STUDIES ON CHEMICAL REGENERATION OF GRANULAR ACTIVATED CARBON

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Executive Summary

The Honolulu Board of Water Supply (BWS) operates granular-activated carbon (GAC) contactors to remove TCP, EDB, and DBCP from well water in central Oahu. These contactors first became operational in 1986. Numerous additional contactors are currently either under construction or in the planning stage. Currently the spent GAC is being disposed of at a local landfill and replaced with virgin GAC at an annual cost of nearly $500,000. A novel chemical regeneration technique has been developed which may reduce these costs by more than 50%. A literature and industry search was conducted into current and emerging regeneration techniques and local disposal alternatives. The result of that effort was to recommend bench-scale followed by pilot-scale chemical regeneration studies.

Bench-scale studies were conducted using rapid small-scale column tests (RSSCT) to determine the best regeneration scheme for dibromoethane (EDB), trichloropropane (TCP), and dibromochloropropane (DBCP) removal from the spent GAC. Short-term studies using BWS’s spent GAC found that many combinations of either an acid or a base and a solvent could desorb all of the pesticides as long as the solvents were used at 100% strength. Side-by-side RSSCTs using Mililani well water and spiked deionized water found that natural organic matter (NOM) competes with the pesticides and reduces GAC adsorption capacity by 30% for DBCP and 49% for TCP. Preliminary RSSCTs using Mililani well water to load the columns found that acetone alone was not an effective regenerant. Long-term RSSCTs are being conducted using Mililani well water. The columns treat the well water until pesticide breakthrough and then are regenerated. After regeneration, they again treat the well water. This has been repeated seven times so far. The use of either an acid or a base plus acetone was effective for 5 load/regeneration cycles. After the fifth cycle the regeneration protocol was modified to include the use of both an acid and a base and acetone. This later protocol seems able to regenerate the GAC to its virgin adsorption capacity. It is not yet clear how many cycles are possible. This indicates that it is technically feasible to chemically regenerate BWS’s GAC such that it can be reused repeatedly and indefinitely. The bench-scale experiments have been very successful and were able to demonstrate that the solvent (acetone) can be reused. Preliminary investigations have been conducted into waste disposal processes including recovery of acetone (via distillation), neutralization of acid/base with disposal to the wastewater system, and chemical destruction of desorbed pesticides followed by disposal to the wastewater system.

Pilot-scale stainless-steel columns (2-inch diameter) have been designed, constructed, and installed in Mililani where they are operated side-by-side with the full-scale contactors. Operation of the pilot columns began on April 8, 1999. Following breakthrough, they are to be regenerated using the protocols developed. These pilot tests will result in directly scaleable chemical use rates, column rinsing requirements, and practicality of proposed waste treatment/disposal techniques.

Based upon the results presented herein, an invention disclosure form was filed with the University of Hawaii Office of Technology Transfer and Economic Development (OTTED) in July, 1999. Patent searches have been conducted and the preliminary assessment from OTTED is that the chemical regeneration protocol is probably patentable. The next step is to determine
what interest BWS has in the patent rights and then to proceed with hiring patent attorneys to file for protection. During this process, no details of the procedure or the results can be publicly disclosed (otherwise patent rights are nullified).

It is recommended that chemical regeneration studies be continued. The bench-scale work should continue in order to determine the number of regenerations that are possible using an acid and a base and an organic solvent; to determine the best order to pass the regenerant fluids through the spent GAC; to determine the most cost effective acid, base, and organic solvent to utilize; and to determine cost effective and legal residuals treatment and disposal alternatives. The pilot-scale studies should continue in order to determine: backpressures generated during regeneration (to design pumps); the amount of post rinsing needed to meet the recommended MCLs for the desorbent chemicals (from health effects study); the feasibility and cost of routine solvent distillation/recovery for reuse; the feasibility of recycling/reusing the acid, base and solvent; the amount of acid/base/solvent lost (to help determine operating costs); and the feasibility of proposed treatment and disposal options for regenerant fluids. This should be followed by a full-scale trial. These experiments will require approximately 3 years.

The ultimate goal of this project is to place into service an on-site chemical regeneration process which will allow the GAC to be reused numerous times (for multiple years) prior to replacement and thereby incurring a significant operations cost savings. All evidence gathered to date indicates that this is both technically and economically feasible.
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1.0 Introduction

1.1 Aquifer Contamination

The discovery and characterization of pesticide contamination in the Pearl Harbor Aquifer in the 1970s and 1980s prompted treatment of water from the aquifer prior to distribution. The pesticides contaminating the aquifer, 1,2-dibromo-3-chloropropane (DBCP), ethylene dibromide (EDB), and 1,2,3-trichloropropane (TCP) are present at low concentrations; however, since their discovery, the concentrations detected have not decreased (Lau and Mink, 1987). Instead, the concentrations of DBCP in the Mililani wells have increased from approximately 10-30 ng/L in 1985 to approximately 25-85 ng/L in 1992 (Oki, et al., 1994). For the same years, the range of TCP concentrations has remained fairly stable at 1200-2400 ng/L. More recent data indicates that in mid-1996, the concentrations at the Mililani wells were 130-150 ng/L for DBCP and 2,500-4,000 ng/L for TCP. In mid-1996, the concentrations at the Waipahu wells were about 40 ng/L for EDB; and at the Kunia wells, the concentrations were 10-15 ng/L for DBCP and 700-800 ng/L for TCP. The maximum contaminant limits (MCLs) for these chemicals are 40 ng/L (EDB, DBCP) and 800 ng/L (TCP). There is evidence that the contamination is spreading rather than subsiding (Lau, et al., 1995). Due to slow desorption and biodegradation rates in the soil, modeling of groundwater transport indicates that the Mililani, Waipahu, and Kunia wells will continue to be contaminated with DBCP, EDB, and TCP for the foreseeable future. In addition, several other well fields in the area are contaminated with these pesticides; however, their concentrations are, for now, below the MCLs.

1.2 Treatment Method

In order to protect the health of water consumers, the Honolulu Board of Water Supply (BWS) commenced treatment of water from the Pearl Harbor aquifer at those locations with the greatest contamination. Remediation of the aquifer is not feasible (and probably impossible) due to its depth and the extent of the contaminant plume. Granular activated carbon (GAC) is utilized to remove DBCP, EDB, and TCP from water pumped out of the aquifer prior to distribution. Adsorption onto GAC is an effective removal method for many organic compounds
including DBCP, EDB, TCP, and background natural dissolved organic matter (NOM). With GAC treatment, DBCP, EDB, and TCP are removed to the limits of detection. All adsorbable organics passed through a GAC column will compete for adsorption sites on the carbon. Generally, competition reduces the adsorptive capacity for any individual compound, and often the reductions are very significant (Jain and Snoeyink, 1973). GAC is known to be an efficient method for removal of NOM as evidenced by promotion of its use for removal of NOM from drinking water prior to chlorination for prevention of trihalomethane formation (Cummings and Summers, 1994). It has been hypothesized that background NOM is responsible for the observed carbon usage rates in Hawaii which have been nearly 10 times greater than expected (Oki, et al., 1994). This has resulted in unexpectedly high operating costs. These costs were reported to be $1.4 million for 1994 (Lau and Mink, 1995), however, it is unclear what costs this estimate included. More recent estimates place the annual costs for carbon replacement at approximately $468,000 per year. This cost estimate is calculated as shown in Table 1 based upon data given in Leon-Guerrero et. al. (1994) and Kawata (1996).

<table>
<thead>
<tr>
<th>Component</th>
<th>Unit Cost ($)</th>
<th>Annual Cost ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC purchase and replacement</td>
<td>2,200</td>
<td>418,000</td>
</tr>
<tr>
<td>GAC analytical testing</td>
<td>49</td>
<td>9,300</td>
</tr>
<tr>
<td>GAC disposal</td>
<td>60</td>
<td>11,400</td>
</tr>
<tr>
<td>Labor</td>
<td>154</td>
<td>29,260</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td><strong>467,960</strong></td>
</tr>
</tbody>
</table>

The BWS currently operates contactors at five locations including Waipahu I (14 contactors, 7 on-line), Waipahu II (4 contactors, 2 on-line), Kunia II (8 contactors, 2 on-line), Mililani Wells I (12 contactors, 6 on-line), and Mililani Wells III (4 contactors, 2 on-line). This gives a total of 42 contactors with 19 on-line. In addition, there are a total of 46 additional contactors either in the design or planning stages for different wells in the area. Each contactor has a diameter of 12 feet and is filled with 20,000 lbs of carbon which has a depth of approximately 10 feet. The empty bed contact time (EBCT) for each of the BWS contactors is approximately 12 minutes.
1.3 Characteristics of Spent Carbon

Activated carbon has been widely used to remove a range of organic compounds from both industrial and municipal water and wastewater. After the exhaustion of its adsorption capacity, activated carbon must be either replaced with virgin carbon or regenerated. In the case of GAC, its high initial cost usually mandates regeneration. It has been estimated that the cost of carbon regeneration (thermally) for a commercial GAC contractor, accounted for approximately 75% of the total operating and maintenance cost (EPA, 1973). Thus, a need exists to develop an economical regeneration process that will suit the City and County of Honolulu BWS.

Currently GAC is exhausted at a rate which requires GAC replacement for all on-line contactors approximately every 11 months. Each contactor contains 20,000 lb of GAC. Spent carbon contains adsorbed EDB, DBCP, TCP as well as NOM. The adsorbed concentrations of the pesticides are likely somewhat variable depending upon which contactor the spent GAC originates from. In addition, the adsorbed concentration of NOM is unknown. Several analyses of spent GAC samples from BWS contactors have found adsorbed concentrations of approximately 1,500 ng/g for EDB, 650 ng/g for DBCP, and 112,000 ng/g for TCP. This means that each 20,000 lb batch of spent carbon might contain a total mass of pesticides of approximately 13.7, 5.9, and 1,014 g of EDB, DBCP, and TCP, respectively. Spent carbon also contains pore water which is also important for some potential regeneration methods which may require its removal. In summary, because there are 19 on-line contactors, each year approximately 190 tons of GAC must be disposed of and replaced or regenerated. This spent GAC contains a total of roughly 0.57 lb of EDB, 0.25 lb of DBCP, and 42.4 lb of TCP.

Regeneration of spent GAC means restoration of adsorption capacity which is different than desorption of target pesticides. The reason for this is the presence of NOM. The NOM may adsorb into carbon pores, block carbon pores due to surface adsorption, and/or cause changes in carbon surface chemistry to adversely impact target compound adsorption. Regeneration will therefore involve removal of pesticides as well as NOM and perhaps restoration of surface chemistry in order to achieve significant restoration of adsorption capacity and facilitate the possibility of multiple regeneration and loading cycles (highly desirable).
1.4 **Regeneration Techniques**

The most common regeneration technique used worldwide is thermal regeneration, which includes thermal desorption followed by hot gas or steam reactivation. Adsorbates are desorbed through volatilization and then oxidized at high temperatures in an afterburner. However, 5-10% of the carbon is usually lost through attrition, excessive burn-off, and washout during each regeneration cycle (Guymont, 1980). This lost carbon must be made up with virgin carbon. Other methods of regeneration have been studied in the literature. These include solvent extraction and chemical oxidation, supercritical fluid extraction, wet air and oxidation, and biological extraction. Of the possibilities listed, steam or hot gas regeneration, supercritical fluid extraction, and wet oxidation can be very effective to remove a broad spectrum of organic compounds, but they require high temperatures and/or high pressures (Sontheimer et al. 1988). In contrast, solvent extractions and advanced oxidation processes (AOPs) can be operated at room temperature and ambient conditions, and are very effective in destroying or mineralizing a wide range of organic compounds (Liu 1996).

1.5 **Study Objectives**

The objectives of the study included evaluation of on-site and off-site regeneration alternatives and local disposal alternatives for the spent GAC, evaluation of on-site chemical regeneration in bench-scale experiments, and use of pilot-scale studies to determine operating capacities and efficiencies for full-scale implementation. To meet these objectives, we first conducted an extensive literature search of available on-site, off-site, and local disposal alternatives and evaluated them against several criteria. We then selected the most promising method (chemical regeneration) for bench-scale experiments. We then designed, set up and conducted bench-scale chemical regeneration experiments. We also designed, constructed, and began operation of pilot-scale columns for proof-of-concept testing.
2.0 Literature Review

2.1 Contaminants

The pesticides of importance to this study are ethylene dibromide (EDB) or 1,2-dibromoethane, 1,2-dibromo-3-chloropropane (DBCP), and 1,2,3-trichloropropane (TCP). The Del Monte Corporation commonly used these three pesticides on their agricultural land. Their properties are listed in Table 1 (Verschueren, 1996; Howard, 1991). 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 (T99) (Taylor et al., 1990).

Table 2 - Properties of DBCP, EDB, and TCP.

<table>
<thead>
<tr>
<th>Property</th>
<th>DBCP</th>
<th>EDB</th>
<th>TCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>236.36</td>
<td>187.88</td>
<td>147.44</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>196.0</td>
<td>131.6</td>
<td>156</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>6.00</td>
<td>9.97</td>
<td>-14</td>
</tr>
<tr>
<td>T99* temperature (°C)</td>
<td>560</td>
<td>545</td>
<td>625</td>
</tr>
<tr>
<td>Vapor pressure @ 20°C (mm HG)</td>
<td>0.58</td>
<td>11</td>
<td>2.0</td>
</tr>
<tr>
<td>Solubility in water (mg/L)</td>
<td>1,230 @ 20°C</td>
<td>4,310 @ 30°C</td>
<td>1,900 @ 25°C</td>
</tr>
<tr>
<td>Density @ 20°C (g/cm³)</td>
<td>2.09</td>
<td>2.18</td>
<td>1.39</td>
</tr>
</tbody>
</table>

* 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:

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{C} \\
\text{Br} & \quad \text{Br} \\
\text{H} & \quad \text{H}
\end{align*}
\]
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 has a volatilization half-life 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.

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/INTP, 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, which is typically found 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:

\[
\begin{array}{cccc}
\text{H} & \text{H} \\
\text{Br} & \text{C} & \text{C} & \text{Br} \\
\text{H} & \text{H}
\end{array}
\]

EDB use began in 1948 and increased use occurred as Dole Company chose it as its primary fumigant in 1978 after DBCP use was banned 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 hydrolyzes 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 used 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:

\[
\begin{array}{c}
\text{H} \\
\text{Cl} \\
\text{H} \\
\text{Cl-C-C-Cl} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

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.

When the pesticides were detected in water samples in Central Oahu in the 1982, 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. 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) of 50 ng/L for EDB and 200 ng/L for DBCP (US EPA, 1989). In 1992, DOH established MCLs of 40 ng/L for EDB and DBCP and 800 ng/L for TCP.

2.2 Competition Between Synthetic Organic Chemicals and Natural Organic Matter

GAC has widely been used to remove trace synthetic organic chemicals (SOCs) and natural organic matter (NOM) from water. The fundamental details on how these compounds interact with each other and how such interaction affects adsorption onto GAC are not completely understood. 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 polyelectrolytically (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). The variation in NOM characteristics can affect pollutant adsorption in several ways (including site utilization and pore blockage) 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). Researchers 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 as the molecule in which there are more contact points and more suitable adsorption energy (i.e., negative $\Delta G$). 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 1997, 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. Carter's hypothesis was also tested 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, Carter et al. (1992) also found that n increased as the carbon was loaded with smaller humic acid molecules.

2.3 Review of Regeneration Methods and Local Disposal Alternatives

An extensive literature review was conducted and submitted to BWS in June, 1998 (Hamura, Sagayaga, and Babcock, 1998). In the literature study, it was found that there are several established and emerging technologies for regeneration of spent GAC that are documented in the literature. To organize their evaluation and comparison, they were categorized as on-site methods (at the wellhead site) and off-site methods (requiring removal...
from the site to be processed elsewhere). Local disposal alternatives were also reviewed. The important criteria that were considered included regeneration efficiency, cost, degree of development, practicality/ease of use, environmental/regulatory issues/permits (emissions, waste residuals), public acceptability, and compatibility with BWS operations/facilities. A great deal of literature was found and summarized. The many possibilities were narrowed down to the best options and conclusions were made regarding the need for bench testing of chemical regeneration.

The literature and industry search found numerous references (42) related to the subject of on-site regeneration of spent GAC. The on-site methods were grouped into chemical methods and other methods. Some of the literature on the effects of NOM was also reviewed (7 citations). The chemical methods discovered included the use of organic solvents, inorganic solvents, and supercritical fluids. Use of either organic or inorganic solvents could potentially occur as an in-vessel (in situ) operation. The use of supercritical CO₂ as the solvent would necessitate ex-situ operation, but presumably on-site at the wellhead locations. For either of these types of systems, a mobile trailer mounted facility that could be transported between the various well sites is envisioned as feasible. The other on-site methods discovered included on-site thermal, biological, photochemical, and electrochemical methods. Each of the on-site methods must be considered as emerging technologies which require further research and development prior to full-scale implementation. However, for the chemical regeneration methods, there exists ample evidence of potential success at substantial cost savings to warrant vigorous pursuit of such research. The other emerging technologies (on-site thermal, biological, photochemical, and electrochemical) do not currently warrant further investigation due to various limitations (Hamura, Sagayaga and Babcock, 1998).

The use of a chemical method may eliminate unloading and transporting of GAC because the regeneration could be conducted in situ with the help of relatively simple equipment to convey the appropriate amount of solvent to the GAC contactor columns. The optimum solvent, or system of solvents and their strengths must be determined. The solvents must be compatible with the existing tank linings or possible replacement linings identified. Other considerations
regarding this in situ method include the volume of post rinse water needed prior to returning the filters to service, and the maximum contaminant levels (MCLs) for residual regenerant solvents appearing in the filtered water due to desorption after return to service. The chosen solvents may also face requirements for permits for purchase and storage. The manner in which the solvent is stored may fall under environmental regulation and the construction for an appropriate storage building may be warranted. Residuals treatment research is required to insure that there will be no impact of waste regenerant compounds and desorbed pesticides. While there are several practical aspects of this method which need to be researched, there do not seem to be any potentially critical roadblocks. The main advantage of chemical regeneration is potential operating cost savings as compared to existing operations (costs are discussed further below). Other advantages of chemical methods include on-site (at wellhead sites) operation, high regeneration efficiencies, the possibility of multiple regeneration/reloading cycles, relative simplicity, good adaptability, compatibility with current operations, and low energy and maintenance requirements. The main disadvantages of chemical regeneration methods are that they have not been demonstrated at full-scale (emerging technology), that many of the bench-scale results have not investigated the effects of NOM on the process, and that there are waste streams generated that must be disposed.

The literature and industry search found numerous references (17) related to the subject of off-site regeneration of spent GAC. The only off-site methods found were thermal methods and these included either constructing a new local thermal regeneration facility or using a mainland thermal regeneration contractor. The literature/industry search found references which give insight into the regeneration efficiency, the need to conduct acid prewashing when calcium deposits occur, and the potential construction and operating costs of such facilities and services. The main advantages of the off-site methods are that these methods are highly developed and accepted technologies for which full-scale operations are in service to look at and learn from. Thermal methods offer high regeneration efficiencies (the GAC is essentially re-made), high reliability, and compatibility with BWS operations. In addition, the use of a mainland contractor has the advantage that the BWS would not have to go into the GAC regeneration business and could instead contract for this service and set the terms of the contract to suite their needs (this
equates to adaptability as well as a desirable relinquishing of regulatory responsibility). On the other hand, it is not clear that there is significant competition in the regeneration contractor industry which could possibly result in undesirable price inflation. The main disadvantages of thermal methods are environmental, regulatory and economic. The construction of a local thermal facility would be very costly and would have environmental costs associated with air pollution. In addition, obtaining all of the necessary permits for a new local facility would be challenging and time consuming at best, and perhaps not feasible at worst.

The literature and industry search found several references (17) related to the subject of local disposal of spent GAC. The local disposal methods were grouped into three categories; landfilling, incineration, and use as construct material. The literature/industry search found information on available alternatives, feasibility of alternatives, and costs of the disposal methods. The main advantages of the disposal methods are that these methods are simple, compatible with existing operations, practical, easy to use, do not require BWS to obtain any new permits, and do not involve any capital costs for facility construction. Local disposal by landfilling is the status quo situation and therefore it is a proven and workable alternative to GAC regeneration. Both landfilling and incineration are highly developed and accepted technologies for which full-scale operations are currently in service. The use of spent GAC as a construction material is an interesting idea and is more environmentally friendly than landfilling or incineration since it is a form of recycling. However, use as a construction material is an emerging technology which would require further research before its true feasibility in Hawaii could be determined. The main disadvantages of the local disposal methods are costs and environmental considerations. Use of landfill space for spent GAC which could be either recycled or destroyed is not optimal for the environment, but is considered environmentally safe. Incineration is considered environmentally safe except in terms of contributing to global warming.

For each of the eleven alternative regeneration and local disposal alternatives, capital and operating costs were estimated and a rating chart (consisting of 13 rating criteria) was constructed to calculate scores (Hamura, Sagayaga and Babcock, 1998). Each of the potential
chemical regeneration methods have estimated operational costs that are significantly lower than those currently incurred by BWS for disposal of spent GAC by landfilling. However, they also each have an associated capital cost for construction of necessary facilities. The operating costs of the off-site methods were all greater than those currently incurred by BWS for disposal of spent GAC by landfilling. The costs for local disposal alternatives indicate that the current practice of landfilling is the least cost local disposal option (compared to local incineration and use as a construction material). Local incineration is not currently feasible and additional research would be required for use of spent GAC as a construction material (potential cost savings are only minimal relative to current practice anyway). The rating chart/scoring system evaluated 8 regeneration alternatives and three local disposal methods and found that the top three scoring alternatives are the mainland thermal regeneration contractor, the on-site chemical regeneration system, and landfill disposal. It was acknowledged that the rating approach is not perfect and the weights assigned to each criteria and the specific scores in each category could be argued. However, if an overall view is taken that the approach is probably somewhat reasonable for greatly narrowing down the pool of alternatives, then it is probably safe to say that the top three scoring alternatives are all good candidates for the best method and then further comparisons can be made. This process selected the current practice (landfilling), the alternative method which is currently being pilot tested (mainland contractor) and the method which we have been researching at UH (chemical regeneration). This was taken to indicate that it is worthwhile to pursue further the inorganic/organic chemical regeneration method. By way of further comparison, it was apparent that if costs alone were examined, a very similar final list would be generated. A major difference in that case would be that the chemical regeneration alternative would end up on top.

Based upon the findings of the literature and industry search, it was recommended that on-site chemical regeneration methods be further investigated in a step-wise manner beginning with laboratory minicolumn studies, followed by pilot-scale trials and finally full-scale trials assuming continued favorable results at each stage. The additional research efforts were recommended to focus on the following areas (Hamura, Sagayaga and Babcock, 1998):
- At the bench-scale: a) focus on determining that near-perfect desorption efficiency can be equated to very high regeneration efficiency when using combinations of organic and inorganic chemical solvents, b) determine the number of regeneration/reloading cycles which are feasible, c) develop methods to recycle solvents and use the least possible amount of fresh organic solvents
- At the pilot-scale: a) verify regeneration efficiencies with realistic scaleable volumes of solvent, b) verify the number of feasible regeneration/reloading cycles, c) refine cost estimates based on findings of (a) and (b)
- At the full-scale trials, the actual feasibility can be determined and this can be followed by generation of the most accurate cost estimates for full system-wide implementation.

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

2.4.1 Description of method

The RSSCT is a method developed by Crittenden and co-workers to rapidly simulate adsorption of a full-scale or pilot-scale column. 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 design of a RSSCT to simulate a full-scale column process can be obtained 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 treated (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.
2.4.2 Important design criteria

The success of the RSSCT depends on the scaling equations used to determine the dimensions and operating parameters for the mini-column. The set of equations established by Crittenden et. al. is 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 3 shows the properties of both cases.

Table 3 - Design criteria for the RSSCT based on surface diffusivity

<table>
<thead>
<tr>
<th>Surface Diffusivity Identical in Full-Scale and Small-Scale Columns</th>
<th>Surface Diffusivity Proportional to Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio of EBCTs equal to Square of Ratio of particle size</td>
<td>Ratio of EBCTs equal to Ratio of particle size</td>
</tr>
<tr>
<td>Peclet and Stanton Numbers equal</td>
<td>Peclet and Stanton Numbers Higher for Small Column</td>
</tr>
<tr>
<td>Minimum Reynolds Number = 1, but can be less if head loss and column length unacceptable</td>
<td>Minimum Reynolds Number = 1, but can be less if head loss and column length unacceptable</td>
</tr>
<tr>
<td>Bed void fractions, particle densities, influent concentrations equal</td>
<td>Bed void fractions and particle densities not required to be equal</td>
</tr>
<tr>
<td>Minimum column diameter to particle-size ratio ≤ 50 to avoid channeling</td>
<td>Minimum column diameter to particle-size ratio ≤ 50 to avoid channeling</td>
</tr>
</tbody>
</table>
2.4.3 Previous studies

In the original study performed by Crittenden et al. (1986), the RSSCT was applied to removal of TCE with background NOM 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 NOM 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 (\( v_i \)) = 3.96 m/h, flow rate = 6.27 cm³/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 4 - RSSCT Design Parameters from Crittenden, et al. (1986) 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 cm³/min                 | Flow rate = 31.5 cm³/min                 |
| \( v_i \) = 19.1 m/h                     | \( v_i \) = 22.4 m/h                     |
Another series of tests conducted by Crittenden, et al. (1991) involved predicting the removal of twelve different SOCs using the RSSCT and then comparing breakthrough curves with those 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 NOM concentration (0.2 mg/L) and high SOC concentration (> 1 mg/L), 2) adsorbable background NOM with high SOC concentration, and 3) adsorbable background NOM 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.
3 Materials and Methods

3.1 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. 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 few grams of sodium sulfate was added (this removes any remaining water). The centrifuge tube was then shaken.

3.2 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 mix and redistribute the carbon.

2. After 30 minutes, the tubes were removed from the bath and placed into a 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.
3.3 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 operating parameters for this GC: electron capture detector 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% CH₄), 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 II 3395. 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 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 with temperature = 325°C, injection port temperature = 210°C, oven temperature = 125°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, the rinsing solvent was methanol since standards were prepared in methanol. For samples, the rinsing solvent was hexane since samples were extracted into hexane.
5. For both GCs, the integrators calculate peak areas at the end of each run. These areas were then used to determine the concentration of pesticide in the sample based upon external standard curves.

### 3.4 Small-Scale Column Design Criteria

Assuming proportional diffusivity, a mini-column was sized and the following dimensions determined.

**Table 5 - Comparison of Design Criteria for Mini-Column and Full-Scale BWS Columns**

<table>
<thead>
<tr>
<th>Design Parameters</th>
<th>Full-scale Column</th>
<th>Mini-column</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Bed Depth</td>
<td>2.1 m</td>
<td>110 mm</td>
</tr>
<tr>
<td>Column Diameter</td>
<td>3.66 m</td>
<td>4.6 mm</td>
</tr>
<tr>
<td>Carbon characteristics</td>
<td>No. 12 x No. 40</td>
<td>No. 80 x No. 100 mesh,</td>
</tr>
<tr>
<td>Hydraulic Loading Rate</td>
<td>314.8 m/d</td>
<td>60.2 mm/min</td>
</tr>
<tr>
<td>EBCT</td>
<td>576.5 sec</td>
<td>111.2 sec</td>
</tr>
<tr>
<td>Flow rate</td>
<td>3312 m³/day</td>
<td>1 cm³/min</td>
</tr>
<tr>
<td>Reynolds Number, Stanton Number,</td>
<td>7.9 x 10⁻³, 4900</td>
<td>0.42, 1.38 x 10⁻⁴, 16000</td>
</tr>
<tr>
<td>Peclet Number</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 cm³/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 for the present work (parameters in Table 5). The
characteristics of the columns used by Dugan (1995), by GMP Associates in the original study (1984), and the present study are shown side-by-side in Table 6.

Table 6 – Mini-Column Design Comparison

<table>
<thead>
<tr>
<th>Column Parameter</th>
<th>Dugan et. al. Column</th>
<th>GMP column</th>
<th>Re-scaled column</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column inner diameter (mm)</td>
<td>2.3</td>
<td>2.1</td>
<td>4.6</td>
</tr>
<tr>
<td>Carbon bed depth (mm)</td>
<td>18</td>
<td>24.5</td>
<td>110</td>
</tr>
<tr>
<td>Carbon size (mesh)</td>
<td>200 x 325</td>
<td>230 x 325</td>
<td>80 x 100</td>
</tr>
<tr>
<td>Flow rate (mL/min)</td>
<td>1.0</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>EBCT (sec)</td>
<td>3.8</td>
<td>3.4</td>
<td>111.2</td>
</tr>
</tbody>
</table>

3.5 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 ¼ of the blender depth). 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 and settling procedure. 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. 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 (containing non-settleable fines) was then discarded carefully so as not to lose any settled 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.

3. 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 repeated 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).

4. 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 labeled and stored in a desiccator until the small-scale columns were prepared.

3.6 Small-Scale Column Preparation

1. Figure 1 (Appendix) shows a schematic diagram of the column set-up and Figure 2 shows a photograph of one actual column.

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

3. 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 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 utilized so as not to scratch the carbon causing flow bypass.

4. After adding glass wool to the bottom of the column, glass beads (No. 11) were carefully poured into the top opening to produce a layer about ½ inch deep. 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 ½ inch depth of wool 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.

5. Once all carbon had been added and packed neatly, a top layer of glass wool (about 1 inch) was added. This was packed down gently.

6. After the column was prepared, it was then set up with the pump and influent/effluent lines as shown in Figures 3 and 4. 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.

3.7 Small-Scale Column Rinsing and 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.

3.8 Short-Term Experiments With Spent Carbon

1. A set of experiments was 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 3. 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 \( \frac{1}{4} \) - \( \frac{1}{2} \) 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 adsorbed pesticides.

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 7 was developed to see which 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 residual adsorbed pesticide concentrations.

Table 7 - Desorbent Aid Matrix for Short-term Loading/Regeneration Experiments

<table>
<thead>
<tr>
<th>EXP.</th>
<th>Solvents Used</th>
<th>Acids Used</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetone</td>
<td>2-propanol</td>
</tr>
<tr>
<td>1a</td>
<td>X</td>
<td>x</td>
</tr>
<tr>
<td>1b</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>3c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>4c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5a</td>
<td>X</td>
<td>x</td>
</tr>
<tr>
<td>5b</td>
<td>X</td>
<td>x</td>
</tr>
<tr>
<td>6a</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>6b</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>7a</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>7b</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>8a</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>8b</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

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**
3.9 Small-Scale Column Operation During Long-Term Experiments

1. After the influent and effluent lines were cleaned and rinsed 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 for 24 hours to wet the carbon and also ensure that the set up was correct and free of leaks.

2. Long-term loading experiments were conducted with either actual contaminated well water from Mililani or spiked deionized water. To determine the effect of NOM on adsorption of pesticides, deionized water spiked with pesticides (spike concentrations were approximately matched to concentrations found in the natural well water) was treated in one column and a separate column treated the natural water side-by-side. Each day of operation, all effluent was collected to determine the amount of water treated. Effluent and influent samples were also collected daily and subjected to microextraction and GC analyses to determine pesticide concentrations. Natural well water samples were also set aside each day for total organic carbon (TOC) analyses to determine removal. TOC samples were stored in small glass tubes (minimum volume = 10 mL) with a couple drops of H$_2$SO$_4$ added.

3. Long-term loading/regeneration experiments were conducted using actual contaminated well water from Mililani. These columns were operated and effluent samples collected daily until breakthrough of both DBCP and TCP were observed. Then pump operation ceased and the columns were chemically regenerated as described below. Following regeneration, the columns were again operated (treating actual contaminated water from Mililani) and effluent samples collected until breakthrough of both pesticides. This second loading cycle was compared to the first loading cycle (in terms of bedvolumes of water treated, mass of each pesticide adsorbed per unit mass of carbon, and mass of NOM adsorbed) to determine regeneration efficiency. This process was repeated for multiple loading/regeneration cycles to determine the feasibility of long-term chemical regeneration.
3.10 Chemical Regeneration Procedures

Two RSSCTs were operated side-by-side and regenerated 6 or 7 times each. Different regeneration protocols were utilized for each column. The protocols were modified after the 5th regeneration. For the 1st through 5th regenerations of Column 1, HCl and acetone were utilized. For the 6th and 7th regenerations of Column 1, HCl, NaOH and acetone were utilized. For the 1st through 5th regenerations of Column 2, NaOH and acetone were utilized. For the 6th regeneration of Column 2, HCl, NaOH and acetone were utilized. Additional details of the protocol are intellectual property and available to BWS upon request and agreement to be kept confidential.

3.11 Pilot-Scale Column Set-Up and Operation

Four pilot-scale columns were constructed from 2-inch inside diameter stainless steel. The columns have a total length of 14 feet with stainless steel flanges welded to each end. Stainless steel caps were also constructed for each end. At the bottom end of each column, a 1-inch thick piece of Plexiglas was fabricated in which a stainless steel wire mesh could be inserted to retain the GAC. These four columns were installed at a Mililani GAC treatment facility on the full-scale contactor support structure (Figures 5-10 show photographs of the set-up). Brass piping was installed to deliver the contaminated water to the top of the pilot columns. Plastic and stainless steel rotameters were installed for flow control. Three of the columns were filled to a depth of 10 feet with virgin GAC available at the site (12x40 mesh), and the fourth column was filled to a depth of 11 feet. Photographs of the pilot-scale columns are included in the appendix. These columns were set up to treat a flow which would give the same empty bed contact time as the full-scale contactors (12 minutes). This equates to a flow of 500 mL/min. This after 4 to 5 months, the flow to two of the columns was doubled to 1,000 mL/min in an attempt to shorten the time to breakthrough and allow pilot-scale chemical regeneration trials.
4 Results and Discussion

4.1 Early Results From This Group

4.1.1 Batch Adsorption/Desorption and Preliminary Mini-Column Studies

Initial work was conducted by a graduate student (Walton-Green, 1997) in 1996 on development and refinement of analytical chemistry methods to quantify DBCP, EDB, and TCP in water (micro-extraction) and on GAC (ultrasonic solvent extraction). This work included batch desorption of BWS's virgin GAC which had been spiked with three pesticides (DBCP, EDB, and TCP). The virgin GAC was contacted with a solution containing the pesticides for a period of time such that approximately the same adsorbed concentration resulted as that found on samples of actual spent GAC from BWS. Batch desorption utilized acetone, methanol, ethanol, propanol, formic acid, acetic acid and heated water separately in Erlenmeyer flasks. In the batch tests, EDB was 100% desorbed by all the solvents. Also, DBCP was 100% adsorbed by all solvents except formic acid (which desorbed 84%). For TCP, the solvents desorbed 32% (acetone), 22% (ethanol), 49% (methanol), 68% (2-propanol), 99.2% (formic acid), and 99.4% (acetic acid). These experiments did not consider the effects of NOM on sorption/desorption.

This work also included preliminary mini-column sorption/desorption experiments with virgin GAC and distilled water spiked with EDB, DBCP, and TCP. Desorption was attempted with a solution of 50% methanol and 50% distilled water and low efficiency was observed (16 to 26% pesticide removal). Again, these experiments did not consider the effects of NOM on sorption/desorption.

4.1.2 Batch TCP, EDB, and DBCP Biodegradation Experiments

Initial work was conducted by a graduate student (Mitch Uehara) in 1996-97 on bench-scale batch biodegradation DBCP, EDB, and TCP. Aerobic, anaerobic, and anoxic cultures were grown and utilized in bioassays. The findings on biodegradability were inconclusive (Babcock, Ewald and Uehara, 1998).
4.2 Short-Term Spent Carbon Desorption Experiments

As stated in Section 3.8, a short-term matrix was developed (Table 7) to evaluate the ability of several acid/base combinations to desorb TCP, EDB, and TCP from spent BWS carbon. Experiments were conducted in roughly 2 weeks time. The selection 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 individually at 100% strength. These include 2-propanol, acetic acid, and formic acid. Also, previously-published work (see for example the extensive literature in Hamura, Sagayaga and Babcock, 1998) served as the basis for the matrix. Also, the matrix incorporates solvents that remove sorbates by different mechanisms. The pesticides, which are organic substances will dissolve into the organic solvents. Similarly, the two carboxylic acids, formic and acetic also form solutions with the pesticides. In contrast, the inorganic desorbents, HCl and NaOH remove sorbates by ionizing in solution and either altering the surface charge causing pesticides to desorb or forming a water-soluble product with the pesticide which is readily flushed from the column. It was important to utilize desorbents whose molecular weight was less than that of the pesticides. This is important so that the desorbents can penetrate the pores behind the sorbates and displace them easily. All the desorbents in Table 7 possess this characteristic as shown in Table 8.

Table 8 – Molecular weights of desorbents and pesticides

<table>
<thead>
<tr>
<th>Pesticide/Desorbent</th>
<th>Molecular Weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBCP</td>
<td>234.45</td>
</tr>
<tr>
<td>EDB</td>
<td>187.88</td>
</tr>
<tr>
<td>TCP</td>
<td>147.44</td>
</tr>
<tr>
<td>Formic acid</td>
<td>46.03</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>60.05</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>60.10</td>
</tr>
<tr>
<td>Acetone</td>
<td>58.08</td>
</tr>
<tr>
<td>HCl</td>
<td>36.45</td>
</tr>
<tr>
<td>NaOH</td>
<td>39.98</td>
</tr>
</tbody>
</table>
It was also 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, formaldehyde, and ethanol (all of which are suitable solvents for the three pesticides). Benzene and formaldehyde are highly toxic carcinogens and ethanol purchase and use is highly restricted. Acetone was included because all three pesticides are soluble in it and it is readily available. However, the remaining desorbents are not without their own restrictions. The acids and bases can cause skin irritations and respiratory problems and acetone can cause respiratory problems under prolonged exposure. Sulfuric acid was not included because others (Gomez-Serrano, et. al., 1996) found that H2SO4 caused a large reduction in pore surface area and adversely affected pore size distribution.

Several tables are presented below listing the pesticide removal percentages for the acids/bases in combination with deionized water. Removal percentage is calculated as the \((\text{amount adsorbed - amount remaining on the carbon})/\text{amount adsorbed}\). It is important to note that this differs from regeneration efficiency because the carbon was not reloaded. Reloading experiments were conducted later as a result of the preliminary findings here. Also, it should be noted that we did not measure desorption of NOM in these experiments. For these desorption experiments in mini-columns, we developed different sequences (acid-solvent-acid-solvent and solvent-acid-solvent), and standardized strengths of desorbents (100% for solvents, 60% (of concentrated) for acids, and 3M for NaOH).

Table 9 shows the first series of data using only an acid or a base in conjunction with deionized water. A total of 10 bedvolumes of acid or base and deionized water were passed through the column. Each acid was at either 100% or 60% of the concentrated form and the NaOH was at 3M concentration. Removal efficiency was determined as \([\text{Ao} - \text{Ar}]/\text{Ao}\)*100%, where Ao is the amount of pesticide onto the carbon before desorption in \(\mu g/g\) and Ar is the amount remaining following desorption in \(\mu g/g\). These are referred to as removal efficiencies because they represent the amount of pesticide removed. Adsorbed pesticide concentrations were determined by ultrasonic extraction and GC. Regeneration efficiency, which is a measure of the carbons restored capacity, was not measured in this portion of the project. Table 9 shows...
that all of the desorbents worked fairly well with the exception of NaOH heated to 40°C. It is not clear why this is so. These results were encouraging, because significant desorption was affected. However, they were also disappointing since no single desorbent was able to remove 100% of all three pesticides.

Table 9 - Removal efficiencies for the sequence acid/base + deionized water (AW)

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Formic Acid (54%)</th>
<th>Acetic Acid (60%)</th>
<th>Hydrochloric Acid (22.2%)</th>
<th>Sodium Hydroxide (3M)</th>
<th>Sodium Hydroxide (3M 40°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDB</td>
<td>99%</td>
<td>81%</td>
<td>74%</td>
<td>30%</td>
<td>3%</td>
</tr>
<tr>
<td>TCP</td>
<td>98%</td>
<td>71%</td>
<td>53%</td>
<td>37%</td>
<td>0%</td>
</tr>
<tr>
<td>DBCP</td>
<td>14%</td>
<td>48%</td>
<td>76%</td>
<td>45%</td>
<td>0%</td>
</tr>
</tbody>
</table>

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

The next series of tables show the results obtained while using alternating cycles of an organic solvent (either acetone or propanol) and either an acid or base. The tables will show two regeneration sequences; solvent/acid/solvent (SAS) and acid/solvent/acid/solvent (ASAS). All solvents were used at 100% strength and 52 bedvolumes were used in the first cycle while 36 bedvolumes were used in the second cycle. The amounts of solvent were chosen arbitrarily. Each 35 mL of solvent that was pumped through the column was analyzed by GC to determine the amount of desorbed pesticides. The determined concentrations were summed and compared to the amount on the GAC prior to the start to determine removal efficiencies. The amount removed by the acid or base was determined by subtraction of the total amount removed by the solvent from the total amount desorbed. The total amount desorbed was determined by ultrasonic extraction of the GAC before and after desorption cycles.
### Table 10 – Removal efficiencies for all experiments with formic acid

<table>
<thead>
<tr>
<th>Formic acid/acetone (SAS)</th>
<th>Formic acid/acetone (ASAS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cycle 1</td>
</tr>
<tr>
<td>EDB</td>
<td>0.95</td>
</tr>
<tr>
<td>TCP</td>
<td>4.92</td>
</tr>
<tr>
<td>DBCP</td>
<td>9.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formic acid/2-propanol (SAS)</th>
<th>Formic acid/2-propanol (ASAS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cycle 1</td>
</tr>
<tr>
<td>EDB</td>
<td>25.5</td>
</tr>
<tr>
<td>TCP</td>
<td>30</td>
</tr>
<tr>
<td>DBCP</td>
<td>37.7</td>
</tr>
</tbody>
</table>

*Cycle 1/Cycle 2 refers to first and second solvent cycles*

### Table 11 – Removal efficiencies for all experiments with acetic acid

<table>
<thead>
<tr>
<th>Acetic acid/acetone (SAS)</th>
<th>Acetic acid/acetone (ASAS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cycle 1</td>
</tr>
<tr>
<td>EDB</td>
<td>99.8</td>
</tr>
<tr>
<td>TCP</td>
<td>100</td>
</tr>
<tr>
<td>DBCP</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Acetic acid/2-propanol (SAS)</th>
<th>Acetic acid/2-propanol (ASAS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cycle 1</td>
</tr>
<tr>
<td>EDB</td>
<td>97.2</td>
</tr>
<tr>
<td>TCP</td>
<td>97.2</td>
</tr>
<tr>
<td>DBCP</td>
<td>99.9</td>
</tr>
</tbody>
</table>

*Cycle 1/Cycle 2 refers to first and second solvent cycles*
### Table 12 – Removal efficiencies for all experiments with hydrochloric acid

<table>
<thead>
<tr>
<th></th>
<th>Hydrochloric acid/acetone (SAS)</th>
<th>Hydrochloric acid/acetone (ASAS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cycle 1 (%)</td>
<td>Cycle 2 (%)</td>
</tr>
<tr>
<td>EDB</td>
<td>99.4</td>
<td>0.01</td>
</tr>
<tr>
<td>TCP</td>
<td>97.8</td>
<td>0</td>
</tr>
<tr>
<td>DBCP</td>
<td>88</td>
<td>12</td>
</tr>
</tbody>
</table>

Cycle 1/Cycle 2 refers to first and second solvent cycles

### Table 13 – Removal efficiencies for all experiments with sodium hydroxide

<table>
<thead>
<tr>
<th></th>
<th>Sodium hydroxide/acetone (SAS)</th>
<th>Sodium hydroxide/acetone (ASAS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cycle 1 (%)</td>
<td>Cycle 2 (%)</td>
</tr>
<tr>
<td>EDB</td>
<td>97.3</td>
<td>2.7</td>
</tr>
<tr>
<td>TCP</td>
<td>97.2</td>
<td>0.82</td>
</tr>
<tr>
<td>DBCP</td>
<td>99.9</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Cycle 1/Cycle 2 refers to first and second solvent cycles

Tables 10-13 present a lot of data which indicates the following:

- Virtually all acid/base + solvent combinations and sequence orders resulted in nearly 100% removal efficiencies
- It seems that formic acid removes most of the pesticides when it is used in any combinations, and that the second solvent cycle could be eliminated
- The formic acid data is not consistent with the other data
- For acetic acid, HCl, and NaOH, the first solvent cycle removes most of the pesticides
- When an acid or base is used prior to the solvent, it tends to reduce pesticide removal during the first solvent cycle.
Given the removal efficiencies observed for the various solvent combinations observed in Tables 10-13, it was decided to determine if the same efficiencies could be obtained when using lower strengths of the organic solvent in order to save on operating costs. A last desorption experiment was conducted using 3M NaOH and a 1% solution of acetone in the ASAS sequence. In addition, for this experiment, only a small volume (5 bedvolumes) of the base and solvent were recycled through the mini-column in a closed-loop for one hour at a time. And the same NaOH and acetone solutions were used in the first and second cycles. The total removal efficiencies (in acetone and NaOH) are shown in Table 14.

Table 14 – Removal efficiencies using 3M NaOH and 1% acetone in a closed-loop desorption experiment

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Removal Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDB</td>
<td>32.6</td>
</tr>
<tr>
<td>TCP</td>
<td>0</td>
</tr>
<tr>
<td>DBCP</td>
<td>92.1</td>
</tr>
</tbody>
</table>

The data in Table 14 shows that only DBCP is effectively removed. The main difference between this experiment and previous ones is the reduced strength of acetone. In agreement with data in Tables 9 and 13, the 3M NaOH does not effectively remove these pesticides on its own and the reduced strength of acetone is responsible for the low overall removal efficiencies. Based upon this finding, long-term regeneration experiments only utilized organic solvents at 100% strength.

Desorption of NOM was not quantified in this portion of the study. In all of these experiments, it was unknown how much, if any, of the NOM was desorbed and hence the possible regeneration efficiency for the actual spent GAC at Mililani (calculated from the amount of pesticides that could be adsorbed during reloading of regenerated carbon) was still unknown. This led us to long-term RSSCT studies in which the GAC would be loaded, regenerated, loaded again, regenerated again, etc.
4.3 Side-by-Side NOM Competition Studies

For this portion of the project we utilized new, correctly-scaled mini-columns to simulate BWS contactors in RSSCTs. Two columns were operated side-by-side to determine the extent to which natural organic matter (NOM) inhibits the adsorption of DBCP and TCP in Mililani well water. One column was set up to treat natural well water from Mililani while the other was set up to treat deionized water spiked with approximately the same concentrations of DBCP and TCP measured in the natural well water. It was anticipated that the well water column would break through first indicating that the two pesticides are indeed competing with NOM.

Figures 11 and 12 display the breakthrough curves for the Mililani well water. Breakthrough of TCP and DBCP occurred after 14,500 and 16,500 bedvolumes of water had been treated, respectively. In contrast, the column with spiked deionized water broke through after 17,500 and 18,000 bedvolumes had passed (Figures 13 and 14) for TCP and DBCP, respectively. The fact that TCP broke through first is a good sign since this also occurs in the full-scale column. Figure 15 shows the cumulative adsorbed mass of the pesticides during the side-by-side experiment. Figure 15 clearly indicates that the NOM competes with the pesticides and reduces the adsorption capacity. The capacity for TCP adsorption is reduced by 49% (from 193 to 97 μg/g) and the capacity for DBCP adsorption is reduced by 30% (from 3.9 to 2.7 μg/g).

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 during the early part of this test and reliable data could not be obtained; however, one portion of the TOC samples was analyzed correctly (see Figure 16). The data indicate that effluent concentrations were generally but not always lower than influent concentrations (influent concentrations vary in the range 0.1 - 0.9 ppm). This result, shows that NOM is being removed; however, some data points show that effluent concentrations exceeded the influent concentration. Discrepancies like these may be attributed to the headspace in the effluent and influent bottles. Gases may be dissolving into the water causing unusually high TOC readings. 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. Figure 16 indicates that overall, at least 2,862 μg of NOM adsorbed onto the GAC. This is equivalent to 2,920 μg/g and is about 30 times greater than the mass of TCP adsorbed indicating effective competition. These results indicate that the key to effective chemical regeneration of the spent GAC is the effective removal of the NOM. If the NOM is not removed, then regeneration will not be successfully accomplished.

4.4 Long-Term Regeneration Studies

Preliminary long-term regeneration studies were conducted in correctly-scaled RSSCTs with spiked (EDB, DBCP, TCP) deionized water and regeneration with 50%, 70%, and 100% acetone. With 50 and 70% acetone, less than 10% of the adsorbed pesticides were desorbed. With 100% acetone, the column was regenerated and reloaded twice and it was found that 45% and then 30% of the adsorption capacity was restored. Further reloadings were not conducted. In these preliminary regeneration experiments with spiked deionized water, it was unknown how much, if any, of the NOM was desorbed and hence the possible regeneration efficiency for the actual spent GAC at Mililani was unknown. Therefore long-term loading/regeneration studies were initiated with natural well water from Mililani.

Cyclic long-term loading-regeneration-loading experiments have been conducted using actual contaminated well water from Mililani beginning since June, 1998. The configuration of the RSSCT columns is as described above in Section 3.4 (80 x 100 mesh size, 110mm bed depth and 1.0 mL/min flow rate). Column 1 has a carbon mass of 0.9167 g and Column 2 contains 0.9173 g of carbon. Influent and effluent samples are collected daily from these columns until breakthrough of both DBCP and TCP is observed. Then pump operation is ceased and the columns are chemically regenerated as described above in Section 3.10 (note that different regeneration protocols are utilized for Columns 1 and 2). Following regeneration, the columns are again operated under the same conditions until breakthrough of both pesticides. This second loading cycle was compared to the first loading cycle (in terms of bedvolumes of water treated,
mass of each pesticide adsorbed per unit mass of carbon, and mass of NOM adsorbed) to determine regeneration efficiency. This process was repeated for 7 cycles of loading plus regeneration to determine the feasibility of long-term chemical regeneration.

Figures 17 through 30 show the breakthrough curves for each of the seven loading cycles. All of these figures look similar and indicate that the effluent concentration of TCP and DBCP are not detectable until breakthrough occurs. When the regeneration protocols were modified after the 5th loading (to include both an acid and a base), the bedvolumes treated increased quite dramatically. Figure 31 shows the cumulative mass of pesticides adsorbed during the seven loading cycles. This figure also indicates that an increased amount of pesticides were adsorbed after the new regeneration protocols were instated and that after 7 loadings, the cumulative mass of pesticides adsorbed is approximately 6 times the mass adsorbed during the initial loading of virgin carbon. Figure 32 shows a summary of the bedvolumes treated in each of the six loading cycles. It should be noted that these columns are still in operation and it is unclear when, if ever, that the chemical regeneration method will cease to be effective (and the carbon will need to be replaced).

These data indicate two things. First, that chemical regeneration at the bench-scale is very effective and seems to completely restore the adsorptive capacity of the GAC. Second, that the chemical regeneration process may allow GAC to be used and reused indefinitely (no end to the number of cycles is evident). These results need to be verified at the pilot-scale where practical operational problems and costs of the process can be more accurately assessed.

4.5 Pilot-Scale Experiments

The pilot columns were brought on-line April 8, 1999 each at a flow rate of 500 mL/min (this gives an EBCT of 12 minutes just like the full-scale contactors). On July 7, 1999 the flow to column No. 3 was increased to 1,000 mL/min. And on August 3, 1999 the flow to column No. 2 was also increased to 1,000 mL/min. These flow increases were instated in an attempt to reduce the time to breakthrough. An influent sample and effluent samples from each column
have been collected weekly and analyzed for EDB, DBCP and TCP by GC and for NOM by NPOC. Breakthrough of these four columns has not yet occurred. Table 15 shows the bedvolumes treated, the DBCP adsorbed, and the TCP adsorbed through December 2, 1999.

Table 15 – Pilot column adsorption data between April 8 and December 2, 1999.

<table>
<thead>
<tr>
<th>Column</th>
<th>Bedvolumes Treated (#)</th>
<th>DBCP Adsorbed (μg/g)</th>
<th>TCP Adsorbed (μg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27,744</td>
<td>4.01</td>
<td>234.9</td>
</tr>
<tr>
<td>2</td>
<td>41,616</td>
<td>6.01</td>
<td>352.4</td>
</tr>
<tr>
<td>3</td>
<td>45,679</td>
<td>6.72</td>
<td>384.8</td>
</tr>
<tr>
<td>4</td>
<td>27,744</td>
<td>3.64</td>
<td>213.6</td>
</tr>
</tbody>
</table>

After the pilot columns breakthrough they will be regenerated using the same protocols devised for the RSSCTs in the long-term regeneration studies.

4.6 Preliminary Desorption Fluids Treatment and Disposal Studies

The desorption fluids that are utilized during chemical regeneration activities will need to be disposed of following treatment. It is anticipated that a regeneration protocol which includes both an acid, a base, and a solvent will be utilized. It is assumed that the acid and base fractions will contain primarily desorbed NOM and a small amount of pesticides. It is likely that the least expensive and least complicated treatment and disposal option will include neutralization of the acid and base fractions, followed by dilution with post rinse water and then disposal into the sanitary sewer. It is anticipated that it will be feasible to distill the solvent for reuse and the retentate will either be disposed as a hazardous waste concentrate or ozonated to break it down and render it readily biodegradable for disposal into the sanitary sewer.

We have conducted preliminary studies investigating neutralization of the acid and base fractions obtained from the 6th regeneration of Column 1 (from the long-term RSSCT regeneration study). When these fractions were combined and neutralized, the mixture took on a yellow tint. If the mixture was allowed to stand, a fluffy brown precipitate formed and settled.
out. It is assumed that this was concentrated NOM. When we extracted the neutralized fluids and analyzed it by GC, we found 250 ppb of TCP and 5.3 ppb of DBCP. We also distilled the solvent fraction from the same regeneration and found that the distillate contained only traces of pesticides (such that it could be reused) and that the yellow-green retentate contained a great deal of water and highly concentrated pesticides. The reason that there was a lot of water in the retentate is because the solvent fraction was not collected carefully and the retained water from the previous rinse cycle was included in it. Preliminary experiments in which the retentate was ozonated found that the pesticides disappeared slowly. The degradation rate is a function of the temperature, the ozone dose, and other factors which need to be systematically investigated to determine feasibility and cost effectiveness.

### 4.7 Health Effects Study

A study was conducted to determine the potential public health effects of chemical regeneration of spent GAC (Fukuda, Babcock and Menon, 1999). The study examined the pertinent environmental regulations, the potential exposure pathways, the properties of all the chemical regenerants utilized in this research, preventative measures, and mitigative measures. The study looked at risks to regeneration process workers, risks to treatment facility neighbors, and risks to the general public who would consume water treated by the regenerated GAC. One aim of the study was to determine allowable concentrations of the various regeneration chemicals in drinking water (most do not have maximum concentration limits, MCLs). This information can be used to determine when sufficient rinsing of the regenerated GAC has occurred and it is safe to distribute the water. The study recommended maximum concentrations of the chemicals in drinking water based upon MCLs, recommended MCLs (these are health-based limits for chemicals which are of a national priority), and local health advisories. The State DOH can issue health advisories (safe water concentrations) for any chemical that has a known value of “no observed adverse effects level” (NOAEL). The safe water concentration is calculated as the safe human dose divided by 2 L/day. The safe human dose is calculated as the NOAEL times the average body weight (70 kg) divided by a safety factor. The safe water concentration (or local health advisory) as just described is the same thing as a preliminary remediation goal (PRG) for
water ingestion. PRGs for water ingestion are available on the EPA Region 9 web page (EPA, 1999). Table 16 shows the recommended values for drinking water from the EPA web page.

Monitoring of residual content is necessary to ensure that the concentrations of the chemicals at acceptable and safe level for distribution. Before distributing the treated water, the concentrations of the chemicals should be less than the recommended concentrations in Table 16. The study found that there would be few, if any, public health risks of conducting chemical regeneration at the wellhead sites near homes, store and schools. The chemicals all biodegrade rapidly in the air, soil, and water. It will be necessary to follow all occupational safety and health standards to prevent any unnecessary exposure to the chemical regeneration process workers and the public. Additional details of the health effects study can be found in the report by Fukuda, Babcock and Menon (1998).

Table 16 – Recommended drinking water concentration limits

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Recommended limit (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>700 (EPA existing MCL)</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>1.28 x 10⁻⁶ (EPA recommended MCL)</td>
</tr>
<tr>
<td>Formic acid</td>
<td>7.3 x 10⁴</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.8 x 10⁴</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.75 x 10⁶*</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>1.75 x 10⁶</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>pH 6.5 – 8.5**</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>pH 6.5 – 8.5**</td>
</tr>
</tbody>
</table>

* These chemicals does not have PRGs. Dr. L. Au (1999) at the Hawaii Department of Health assisted us. Given a dose with least effects known (1 g/kg body weight), we calculated the given value for ethanol. For 2-propanol, Dr. Au recommended using the PRG of a similar chemical. Therefore the recommended limit for ethanol was used for 2-propanol.
** Hydrochloric acid and sodium hydroxide dissociate in water, thus changing the acidity of the water. The pH values are secondary MCLs for drinking water.

We do not yet know what concentrations, if any, will be detected in the rinse water from the freshly regenerated GAC. It is unclear what volume of rinsing will be required. These questions cannot be answered in the bench scale experiments due to the small volumes involved. However, the pilot-scale column study should offer insight into this unresolved issue.
4.8 Full-Scale Chemical Regeneration Preliminary Process Design Considerations

Initial efforts to determine the potential design for the chemical regeneration treatment system were completed during the literature search and included in the Hamura, Sagayaga and Babcock (1998). In that work, a system was conceived and described and then evaluated for compatibility with BWS operations, degree of development, practicality, ease of use, environmental issues, regulatory permits, public acceptability, and economics. The conceptual design included a trailer-mounted system that could be driven to any of the BWS treatment facilities for use. That work also considered in situ regeneration which may be feasible. However, current thinking has evolved to favor ex situ regeneration on a trailer-mounted system of tanks, pumps, and piping (see Figure 33). The reason for this is two-fold. First, the current practice involves inspection and repair of the contactor lining whenever spent GAC is removed from the contactors. It is desirable to allow this process to continue rather than leaving the GAC in the same vessel for many years without removal for inspection as would be possible with in situ regeneration. Second, an ex situ regeneration tank could be constructed out of chemically inert materials and considering chemical regeneration requirements. Thus the ex-situ regeneration tank would have a smaller headspace than the full-scale contactors and would be designed to allow the pressurized pumping of concentrated acid, base, and organic solvents.

The general design concept is described as follows:

1) Ex-situ chemical regeneration is selected because it is easy to control and to make sure that no corrosion occurs in the GAC contactor system.

2) The BWS backwash tank at each treatment facility is used to receive rinse water.

3) The steps of regeneration are conducted serially as follows: acid, rinse, base, rinse, solvent, rinse, acid, rinse, base, rinse, solvent, and final rinse.

   Where as, 90 minutes for acid, base, or solvent step
   10 minutes for rinse step
   20 minutes for final rinse step

   Therefore, total completed time = \( (90 \times 6) + (10 \times 5) + (20) \)
   = 610 minutes
4) Used acid and used base are sent to neutralization tank to adjust pH before sending to the backwash tank.

5) Used solvent is sent to a distillation unit to purify it for later reuse.

6) The condensate of distillation unit is sent to temporary hazardous waste drum before being sent to the mainland for disposal.

7) The piping system of acid tank, base tank, and neutralization tank must be made of stainless steel or material types that cannot be corroded by acid and base.

8) The quantity of acid, base and solvent must be enough to fill the regeneration tank and remain some level in the liquid (acid, base, or solvent) tanks and piping system.

9) Solvent tank, distillation unit and their piping system can be carbon steel because pH is not corrosive.

10) Solvent is added into the tank if some quantity is lost during the process. How many times acid, base, or solvent should be used depends on cost of chemical and service time of GAC system.

11) Drain lines are included for all tanks.

12) The elevation of neutralization tank must be lower than other units.

13) Flexible hoses may be used for connection during feeding clean water or filling acid, base and solvent to the system.

The general design concept dictates the following major equipment:

1) Regeneration Tank (stainless steel, 5,900 gal)

2) Temporary Tank (carbon steel, 5,900 gal)

3) Acid Tank (stainless steel, 6,200 gal)

4) Base Tank (stainless steel, 6,200 gal)

5) Solvent Tank (carbon steel, 5,000 gal)

6) Neutralization Tank (stainless steel, 6,000 gal)

7) Distillation Unit (Including Condenser)

8) Regeneration Pump (stainless steel and Teflon, 35 gpm)

9) Acid Pump (stainless steel and Teflon, 160 gpm)

10) Base Pump (stainless steel and Teflon, 160 gpm)
11) Solvent Pump (stainless steel and Teflon, 160 gpm)
12) Neutralization Pump (stainless steel and Teflon, 160 gpm)
13) Distillation Pump (stainless steel and Teflon, 35 gpm)

Capital costs are to be computed from the following list of items: Direct Costs: 1) Purchased equipment (acid tank, base tank, solvent tank, neutralization tank, acid pump, base pump, solvent pump, neutralization pump, distillation unit, distillation pump, spare parts, freight charges, taxes, insurance, duties, allowance for modification during start-up; Purchased-equipment installation (installation, structural supports, insulation, paint); Instrumentation and control (purchases, installation, calibration); Piping (process piping, pipe hangers, fittings, valves, insulation); Electrical equipment (switches, motors, conduits, wire, fittings, feeders, grounding, instrument and control wiring, panels, labor); Process trailer; and Indirect Costs: engineering and supervision, construction expenses, contingency. Operating costs will also be estimated from Direct Production Costs: 1) Raw materials (acid, base, solvent), 2) Operating labor, 3) Utilities, 4) Maintenance and Repairs, and 5) Laboratory Charges plus Fixed Charges (Depreciation and Insurance).

Figure 33 shows a conceptual schematic diagram of the ex-situ low pressure chemical regeneration system. Significant additional design and cost estimate work needs to be conducted for this GAC regeneration technique. Preliminary capital and operating cost estimates for the proposed system were made in the report by Hamura, Sagayaga and Babcock (1998). in-situ protocol. The current thinking involves an ex-situ protocol (additional tanks), neutralization facilities (additional tank and pumps), and a solvent distillation system. The earlier estimate of approximately $55,000 per year for an in-situ acid plus base plus acetone system is surely somewhat low. It is now estimated that the annual costs (including contractor costs) would be closer to $200,000. However, this is still less than 50% of the current disposal/replacement costs. There are many assumptions which go into these preliminary estimates which must be verified and updated based upon pilot-scale test results and full-scale trials.
4.9 *Patent Protection*

Based upon the results presented herein, an invention disclosure form was filed with the University of Hawaii Office of Technology Transfer and Economic Development (OTTED) in July, 1999. Patent searches have been conducted and the preliminary assessment from OTTED is that the chemical regeneration protocol is probably patentable. The next step is to determine what interest BWS has in the patent rights and then to proceed with hiring patent attorneys to file for protection. During this process, no details of the procedure can be publicly disclosed (otherwise patent rights are nullified).
5 Conclusions and Recommendations

Based upon the findings of this study, the following conclusions can be drawn:

1. From the literature and industry search into current and emerging regeneration techniques and local disposal alternatives, it can be concluded that it is worthwhile to pursue experimental research into chemical regeneration of BWS’s spent GAC through bench-scale followed by pilot-scale studies.

2. From the short-term spent carbon desorption experiments, it can be concluded that either an acid or a base in combination with an organic solvent can remove essentially 100% of the TCP, DBCP, and EDB from BWS’s spent GAC. However, this finding cannot be equated to 100% regeneration efficiency, since desorption of NOM was unknown. Also, relatively inexpensive HCl and NaOH can be effectively utilized. Finally, the strength of the organic solvent should be very high (preferably 100%) for maximum effectiveness.

3. From the side-by-side NOM competition studies, it can be concluded that NOM in Mililani well water effectively competes with TCP and DBCP for GAC adsorption sites. The adsorption capacity is reduced by 30% and 49% for DBCP and TCP, respectively. This also indicates that if the NOM is not removed, then regeneration cannot be successfully accomplished.

4. From the long term bench-scale regeneration studies, it can be concluded that the use of an organic solvent alone cannot effectively regenerate BWS’s spent GAC; that chemical regeneration using an acid or a base and an organic solvent is very effective for approximately 5 regeneration cycles for BWS’s spent GAC; that chemical regeneration using an acid and a base and an organic solvent seems to completely restore the adsorptive capacity of the GAC used by BWS which may allow the GAC to be used and reused indefinitely.
5. From the health effects study, it can be concluded that there would be few, if any, public health risks of conducting chemical regeneration at the wellhead sites near homes, stores and schools. The chemicals all biodegrade rapidly in the air, soil, and water. It will be necessary to follow all occupational safety and health standards to prevent any unnecessary exposure to the chemical regeneration process workers and the public. It remains unclear how much post chemical regeneration rinsing will be required in order to achieve the recommended MCLs for the regenerant chemicals.

6. From the preliminary process design considerations, it can be concluded that the proposed chemical regeneration system should be transportable to each BWS well-field site, should be an ex situ system where the carbon is first off-loaded to a regeneration tank, and will consist of several tanks, pumps, and a solvent distillation system. Considerable additional design work is needed.

7. Unfortunately, no conclusions can yet be drawn from the pilot-scale studies because the columns have not yet broken through on their first loading cycle.

The following recommendations are provided:

1. Additional bench-scale experiments to determine the number of regenerations that are possible using an acid and a base and an organic solvent; to determine the best order to pass the regenerant fluids through the spent GAC; to determine the most cost effective acid, base, and organic solvent to utilize; to determine cost effective and legal residuals treatment and disposal alternatives.

2. Additional work on NOM quantification methods for desorption fluids to allow development of a sorption/desorption mechanistic model which would lead to improvements in the choice of chemicals or protocols for chemical regeneration.
3. Complete the pilot-scale studies to determine: backpressures generated during regeneration (to design pumps); the amount of post rinsing needed to meet the recommended MCLs for the desorbent chemicals (from health effects study); the feasibility and cost of routine solvent distillation/recovery for reuse; the feasibility of recycling/reusing the acid, base and solvent; the amount of acid/base/solvent lost (to help determine operating costs); the feasibility of proposed treatment and disposal options for regenerant fluids. These experiments will require approximately 2 years.

4. Following successful completion of pilot-scale regeneration trials and appropriate chemical regeneration protocol modifications, conduct a full-scale trial of the optimized chemical regeneration process to determine practicality issues and obtain a firm operating cost estimate. This will require approximately an additional year.

5. Pursue patent protection for the proposed chemical regeneration method.
6 References


22. Kawata, E., Board of Water Supply, City and County of Honolulu., Personal communication. 1996.


28. 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.


http://www.epagov/region09/wastelsfundlprg


Figure 1 – Mini-column set-up and dimensions

- Pulverized activated carbon (PAC) No. 80 x No. 100 mesh
- Glass beads: Size 11
- Glass wool

Bed depth: 110 mm
Column inner diameter: 4.6 mm
Figure 2 – Schematic of mini-column system set-up
Figure 3 – Photograph of laboratory mini-column
Figure 4 – Photograph of laboratory minicolumn systems
Figure 5 – Overall view of pilot columns at Mililani
Figure 6 – Top of pilot columns with inlet hardware
Figure 7 – Bottom of pilot columns with GAC retainer ring, outlet hardware, sampling ports and effluent piping
Figure 8 – Pilot column rotameters
Figure 9 – Side view of pilot columns with rotameters, and inlet piping including pressure reducing valve
Figure 10 - Raw water tap and piping for pilot columns
Figure 11 - Breakthrough curve for TCP using Millamino Well Water
Figure 12 - Breakthrough curve for DBCP using Milliani well water.
Figure 13 - Breakthrough curve for TCP using spiked denitrified water
Effluent •
Influent • ▼
Average Influent

Figure 14 - Breakthrough curve for DBCP using spiked deionized water
Figure 15 - Cumulative adsorption of TCP and DBCP during side-by-side RSSCTs
Figure 16 - Influent and Effluent NPOC for RSSST treating Milliman Well Water

Amount in influent: 8050 ug
Amount in effluent: 5188 ug

Bedvolumes Treated

NPOC, ppm

0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

0
2000
4000
6000
8000
10000
12000
14000
16000

Influent - - - Effluent
Figure 17 – TCP breakthrough curve for first loading using Mililani well water

Figure 18 – DBCP breakthrough curve for first loading using Mililani well water
Figure 19 - TCP breakthrough curve for second loading using Mililani well water

Figure 20 - DBCP breakthrough curve for second loading using Mililani well water
Figure 21 – TCP breakthrough curve for third loading using Mililani well water

3rd Loading - Breakthrough Curve for TCP

- col 1 TCP — col 2 TCP

Figure 22 – DBCP breakthrough curve for third loading using Mililani well water

3rd Loading - Breakthrough Curve for DBCP

- col 1 DBCP — col 2 DBCP
Figure 23 - TCP breakthrough curve for fourth loading using Mililani well water

![4th Loading - Breakthrough Curve for TCP](image)

Figure 24 - DBCP breakthrough curve for fourth loading using Mililani well water

![4th Loading - Breakthrough Curve for DBCP](image)
Figure 25 - TCP breakthrough curve for fifth loading using Mililani well water

5th Loading - Breakthrough Curve for TCP

--- col 1 TCP -- col 2 TCP

Effluent Conc. of TCP (μg/L)

Bedvolumes Treated (#)

Figure 26 - DBCP breakthrough curve for fifth loading using Mililani well water

5th loading - Breakthrough Curve for DBCP

--- col 1 DBCP -- col 2 DBCP

Effluent Conc. of DBCP (μg/L)

Bedvolumes Treated (#)
Figure 27 - TCP breakthrough curve for sixth loading using Mililani well water

![6th loading - Breakthrough Curve for TCP](image)

Figure 28 - DBCP breakthrough curve for sixth loading using Mililani well water

![6th Loading - Breakthrough Curve for DBCP](image)
Figure 29 – TCP breakthrough curve for seventh loading using Mililani well water

Figure 30 – DBCP breakthrough curve for seventh loading using Mililani well water
Figure 31 – Cumulative adsorption of TCP and DBCP

Cumulative Adsorption

<table>
<thead>
<tr>
<th>DBCP - Col 1</th>
<th>DBCP - Col 2</th>
<th>TCP - Col 1</th>
<th>TCP - Col 2</th>
</tr>
</thead>
</table>

DBCP adsorbed (mg/g) vs. Loading Number (＃)

Figure 32 – Bedvolumes treated during long-term regeneration study

Bedvolumes Treated

Bedvolumes (＃) vs. Loading Number (＃)
Figure 33 – Concept schematic for ex-situ low pressure chemical regeneration system