = \frac{KfEBCT(1-\varepsilon)}{R\varepsilon}$$

$$Pe = \frac{Lv}{De}$$

Annotations for Equations:

R	=	average particle radius
d1	=	diameter of carbon particle in large column (mm)
d2	=	diameter of carbon particle in small column (mm)
V	=	interstitial velocity (m/d)
Q	=	liquid flow rate (m^3/d)
A	=	area of column (m^2)
n	=	constant (assume n= 0.39)
Re	=	Reynolds number
v	=	velocity (m/d)
d	=	particle diameter
ρ	=	density of water (g/cm^3)
μ	=	viscosity of water (centipoise)
EBCTsc	=	Empty bed contact time of small column (seconds)
EBCTlc	=	Empty bed contact time of large column (seconds)
dp,sc	=	diameter of carbon particle in small column (mm)
dp,lc	=	diameter of carbon particle in large column (mm)
Resc,min	=	Minimum recommended Reynolds Number for small column
Vsc	=	Hydraulic Loading Rate for small column (m/d)
Vlc	=	Hydraulic Loading Rate for large column (m/d)
Re,lc	=	Reynolds Number for large column
Lsc	=	Bed Length for small column (cm)
Asc	=	Area of small column (cm^2)
Volsc	=	Volume of small column (cm^3)
x	=	Proportionality constant (x =1)
Qsc	=	Flow rate in small column (cm^3/min)
Pacmass	=	Mass of carbon required for small column
ρ(b,lc)	=	Bulk density of carbon in large column (g/l)
Sc	=	Schmidt number
D	=	Diffusivity
φ	=	Diffusivity constant (=2.6 for water)
M	=	Molecular weight of water (g/mol or kg.mass/kg.mol)
T	=	Absolute temperature
St	=	Stanton Number
Kf	=	Mass transfer coefficient
ε	=	Void fraction (= 0.4)
Pe	=	Peclet Number
L	=	Length of fixed bed (for either large or small column)
De	=	Axial dispersivity (L^2/t - based on adsorber length and interstitial velocity)