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[12] ABSTRACT (PURPOSE, METHOD, RESULTS, CONCLUSIONS)

During 1986 and 1987, the City and County of Honolulu Board of Water Supply (BWS) placed granular activated carbon (GAC) water treatment plants in service at Mililani, Waipahu, and Kunia on the island of Oahu, Hawaii. The GAC treatment plants were designed to remove target organic chemicals DBCP, EDB, and TCP from well water in central Oahu. Original operational cost estimates for the GAC treatment plants were based on carbon requirements determined through laboratory minicolumn experiments. Actual carbon usage rates, however, have proved to be several times higher than originally estimated. This study, which represents the first phase of a two-phase study to determine the potential for extending the effective life of GAC used to remove target organic chemicals from groundwater in central Oahu, addresses the basic information necessary to understand the problem. Levels of target organic compounds in groundwater in the Pearl Harbor aquifer of central Oahu do not appear to be decreasing significantly. In fact, based on the analysis of spent GAC samples from contactors at the Waipahu treatment facility, DBCP, which was previously undetected at the Waipahu wells, now appears to be occurring at low levels of a few nanograms per liter in groundwater near Waipahu. Analyses of spent carbon samples also indicate that the adsorptive capacity of the GAC for a particular compound is directly related to the concentration of that compound in the influent water. Total organic carbon (TOC) levels in groundwater samples from the Pearl Harbor basaltic aquifer are typically a few tenths of a milligram per liter. This concentration of background organics is two to three orders of magnitude greater than TCP, which is the target organic compound typically found at the highest concentrations in groundwater in the study area. TOC and infrared analyses indicate the presence of background organic compounds in groundwater, a factor which could shorten the service life of GAC contactors. Results of this study seem to indicate that inorganic cations and anions are not significantly adsorbed by the GAC. In addition to chemical effects, bacterial growth may also play a role in the adsorption of target organic compounds. Although attached bacteria were recovered from spent GAC samples, subsequent scanning electron microscope analysis did not reveal a significant biological slime layer which may inhibit adsorption.

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EXTENDING THE EFFECTIVE LIFE OF THE GAC USED TO TREAT WELL WATER: PHASE I OF EVALUATIVE STUDY AT MILILANI

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Project Report PR-95-02

July 1994

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Principal Investigator: Gordon L. Dugan

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ABSTRACT

During 1986 and 1987, the City and County of Honolulu Board of Water Supply (BWS) placed granular activated carbon (GAC) water treatment plants in service at Mililani, Waipahu, and Kunia on the island of O'ahu, Hawai'i. The GAC treatment plants were designed to remove target organic chemicals DBCP, EDB, and TCP from well water in central O'ahu. Original operational cost estimates for the GAC treatment plants were based on carbon requirements determined through laboratory minicolumn experiments. Actual carbon usage rates, however, have proved to be several times higher than originally estimated. This study, which represents the first phase of a two-phase study to determine the potential for extending the effective life of GAC used to remove target organic chemicals from groundwater in central O'ahu, addresses the basic information necessary to understand the problem.

Levels of target organic compounds in groundwater in the Pearl Harbor aquifer of central O'ahu do not appear to be decreasing significantly. In fact, based on the analysis of spent GAC samples from contactors at the Waipahu treatment facility, DBCP, which was previously undetected at the Waipahu wells, now appears to be occurring at low levels of a few nanograms per liter in groundwater near Waipahu. Analyses of spent carbon samples also indicate that the adsorptive capacity of the GAC for a particular compound is directly related to the concentration of that compound in the influent water.

Total organic carbon (TOC) levels in groundwater samples from the Pearl Harbor basaltic aquifer are typically a few tenths of a milligram per liter. This concentration of background organics is two to three orders of magnitude greater than TCP, which is the target organic compound typically found at the highest concentrations in groundwater in the study area. TOC and infrared analyses indicate the presence of background organic compounds in groundwater, a factor which could shorten the service life of GAC contactors. Results of this study seem to indicate that inorganic cations and anions are not significantly adsorbed by the GAC.

In addition to chemical effects, bacterial growth may also play a role in the adsorption of target organic compounds. Although attached bacteria were recovered from spent GAC samples, subsequent scanning electron microscope analysis did not reveal a significant biological slime layer which may inhibit adsorption.

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INTRODUCTION

Background

In 1977, a spill of approximately 1.9 m^3 (500 gal) of 1,2-dibromoethane (EDB) within 18 m (60 ft) of the Del Monte Corporation's water-supply well at Kunia (2703-01) focused attention for the first time on the possibility of pesticide contamination of groundwater in Hawai'i. Subsequently, numerous wells located in the Pearl Harbor aquifer, O'ahu, Hawai'i, were found to be contaminated with trace amounts of organic chemicals. In 1980, the Del Monte Kunia well was closed following the discovery of both 1,2-dibromo-3-chloropropane (DBCP) and EDB in water samples. From 1982 to 1983, following detection of DBCP or EDB in well samples, nine additional potable water wells in central O'ahu were closed due to potential adverse health risks associated with long-term exposure to contaminated water. Affected well sites included Mililani Wells I (2800-02, -04) and II (2859-01), Kunia Wells II (2402-01, -02), and the Waipahu Wells (2400-01 to -04). Following the well closures, a third contaminant, 1,2,3-trichloropropane (TCP), was detected in water samples at all nine wells.

DBCP is a soil fumigant that was first used on a significant commercial basis by Dole Company in central O'ahu in 1959. Del Monte Corporation did not use DBCP on O'ahu except on an experimental basis (Hawaii Department of Agriculture 1983). DBCP use on O'ahu by Dole Company was phased out in the 1977 planting season in response to findings of the potential health risks associated with the compound.

EDB was used in a tetraethyl lead mixture added to aviation fuels (Lau 1985). EDB was also used as a fumigant to control nematodes in pineapple fields. On O'ahu, EDB was the primary soil fumigant of Del Monte Corporation since about 1948. Dole Company only began using EDB on O'ahu on a significant commercial scale in 1978 after it phased out the use of DBCP in 1977 (Hawaii Department of Agriculture 1983). In September 1983, the U.S. Environmental Protection Agency (EPA) announced its intent to cancel registrations of pesticide products containing EDB and ordered an emergency suspension of registrations of EDB for use as a soil fumigant. Under the terms of the cancellation order, the use of EDB on pineapple fields in Hawai'i would be allowed until September 1, 1984. However, use of EDB on O'ahu by pineapple growers effectively stopped by the end of 1983.

Excluding the Del Monte Kunia well, EDB contamination of groundwater on O'ahu is limited to the Waipahu area. EDB may have entered the groundwater as a result of use and handling by pineapple growers. However, the occurrence of large fuel pipeline leaks in the vicinity of the contamination makes it difficult to identify the source of EDB in groundwater at this time.

TCP is used as a paint and varnish remover, a solvent, and a degreasing agent (U.S. EPA 1980). Also, it occurred as an impurity during the manufacturing process of the Shell Chemical Company product DD, which was introduced in 1942. Shell DD became the primary soil fumigant of Dole Company in 1948 and was later used as a pre-plant nematicide in conjunction with DBCP. DD has not been used on pineapple fields on O'ahu since 1977 (*Honolulu Advertiser,* October 6, 1983).

At the time of the well closures, no state or federal drinking water standards existed for DBCP, EDB, or TCP. Consequently, the Hawaii Department of Health (DOH) set an interim limit of 20 ng/l for DBCP and EDB. The accepted detection limit for both DBCP and EDB during the period of contaminant discovery was 20 ng/l. DOH did not have an action limit for TCP based on the assumed lesser risk associated with its consumption. Currently, EPA is proposing enforceable maximum contaminant levels (MCLs) of 50 and 200 ng/l for EDB and DBCP, respectively (Federal Register, May 22, 1989, 54(97):22062–22160). DOH is proposing to set stricter MCLs of 40 ng/l for both EDB and DBCP. In addition, DOH is currently proposing a standard of 800 ng/l for TCP in its 1990 draft of Hawaii Administrative Rules, Title 11, Chapter 20. However, in light of a recent National Toxicology Program draft report on the toxicology and carcinogenesis of TCP in rats and mice (U.S. Department of Health and Human Services 1991), DOH may set a stricter MCL for TCP (*Honolulu Star-Bulletin,* 23 July 1991).

The immediate response to the well closures by the City and County of Honolulu Board of Water Supply (BWS) was to increase production at well sites less affected by contamination. In the Mililani area, however, Mililani Wells I, Pumps 1 (2800-01) and 3 (2800-03) remained open despite evidence of trace amounts of DBCP, since no other wells were available to serve the area. In addition, uncontaminated water was delivered to the Mililani area in water trucks.

A number of studies were conducted to identify the best practicable treatment technology to reduce contaminant concentrations to below detectable levels (Dugan et al. 1984; Oshiro 1986; GMP Associates, Inc. 1984). Dugan et al. (1984) conducted a series of laboratory bench-scale experiments in which EDB- and/or DBCP-spiked water was treated by passing various quantities through different types of granular activated carbon (GAC). Oshiro (1986) studied thin-film volatilization and heat volatilization as possible treatment alternatives. GMP Associates, Inc. (1984) examined GAC, packed tower air stripping, and cooling tower treatments. Despite its greater capital cost, GAC treatment was recommended because it provided (1) improved performance and comparable operational costs relative to that attained with air stripping, (2) performance stability under varying influent conditions, (3) operational

ease and reliability, (4) enclosed treatment, and (5) no air emissions (GMP Associates, Inc. 1984).

Based on the recommendations of the GMP Associates, Inc. (1984) study, BWS installed GAC treatment facilities at Mililani, Kunia, and Waipahu (Figure 1). The treatment plants at Mililani, Kunia, and Waipahu were placed in service in March 1986, May 1986, and July 1987, respectively (Ishihara and Astrab 1989).

Problem Identification

Original operational cost estimates for the GAC treatment plants at Mililani and Waipahu were based on assumed carbon requirements of 0.0028 and 0.0043 kg/m^3 (23 and 36 $lb/10^6$ gal), respectively (GMP Associates, Inc. 1984). Original carbon requirements were estimated based on breakthrough of TCP from laboratory minicolumns. However, operational experience from the time the treatment units were placed in service to September 1991 indicates actual carbon usage rates of approximately 0.014 and 0.016 kg/m^3 (120 and 130 $lb/10^6$ gal) for Mililani and Waipahu, respectively. The actual carbon usage rate represents the ratio of carbon quantity to volume of water treated between successive carbon replacements. The GAC in the contactors are typically changed upon breakthrough of target organic compounds. Because actual carbon usage is significantly greater than originally predicted, operational costs are much greater than anticipated.

Nature and Scope

Recognizing the need to reduce operational costs associated with its GAC facilities, BWS contracted the University of Hawai'i Water Resources Research Center (WRRC) to address the current problem of extending the effective life of GAC used for the removal of target organic chemicals from well water in central O'ahu. The study consists of two related phases. The scope of Phase I is to obtain the basic information necessary to understand the problem, so that in Phase II the best practicable means of extending the effective life of the GAC used to remove the target organic chemicals from affected wells can be determined.

The project objectives of the one-year evaluative Phase I study are listed below.

1. Examine the operations of the GAC facilities at the Mililani, Waipahu, and Kunia well sites
2. Employ and train a toxic chemist to effectively and reliably assay for the various target organic chemicals of importance in the well waters and GAC
3. Conduct physical, chemical, and biological tests to characterize the influent water, effluent water, and GAC in various stages of operation
4. Test and characterize the spent carbon to determine its total sorptive capacity and ability to be reused

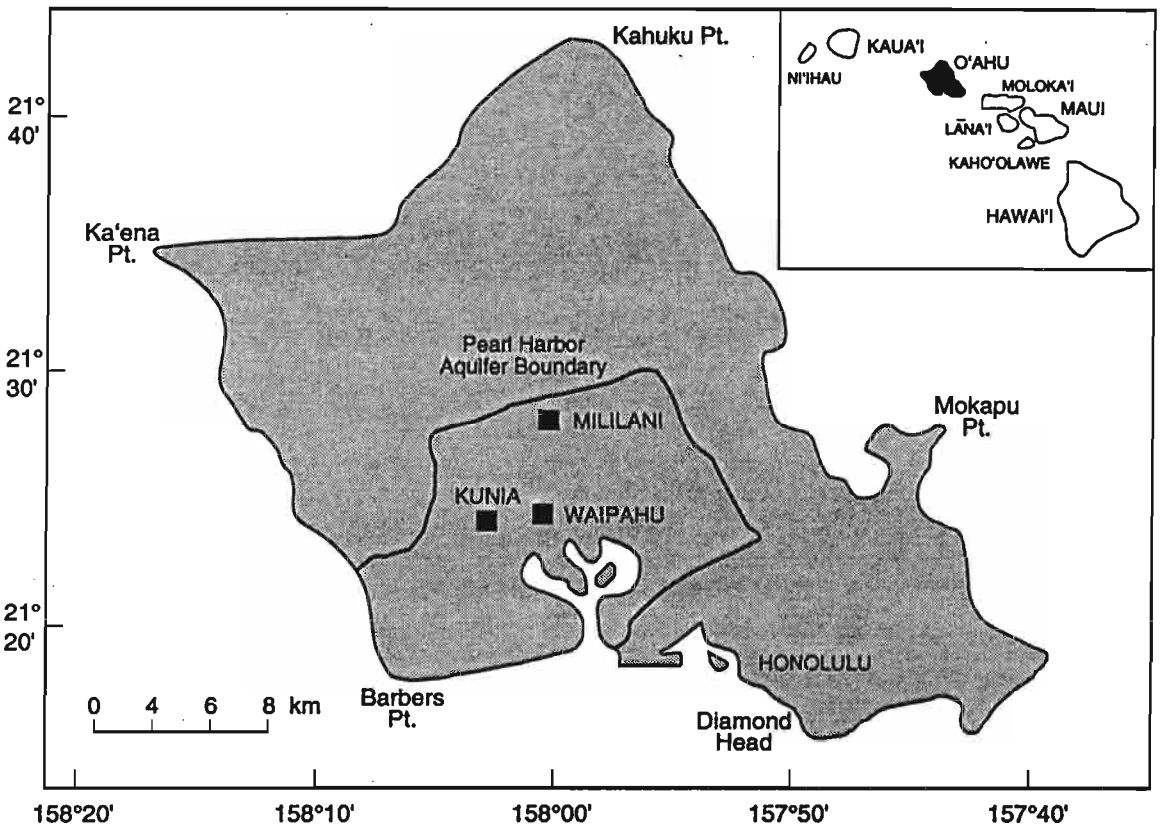

FIGURE 1. GAC treatment sites, O'ahu, Hawai'i

5. Conduct pretreatment tests of the influent water to extend the life of the GAC

This document is the final report of Phase I of the evaluative study initiated in May 1990. The methodology, field and laboratory work performed, and results of activities completed as of October 1991 are documented. Phase II of this project, which represents a continuation and expansion of Phase I, is scheduled to be completed in 1992. The Phase II goals are:

1. To sample and analyze spent carbon samples from existing contactors to determine chemical profiles
2. To analyze influent and effluent water samples for target organic compounds, identifiable nontarget organic compounds and total organic carbon to fully characterize the water quality
3. To quantify humic acids and other naturally occurring organics to assess the importance of humic substances and background organic matter in the adsorption process
4. To run tests not conducted in Phase I to determine the efficacy of certain pretreatment methods (possibly ozonation)
5. To suggest and implement, if possible, different operation strategies, such as parallel operation of contactors instead of serial operation, and to determine the impact on GAC service life

Project Management and Personnel

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Dr. Roger S. Fujioka	Co-Principal Investigator
Dr. L. Stephen Lau	Co-Principal Investigator
Mr. Henry K. Gee	Research Associate, WRRC
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Dr. Gerald H. Takei	Toxic Chemist, WRRC
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PESTICIDE ANALYSIS OF WATER SAMPLES

Untreated groundwater samples collected from the Mililani wells and treated water samples collected at the Mililani GAC treatment facility were analyzed for target organic compounds. The samples were collected (1) to ensure capability of the WRRC laboratory in the analysis of pesticides, (2) to quantify the levels of target organic compounds in well samples, and (3) to determine any previously unidentified organic compounds present in source waters.

Sampling

Water samples were collected from wellhead taps at Mililani Wells I and II and from influent, effluent, and contactor taps at the Mililani GAC treatment facility. Water was allowed to discharge from the tap for several minutes prior to sampling. Water samples were collected in 1-liter glass bottles with teflon-lined caps in a manner which minimizes volatilization losses. Sample bottles were angled during collection to allow water to flow calmly down along the sides, avoiding excessive turbulence and aeration. Sample bottles were filled to minimize head space. Samples were then stored in an ice chest and transported to the University of Hawai'i WRRC laboratory for analysis. Analyses were generally completed within six hours of collection.

Solvents

All glassware was rinsed in Fisher Optima-grade acetone prior to use. Codistillation extraction of water samples was conducted with Fisher Optima-grade hexane.

Analytical Methodology

Codistillation

Water samples were codistilled by placing 600 ml of sample and 10 ml of hexane in a 1-liter round-bottom boiling flask with 24/40 ground glass joint. Boiling chips were added to the flask, which was then connected to a Barrett distillation receiver with an Allihn condenser. The solution was heated in a heating mantle to distill over the hexane and associated organic compounds. The recovered hexane was dried with sodium sulfate. A 5-µl aliquot of the extract was injected into the gas chromatograph for analysis.

Gas Chromatography

A Hewlett-Packard Model 5700A gas chromatograph equipped with a nickel 63-electron capture detector was used for pesticide analyses. A 1.83 m × 4 mm I.D. glass column packed with 4% SE-30 and 6% OV-210 on 100/120 Chromosorb W (Supelco) was primarily used in the gas chromatograph. A similar column with only 5% OV-210 was used for confirmation analyses. In June 1991 a J&W Scientific DB-624 75 m × 0.53 mm I.D. megabore column (3 µm film thickness) was installed in the gas chromatograph. Injector and detector temperatures were set at 250°C and 300°C, respectively. Oven temperature was set at 65°C or 100°C (95°C or 135°C with J&W Scientific DB-624 column), depending on the compound being analyzed. Carrier gas, 95% argon and 5% methane, was maintained at a flow rate of 35 ml/min at 4.1 bar (60 psi). Chromatograms were plotted on a Hewlett-Packard Model 3390A integrator.

Results and Discussion

The results of WRRC analyses of Mililani and Waipahu wells and contactors samples are presented in Tables 1 and 2, respectively. Concentrations of DBCP and TCP in well and treatment plant water samples are within the expected range. Typically, DBCP concentrations at Mililani Wells I and II and in the influent water to the GAC treatment facility are between 20 and 100 ng/l (Figures 2 and 3), whereas TCP concentrations are generally between 1000 and 3000 ng/l (Figures 4 and 5). Interestingly, the DBCP time series of the influent water seems to exhibit an upward trend prior to mid-1990; this may be related to the increased pumpage from Mililani Wells II since 1986 (Figure 6). As depicted by the concentration time series (Figures 2–5), TCP behavior differs from DBCP behavior; this may indicate that, among other reasons, (1) DBCP and TCP source areas differ, (2) behavior of the two compounds in the unsaturated and/or saturated zones differs, or (3) timing of DBCP and DD applications differed. Analysis for 1,2-dichloropropane (DCP) was initiated with the samples collected in August 1991.

TABLE 1. Pesticide Concentrations of Mililani and Waipahu Well Water Samples

Sample	Sampling Date	Concentration (ng/l)		
		DBCP	EDB	TCP
Mililani Wells I				
Pump 2 (2800-02)	07/23/90	50		1730
	07/26/90	58		1710
	07/30/90	79		1760
	10/11/90	47		760
	08/21/91	25	ND	1070
Pump 3 (2800-03)	07/23/90	49		3040
	07/26/90	39		2330
	07/30/90	27		1640
	10/11/90	45		2150
	08/12/91	NQ	ND	1040
	08/21/91	23	ND	1860
Mililani Wells II				
Pump 1 (2859-01)	07/23/90	140		3520
	07/26/90	75		1530
	07/30/90	84		1860
	10/25/90	81		2020
	08/21/91	55	ND	1270
Pump 2 (2859-02)	10/25/90	110		2310
	08/06/91	28	ND	1160
	08/21/91	46	ND	1490
Waipahu Wells				
Pump 1 (2400-02)	10/25/90	NQ	52	560
Pump 2 (2400-01)	06/12/91		NQ	150
Pump 3 (2400-04)	06/12/91		38	230
Pump 4 (2400-03)	06/12/91		46	170

NOTE: Detection limit for DBCP ≈ 20 ng/l, for EDB ≈ 20 ng/l, and for TCP ≈ 100–200 ng/l; ND = not detected, NQ = not quantifiable. All samples extracted by codistillation with hexane and analyzed with a gas chromatograph equipped with an electron capture detector. Quantitated results not corrected for percent recovery.

TABLE 2. Pesticide Concentrations of Mililani Influent, Effluent, and Contactor Water Samples

Sample	Position	Sampling Date	Concentration (ng/l)		
			DBCP	EDB	TCP
Contactor 2	Lag	06/21/90	ND		NQ
	Lag	08/07/90	ND		a
Contactor 3	Lead	10/25/90	NQ		510
	Lead	04/19/91	ND		ND
Contactor 4	Lead	06/21/90	ND		NQ
	Lead	08/07/90	ND		470
	Lead	06/28/91	ND		ND
Contactor 5	Lead	06/21/90	ND		NQ
	Lead	07/26/90	ND		150
	Lead	08/07/90	ND		180
	Lag	01/16/91	ND	ND	220
	Lag	04/12/91	ND		ND
Contactor 6	Lead	10/11/90	ND		650
	Lead	10/25/90	ND		620
	Lead	04/19/91	ND		480
Contactor 7	Lag	06/21/90	ND		NQ
	Lag	07/26/90	ND		140
	Lag	08/07/90	ND		260
	Lead	01/16/91	ND	ND	380
	Lead	04/12/91	ND		400
	Lead	04/19/91	ND		760
Contactor 8	Lag	10/11/90	ND		620
	Lag	10/25/90	NQ		510
	Lead	04/12/91	ND		ND
Contactor 9	Single	04/19/91	ND		ND
	Single	08/06/91	ND	ND	ND
Contactor 12	Single	04/19/91	ND		ND
	Single	08/06/91	ND	ND	ND
	Single	08/12/91	ND	ND	ND
Influent		06/21/90	33		1080
		08/07/90	ND		850
		11/23/90	64		2240
		01/16/91	53	ND	1970
		04/12/91	85		2260
		04/19/91	41		2000
		06/28/91	51		2490
		07/03/91	49	ND	2140
		08/06/91	41	ND	1220
		08/12/91	85	ND	2730
		08/21/91	23	ND	920
Effluent (even contactors)		08/07/90	ND		a
		11/23/90	ND	ND	100
		04/12/91	ND		ND
		06/28/91	ND		ND
		07/03/91	ND	ND	ND
Effluent (odd contactors)		11/23/90	ND		ND
		04/12/91	ND		ND
		07/03/91	ND	ND	ND

NOTE: Detection limit for DBCP ≈ 20 ng/l, for EDB ≈ 20 ng/l, and for TCP ≈ 100–200 ng/l.; ND = not detected, NQ = not quantifiable. All samples extracted by codistillation with hexane and analyzed with a gas chromatograph equipped with an electron capture detector. Quantitated results not corrected for percent recovery.

[a]Peak occurring at the approximate retention time for TCP most likely does not represent TCP.

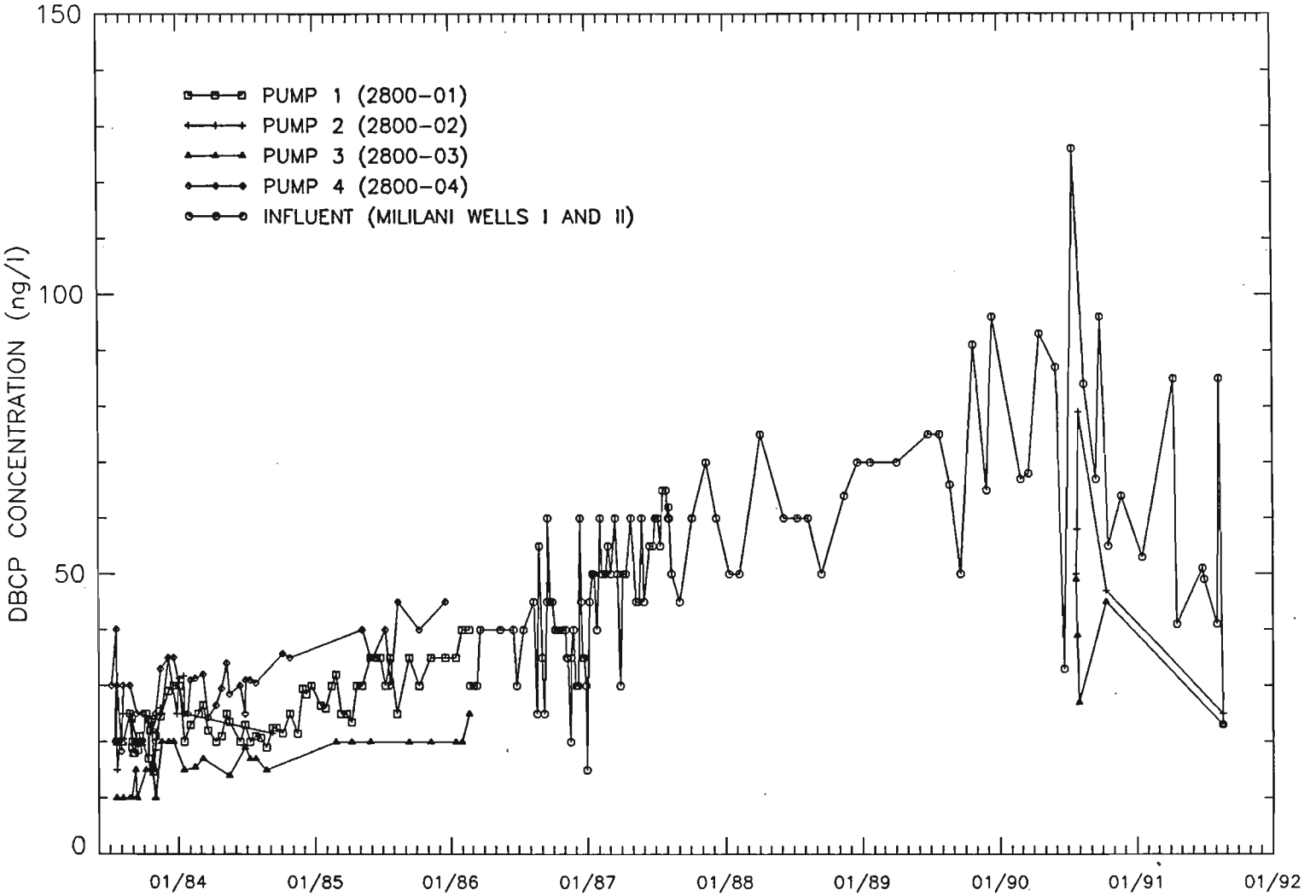


FIGURE 2. DBCP concentration time series, Mililani Wells I, O'ahu, Hawai'i

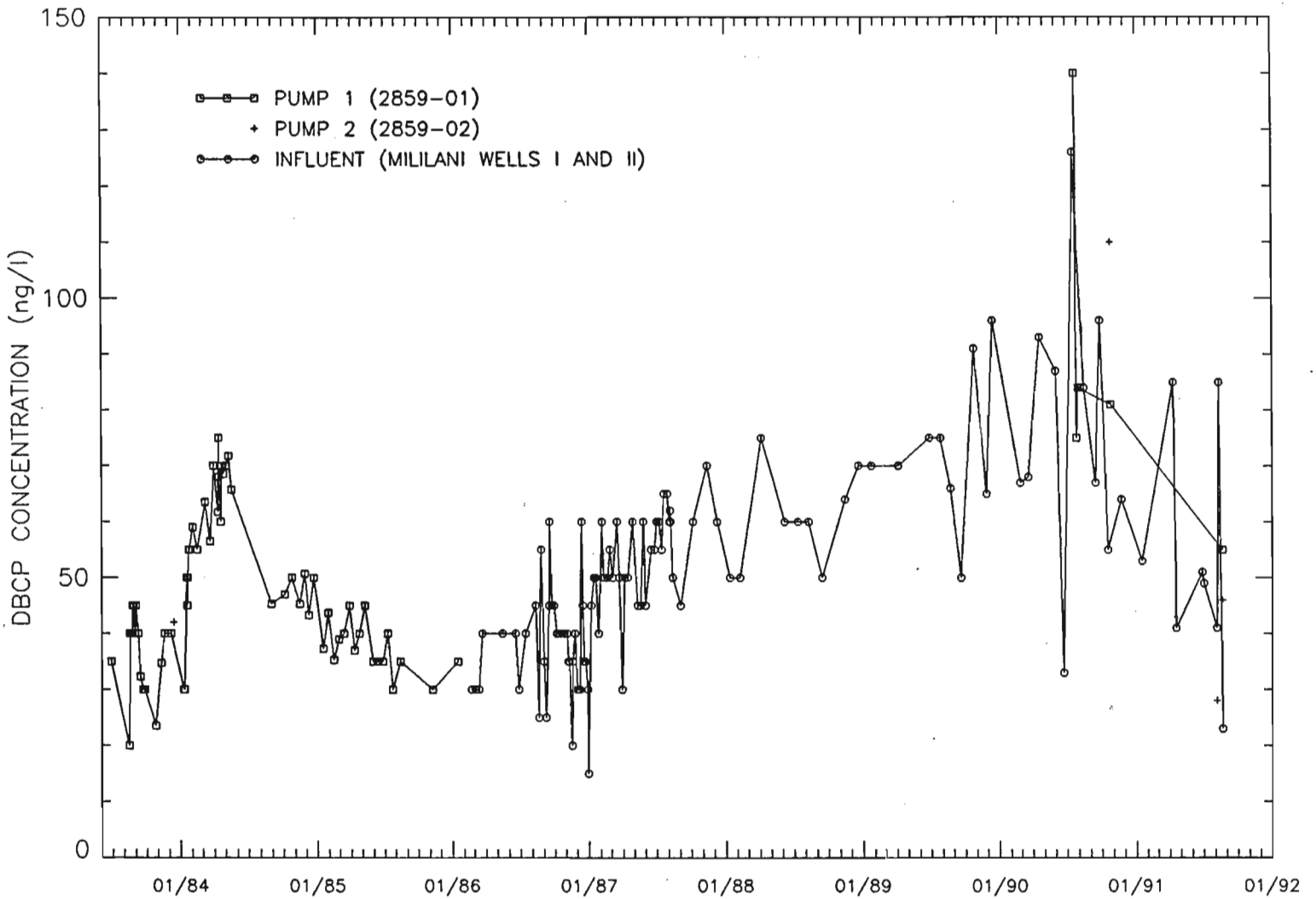


FIGURE 3. DBCP concentration time series, Mililani Wells II, O'ahu, Hawai'i

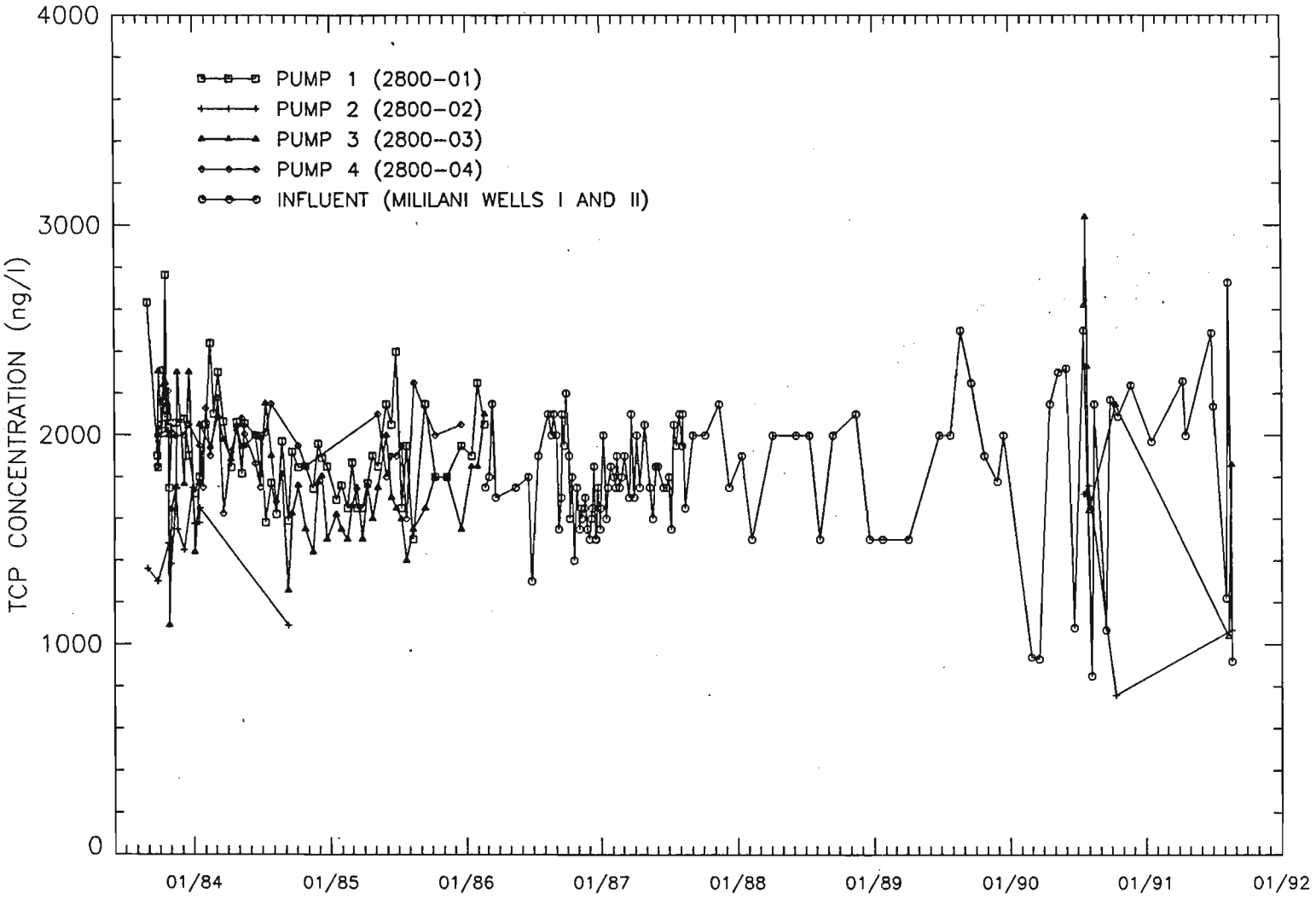


FIGURE 4. TCP concentration time series, Mililani Wells I, O'ahu, Hawai'i

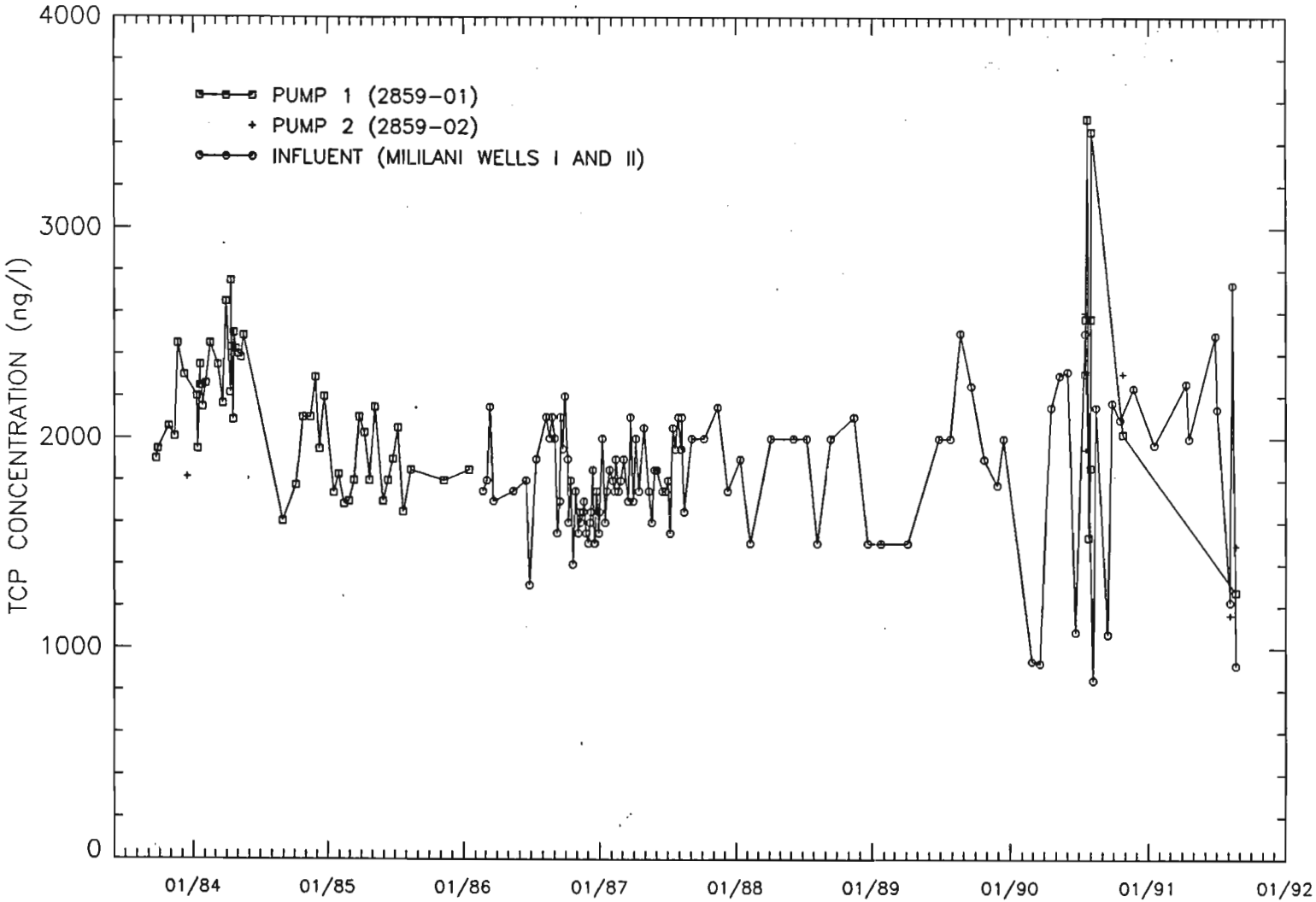


FIGURE 5. TCP concentration time series, Mililani Wells II, O'ahu, Hawai'i

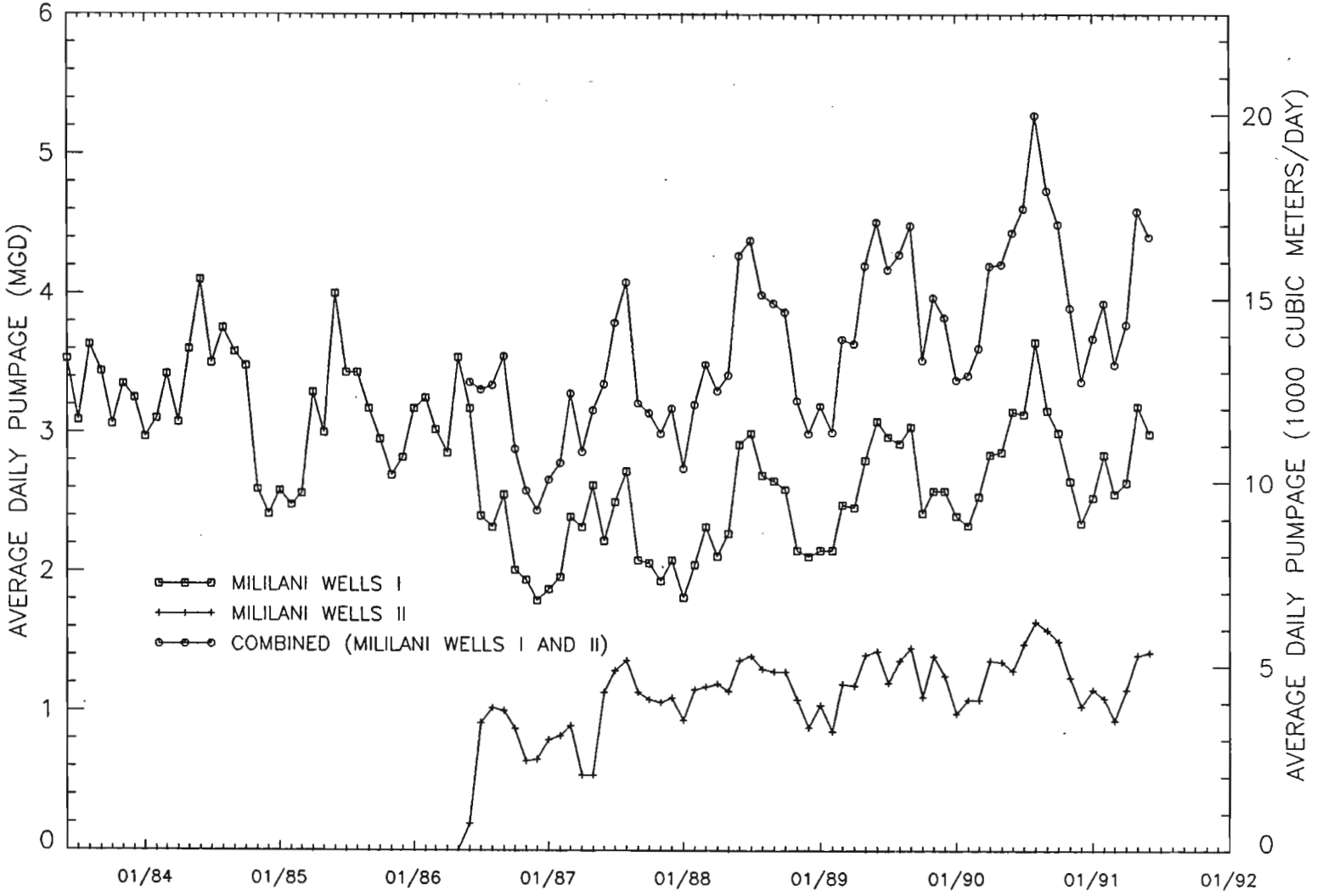


FIGURE 6. Pumpage time series, Mililani Wells I and II, O'ahu, Hawai'i

An effort is currently being made to identify organic compounds other than DBCP, TCP, and DCP which may be present in Mililani well waters. This identification effort is being conducted with a Hewlett-Packard Model 5890 gas chromatograph equipped with a 5970 Series Mass Selective Detector. Unfortunately, the sensitivity of the gas chromatograph/mass spectrometer (GC/MS) system is less than the gas chromatograph/electron capture (GC/EC) system (nanogram levels vs. picogram levels). This shortcoming and the difficulties associated with concentrating and "cleaning" the extracts, particularly with volatile organic chemicals, are the primary impediments for identification of these other compounds by GC/MS. However, special processes involving solid-phase chromatography cartridges and inert gas blow-down systems are being developed for the preparation of these extracts for GC/MS analysis.

PESTICIDE ANALYSIS OF GAC SAMPLES

GAC samples from contactors at Mililani, Waipahu, and Kunia were collected and analyzed for target organic compounds. The samples were analyzed (1) to ensure that the WRRC laboratory is capable of extracting target organic compounds from GAC, (2) to quantify the levels of target organic compounds adsorbed on spent GAC, and (3) to determine whether any previously unidentified organic compounds are occupying sorption sites on the GAC. Samples were collected by both BWS and WRRC personnel.

Sampling

BWS Sampling

Prior to collecting GAC, the contactor was drained of water to facilitate sampling. Sampling of spent GAC by BWS personnel was conducted in a cased hole with a hand auger. A 15-cm (6-in.) diameter steel casing was first lowered vertically into the GAC bed within the contactor using a hydraulic jack. The GAC bed in the contactor is typically about 1.2 m (4 ft) deep. GAC samples collected at 15 cm (6 in.) increments were placed in 3.8-liter (1-gal) clear glass jars with aluminum foil-lined caps. At each sampling depth, the auger was filled several times.

WRRC obtained access to the GAC samples after BWS removed a representative subsample for analysis by an independent laboratory. The GAC obtained by WRRC was placed in 400-ml glass jars wrapped in aluminum foil to avoid photodegradation. Covers were lined with aluminum foil. Upon returning to the University of Hawai'i, all GAC samples were refrigerated for later analysis.

WRRC Sampling

Sampling was conducted from the top of the drained contactor through an eccentrically located access hole. The top of the GAC bed is typically about 1 m below the opening of the contactor.

GAC samples were collected with sterilized bucket augers. A telescoping casing system was used to minimize inter-sample contamination. Samples were homogenized in the field and placed in appropriate collection bottles. GAC samples to be analyzed for adsorbed organic compounds were collected in 400-ml clear glass bottles lined with aluminum foil to prevent photodegradation. Plastic covers were also lined with aluminum foil. GAC samples to be analyzed for bacteria were collected in sterile 1-liter Nalgene bottles. All samples were stored in an ice chest for transport to the University of Hawai'i.

The initial GAC sample was collected with a 10.2-cm (4-in.) bucket auger. If necessary, sterile deionized water was poured onto the GAC surface to enhance particle cohesion so that the loose granular material did not fall out of the auger when it was lifted. The collected GAC was emptied onto a piece of sterile aluminum foil, homogenized, and then placed into appropriate sample bottles.

Prior to reinserting the 10.2-cm auger into the sample hole, it was cleaned of any adhering GAC with sterile, deionized water. The top of the second GAC sample in the bucket auger, which represents material from the upper sampling interval, was disposed. The GAC sample was emptied onto a new piece of sterile aluminum foil, homogenized, and placed into appropriate sample bottles.

To prevent near-surface GAC from falling into the hole and contaminating deeper samples, a 1.37 m (54 in.) length of 10.2-cm (4-in.) PVC casing was placed into the hole at a sample depth of about 30 cm and secured in place with wire. The next sample was then collected with a 7.6-cm (3-in.) bucket auger within the cased hole. The top few centimeters of GAC in the auger was typically disposed, and the remaining GAC homogenized and placed into an appropriate sample bottle. After rinsing the 7.6-cm auger with sterile deionized water, the next sample was collected.

At a sample depth of about 75 cm, a second PVC casing (7.6 cm diameter) was placed within the larger 10.2-cm casing. The remaining GAC samples were then collected with a 5.1-cm auger. Note that the bottom of the sampled hole actually does not extend to the bottom of the contactor since a 30-cm stainless steel pipe occurs within the contactor and prevents further sampling. The depth of GAC beneath the stainless steel pipe is approximately 1 m.

Solvents

All glassware was rinsed in Fisher Optima-grade acetone prior to use. Fisher Optima-grade methanol and hexane were used for ultrasonic and codistillation extraction methods, respectively.

Analytical Methodology

The two methods considered for desorption and recovery of organic compounds from spent GAC samples were ultrasonic solvent extraction and codistillation. Each method is described below. Since ultrasonic solvent extraction of GAC samples had not been conducted previously in Hawai'i, the methodology required considerable development.

Ultrasonic Solvent Extraction

GAC samples were weighed into 18 mm O.D. × 150 mm long glass test tubes. Methanol was then added to the GAC samples in the test tubes. Initially, solvent to GAC (dry weight) ratios tested ranged from about 20 to 2000 ml/g. All test tubes were capped with teflon-lined screw caps, immersed in a water bath of a Bransonic 32 ultrasonic cleaner, and sonicated for 30 minutes. Samples were inverted at 5-minute intervals during sonication to enhance GAC-solvent interaction. Following sonication, samples were allowed to stand in a refrigerator under quiescent conditions for approximately 24 hours to encourage further GAC-solvent interaction and to allow the GAC to settle. After settling, 2 ml of the solvent extract were transferred to a glass vial, which was then capped to minimize volatilization losses. Sodium sulfate was added to dry the solvent extract, and 5 µl of the extract were then injected into a gas chromatograph for analysis.

The dry weight of each GAC sample was subsequently obtained by removing as much of the solvent extract from the test tubes as possible prior to placing the tube in an oven. To avoid GAC loss due to boiling, the oven temperature was maintained at 70° to 80°C for 1 to 2 hours and then raised to 105°C for about 1 hour more until constant weight was achieved.

Codistillation

Approximately 2 g (wet weight) of GAC were placed in a 1-liter round-bottom boiling flask with 24/40 ground glass joint. Six hundred milliliters of tap water and 10 ml of hexane were added to the flask. The boiling flask was attached to a distilling receiver Barrett trap, which was then connected to an Allihn condenser. The solution was heated in a heating mantle to distill over the hexane and associated desorbed organic compounds. The recovered hexane was dried with sodium sulfate. Five microliters of the extract were injected into the gas chromatograph for analysis.

Gas Chromatography

A Hewlett-Packard Model 5700A gas chromatograph equipped with a nickel 63-electron capture detector was used for pesticide analyses. A 1.83 m × 4 mm I.D. glass column packed with 4% SE-30 and 6% OV-210 on 100/120 Chromosorb W (Supelco) and a confirming column packed with 5% OV-210 were used in the gas chromatograph. In June 1991 a J&W Scientific DB-624 75 m × 0.53 mm I.D. megabore column (3 μm film thickness) was installed in the gas chromatograph. Injector and detector temperatures were set at 250°C and 300°C, respectively. Oven temperature was set at 65°C or 100°C, depending on the compound being analyzed. Carrier gas (95% argon and 5% methane) was maintained at a flow rate of 35 ml/min at 4.1 bar (60 psi). Chromatograms were plotted on a Hewlett-Packard Model 3390A integrator.

Results and Discussion

Ultrasonic Solvent Extraction

Initially, samples obtained from Mililani contactor no. 3 during August 1990 were extracted using a solvent to GAC (dry weight) ratio of approximately 15 to 25 ml/g. The approximate wet weight of GAC added to each test tube was 2 g. Results of the initial extraction, presented in Table 3, indicate that DBCP and TCP concentrations generally decrease with depth. Note that the amounts of DBCP and TCP in the sorbed phase are much greater than the amounts in the water being treated; therefore, the contributions of these materials from the pore water associated with the wet GAC are neglected.

The results for the GAC sample from the 0- to 15-cm depth interval, which was extracted using solvent to GAC ratios of 12.4 ml/g and 18.5 ml/g, indicate that DBCP and TCP are extracted more efficiently using the higher ratio. Thus solvent to GAC (dry weight) ratios of 2000 ml/g were also tested. In addition, trial runs using successive ultrasonic extractions of a GAC sample were conducted to determine the efficiency of the first extraction.

Before running successive extractions on a GAC sample, methanol remaining in the test tube following the initial extraction is removed and the total volume of methanol removed from the tube recorded. The volume of unrecoverable methanol, which is the difference between the original amount added (approximately 25 ml) and the total amount removed, has the same characteristics as the methanol removed for the gas chromatograph analysis with similar concentrations of DBCP and TCP. For the second extraction, approximately 25 ml of methanol are added to the test tube containing both GAC and a small amount of residual methanol remaining from the initial extraction. The methodology for the second extraction is the same as for the initial extraction. The total amounts of DBCP and TCP desorbed during the second

TABLE 3. Ultrasonic Solvent Extraction of Mililani Contactor No. 3 GAC: Approximate Sample Size 2 g (Wet Weight); Approximate Solvent to GAC (Dry Weight) Ratio 20 ml/g

Sampling Depth (cm)	GAC Sample Size		Moisture Content[a] (g/g)	Methanol (ml)	Solvent: GAC Ratio[a] (ml/g)	Concentration[a]	
	Wet (g)	Dry (g)				TCP (µg/g)	DBCP (µg/g)
0–15	2.00	1.31	0.53	24.3	18.5	300	16.0
0–15	2.00	1.26	0.59	15.6	12.4	200	11.4
15–30	2.00	1.29	0.55	24.5	19.0	318	14.3
30–46	2.07	1.29	0.60	24.5	19.0	284	11.1
46–61	2.04	1.22	0.67	25.6	21.0	276	5.5
61–76	2.08	1.31	0.59	15.2	11.6	173	3.1
76–91	2.00	1.27	0.57	15.5	12.2	139	2.2
91–107	2.14	1.35	0.59	15.4	11.4	129	1.3
107–122	2.09	1.22	0.71	15.4	12.6	106	1.0

NOTE: Mililani contactor no. 3 GAC samples collected on 07 August 1990 by Board of Water Supply and extracted on 08 August 1990.
[a]Dry weight basis.

sonication extraction include the carry-over amounts of DBCP and TCP remaining from the first extraction.

Results of a double ultrasonic solvent extraction using solvent to GAC (dry weight) ratios of about 2000 ml/g are presented in Table 4. The wet weight of GAC used for each sample was 0.02 g. Based on the first extraction, it is clear that DBCP concentrations generally decrease with bed depth. TCP concentrations, however, do not follow any clear trend with bed depth. The second ultrasonic extraction is generally unable to desorb additional DBCP and TCP from the GAC. The only exception occurs in the 0- to 15-cm sample from which a small amount of DBCP is desorbed.

Based on the results presented in Table 4, a second sonication extraction is apparently not necessary with 0.02-g (wet weight) GAC samples. However, a small sample size of 0.02 g may not be representative of the GAC contactor bed, and this may explain why the TCP concentrations fluctuate with bed depth. The concentrations of both DBCP and TCP are typically expected to decrease with bed depth (unless during operation the entire profile becomes exhausted or desorption occurs). However, the 0.02-g GAC samples fail to show this trend for TCP in Table 4.

The concept of double ultrasonic extraction was continued using 2-g (wet weight) GAC samples at solvent to GAC (dry weight) ratios of about 20 ml/g (Table 5). Based on the initial

ABLE 4. Double Ultrasonic Extraction of Mililani Contactor No. 3 GAC: Approximate Sample ize 0.02 g (Wet Weight); Approximate Solvent to GAC (Dry Weight) Ratio)00 ml/g

ampling Depth (cm)	GAC Sample Size		Moisture Content[a] (g/g)	First Extraction[a]		Second Extraction[a]	
	Wet (g)	Dry (g)		TCP (µg/g)	DBCP (µg/g)	TCP (µg/g)	DBCP (µg/g)
0–15	0.0200	0.0123[b]	0.63[b]	302	26.5	ND	4.1
15–30	0.0200	0.0122[b]	0.64[b]	309	24.9	ND	ND
30–46	0.0200	0.0110	0.82	422	23.9	ND	ND
46–61	0.0200	0.0150	0.33	149	6.0	ND	ND
61–76	0.0200	0.0115	0.74	390	11.1	ND	ND
76–91	0.0200	0.0130	0.54	229	4.9	ND	ND
)1–107	0.0200	0.0095	1.11	319	3.4	ND	ND
07–122	0.0200	0.0122[b]	0.64[b]	156	1.9	ND	ND

)TE: ND = not detected. Mililani contactor no. 3 GAC samples collected on 07 August 1990 by Board of Water Supply d extracted on 14–15 August 1990. Results for second extraction are corrected for the amount of methanol and sociated DBCP and TCP remaining in each test tube as a result of the first extraction.

)ry weight basis.

stimated from 2-g samples (Table 3).

ABLE 5. Double Ultrasonic Extraction of Mililani Contactor No. 3 GAC: Approximate Sample ze 2 g (Wet Weight); Approximate Solvent to GAC (Dry Weight) Ratio 20 ml/g

ampling Depth (cm)	GAC Sample Size		Moisture Content[a] (g/g)	First Extraction[a]		Second Extraction[a]	
	Wet (g)	Dry (g)		TCP (µg/g)	DBCP (µg/g)	TCP (µg/g)	DBCP (µg/g)
0–15	2.00	1.23	0.63	115	7.9	71	5.8
51–76	2.00	1.22	0.64	83	2.2	79	3.0
)7–122	2.00	1.22	0.64	42	0.7	44	1.0

)TE: Mililani contactor no. 3 GAC samples collected on 07 August 1990 by Board of Water Supply and extracted on -17 August 1990. Results for second extraction are corrected for the amount of methanol and associated DBCP and P remaining in each test tube as a result of the first extraction.

ry weight basis.

extraction, it is clear that both DBCP and TCP concentrations decrease with bed depth. However, the initial extraction desorbed considerably lower amounts of DBCP and TCP than the corresponding 0.02-g samples run at a higher solvent to GAC ratio (Table 4) and recovered significantly lower amounts of the compounds than in the previously run single sonication extractions with 2-g samples (Table 3). These results were somewhat unexpected. Furthermore, the low initial extraction efficiencies most likely caused the recovery of higher amounts of DBCP and TCP during the second ultrasonic extractions with certain samples.

Results from the extractions of 0.02- and 2-g samples indicate that higher solvent to GAC ratios yield better recoveries of target organic compounds. However, small GAC samples associated with the high solvent to GAC ratios may not be representative of the contactor bed and may yield misleading results. Thus 0.2 g (wet weight) of GAC is considered an appropriate compromise for sample size and optimum extraction efficiency.

Results of a double ultrasonic solvent extraction using 0.2-g (wet weight) samples are presented in Table 6. Solvent to GAC (dry weight) ratios are approximately 200 ml/g. Based on the first extraction, it is clear that both DBCP and TCP concentrations decrease with bed depth. The second ultrasonic extraction is able to desorb additional DBCP and TCP from the GAC. However, the amounts of DBCP and TCP recovered in the first extraction are generally at least an order of magnitude greater than the amounts recovered in the second extraction.

Based on the results presented in Table 6, it appears that TCP is more readily desorbed in the first extraction than DBCP; that is, assuming that the two extractions recover 100% of the adsorbed DBCP and TCP, a greater percentage of the adsorbed TCP is recovered during the initial extraction. Furthermore, over 90% of each of the adsorbed compounds is recovered with one extraction, and perhaps this is all that is necessary for our study. More work will be conducted in the future to determine the recovery efficiency of the ultrasonic extraction method.

The GAC samples collected from Mililani contactor no. 3 by BWS in August 1990 were used to develop the ultrasonic extraction methodology. All subsequent ultrasonic extraction analyses were conducted using a GAC sample size of about 0.2 g. Results of the duplicate analyses of the Waipahu west contactor no. 3 GAC profile sampled in September 1990 by WRRC are presented in Tables 7 and 8. Composite samples collected by BWS in April 1991 from Mililani contactor no. 2 were analyzed in duplicate by WRRC, and the results are presented in Table 9. The GAC profile of Kunia contactor no. 1, sampled in May 1991, is presented in Table 10. Results of the triplicate analyses of the GAC profile of Mililani contactor no. 3 sampled in May 1991 are presented in Tables 11 to 13, and those for the duplicate analyses of the GAC profile of Waipahu east contactor no. 2 sampled in June 1991 are presented in Tables 14 and 15.

TABLE 6. Double Ultrasonic Extraction of Mililani Contactor No. 3 GAC: Approximate Sample Size 0.2 g (Wet Weight); Approximate Solvent to GAC (Dry Weight) Ratio 200 ml/g

Sampling Depth (cm)	GAC Sample Size		Moisture Content[a] (g/g)	First Extraction[a]		Second Extraction[a]	
	Wet (g)	Dry (g)		TCP (µg/g)	DBCP (µg/g)	TCP (µg/g)	DBCP (µg/g)
0–15	0.2326	0.1390	0.67	409	22.3	7.8	1.5
15–30	0.2523	0.1544	0.63	388	19.8	12.3	1.8
30–46	0.2400	0.1443	0.66	365	18.1	10.3	1.5
46–61	0.2491	0.1383	0.80	364	12.5	—	—
61–76	0.2690	0.1493	0.80	313	9.0	6.4	0.8
76–91	0.2800	0.1630	0.72	289	6.1	10.0	0.7
91–107	0.2366	0.1319	0.79	241	3.5	8.0	0.3
107–122	0.2415	0.1416	0.71	195	3.2	6.4	0.3

NOTE: Mililani contactor no. 3 GAC samples collected on 07 August 1990 by Board of Water Supply and extracted on 22–23 August 1990. Results for second extraction are corrected for the amount of methanol and associated DBCP and TCP remaining in each test tube as a result of the first extraction.

[a]Dry weight basis.

TABLE 7. Waipahu West Contactor No. 3 GAC Profile, Replicate 1

Sampling Depth (cm)	GAC Sample Size		Moisture Content[a] (g/g)	Methanol (ml)	Concentration[a]		
	Wet (g)	Dry (g)			EDB (µg/g)	TCP (µg/g)	DBCP[b] (µg/g)
0–25	0.2000	0.1210	0.65	26.0	4.2	40	0.41
25–41	0.2000	0.1290	0.55	26.0	3.3	33	0.21
41–48	0.2000	0.1125	0.78	26.0	3.8	38	0.24
48–64	0.2000	0.1225	0.63	26.0	2.9	32	0.19
64–81	0.2000	0.1690	0.18	26.0	1.8	23	0.08
81–102	0.2000	0.1195	0.67	26.0	2.6	27	0.12
102–122	0.2000	0.1235	0.62	26.0	2.1	17	0.04
122–147	0.2000	0.1335	0.50	20.0	0.1	10	ND

NOTE: ND = not detected. Waipahu west contactor no. 3 GAC samples collected on 19 September 1990 by Water Resources Research Center and extracted on 03 October 1990.

[a]Dry weight basis.

[b]Compound retention time similar to DBCP, but compound not identified or confirmed by GC/MS.

TABLE 8. Waipahu West Contactor No. 3 GAC Profile, Replicate 2

Sampling Depth (cm)	GAC Sample Size		Moisture Content[a] (g/g)	Methanol (ml)	Concentration[a]		
	Wet (g)	Dry (g)			EDB (µg/g)	TCP (µg/g)	DBCP[b] (µg/g)
0–25	0.2000	0.1125	0.78	26.0	4.5	43	0.36
25–41	0.2000	0.1185	0.69	26.0	3.1	34	0.24
41–48	0.2000	0.1155	0.73	26.0	3.5	41	0.24
48–64	0.2000	0.1120	0.79	26.0	3.5	38	0.18
64–81	0.2000	0.1120	0.79	26.0	3.1	33	0.14
81–102	0.2000	0.1145	0.75	26.0	3.4	37	0.10
102–122	0.2000	0.1105	0.81	26.0	2.4	25	ND
122–147	0.2000	0.1095	0.83	26.0	1.8	18	ND

NOTE: ND = not detected. Waipahu west contactor no. 3 GAC samples collected on 19 September 1990 by Water Resources Research Center and extracted on 09 October 1990.

[a]Dry weight basis.

[b]Compound retention time similar to DBCP, but compound not identified or confirmed by GC/MS.

TABLE 9. Mililani Contactor No. 2 GAC Profile, Composite Samples

Sample	GAC Sample Size		Moisture Content[a] (g/g)	Methanol (ml)	Solvent: GAC Ratio[a] (ml/g)	Concentration[a]	
	Wet (g)	Dry (g)				TCP (µg/g)	DBCP (µg/g)
Composite 1	0.2684	0.1565	0.72	25.0	160	186	10.3
Composite 2	0.2353	0.1375	0.71	25.0	182	189	10.0

NOTE: Mililani contactor no. 2 GAC samples collected on 09 April 1991 by Board of Water Supply and extracted on 10 April 1991.

[a]Dry weight basis.

TABLE 10. Kunia Contactor No. 1 GAC Profile

Sampling Depth (cm)	GAC Sample Size		Moisture Content[a] (g/g)	Methanol (ml)	Solvent: GAC Ratio[a] (ml/g)	Concentration[a]	
	Wet (g)	Dry (g)				TCP (µg/g)	DBCP (µg/g)
0–10	0.2569	0.1351	0.90	25.0	185	36	0.3
10–17	0.3723	0.1849	1.01	25.0	135	26	ND
17–27	0.2575	0.1449	0.78	25.0	172	14	ND
27–36	0.2698	0.1461	0.85	25.0	171	6	ND
36–56	0.3129	0.1756	0.78	25.0	142	0.3	ND
56–67	0.2455	0.1439	0.71	25.0	174	ND	ND
67–95	0.2753	0.1523	0.81	25.0	164	ND	ND
95–131	0.2636	0.1485	0.78	25.0	168	ND	ND
131–164	0.2830	0.1643	0.72	25.0	152	ND	ND
164–170	0.2900	0.1561	0.86	25.0	160	ND	ND

NOTE: ND = Not detected. Kunia contactor no. 1 GAC samples collected on 06 May 1991 by Water Resources Research Center and extracted on 06 May 1991.
[a]Dry weight basis.

TABLE 11. Mililani Contactor No. 3 GAC Profile, Replicate 1

Sampling Depth (cm)	GAC Sample Size		Moisture Content[a] (g/g)	Methanol (ml)	Solvent: GAC Ratio[a] (ml/g)	Concentration[a]	
	Wet (g)	Dry (g)				TCP (µg/g)	DBCP (µg/g)
0–25	0.2662	0.1231	1.16	25.0	203	458	29.1
25–39	0.2627	0.1064	1.47	25.0	235	479	12.8
39–51	0.2821	0.1219	1.31	25.0	205	470	13.1
51–69	0.2780	0.1172	1.37	25.0	213	357	1.7
69–93	0.2153	0.0939	1.29	25.0	266	281	1.6
93–116	0.2603	0.1114	1.34	25.0	224	180	0.48
116–123	0.2754	0.1195	1.30	25.0	209	122	0.45

NOTE: Mililani contactor no. 3 GAC samples collected on 15 May 1991 by Water Resources Research Center and extracted on 15 May 1991.
[a]Dry weight basis.

TABLE 12. Mililani Contactor No. 3 GAC Profile, Replicate 2

Sampling Depth (cm)	GAC Sample Size		Moisture Content[a] (g/g)	Methanol (ml)	Solvent: GAC Ratio[a] (ml/g)	Concentration[a]	
	Wet (g)	Dry (g)				TCP (µg/g)	DBCP (µg/g)
0–25	0.2625	0.1442	0.82	25.0	173	356	26.6
25–39	0.2741	0.1648	0.66	25.0	152	317	10.3
39–51	0.2578	0.1495	0.72	25.0	167	298	8.5
51–69	0.2535	0.1485	0.71	25.0	168	196	1.3
69–93	0.2405	0.1406	0.71	25.0	178	165	1.2
93–116	0.2700	0.1573	0.72	25.0	159	109	0.31
116–123	0.2541	0.1474	0.72	25.0	170	58	0.22

NOTE: Mililani contactor no. 3 GAC samples collected on 15 May 1991 by Water Resources Research Center and extracted on 27 May 1991 for replication.
[a]Dry weight basis.

TABLE 13. Mililani Contactor No. 3 GAC Profile, Replicate 3

Sampling Depth (cm)	GAC Sample Size		Moisture Content[a] (g/g)	Methanol (ml)	Solvent: GAC Ratio[a] (ml/g)	Concentration[a]	
	Wet (g)	Dry (g)				TCP (µg/g)	DBCP (µg/g)
0–25	0.2972	0.1380	1.15	25.0	181	344	23.7
25–39	0.2863	0.1190	1.41	25.0	210	404	11.8
39–51	0.2512	0.1113	1.26	25.0	225	358	10.7
51–69	0.2781	0.1172	1.37	25.0	213	286	1.7
69–93	0.2683	0.1117	1.40	25.0	224	204	1.4
93–116	0.2672	0.1123	1.38	25.0	223	130	0.15
116–123	0.3371	0.1447	1.33	25.0	170	74	0.28

NOTE: Mililani contactor no. 3 GAC samples collected on 15 May 1991 by Water Resources Research Center and extracted on 08 July 1991 for replication.
[a]Dry weight basis.

TABLE 14. Waipahu East Contactor No. 2 GAC Profile, Replicate 1

Sampling Depth (cm)	GAC Sample Size		Moisture Content[a] (g/g)	Methanol (ml)	Concentration[a]		
	Wet (g)	Dry (g)			EDB (µg/g)	TCP (µg/g)	DBCP[b] (µg/g)
0–17	0.2843	0.1307	1.18	25.0	2.8	29	0.30
17–34	0.2400	0.1143	1.10	25.0	3.0	30	0.34
34–38	0.2687	0.1270	1.12	25.0	3.1	31	0.35
38–43	0.2662	0.1217	1.19	25.0	3.4	31	0.40
43–71	0.2711	0.1274	1.13	25.0	4.8	46	0.58
71–91	0.3081	0.1482	1.08	25.0	2.9	27	0.26
91–144	0.3169	0.1491	1.13	25.0	3.8	27	0.23

NOTE: Waipahu east contactor no. 2 GAC samples collected on 12 June 1991 by Water Resources Research Center and extracted on 12 June 1991.

[a]Dry weight basis.

[b]Compound retention time similar to DBCP, but compound not identified or confirmed by GC/MS.

TABLE 15. Waipahu East Contactor No. 2 GAC Profile, Replicate 2

Sampling Depth (cm)	GAC Sample Size		Moisture Content[a] (g/g)	Methanol (ml)	Concentration[a]		
	Wet (g)	Dry (g)			EDB (µg/g)	TCP (µg/g)	DBCP[b] (µg/g)
0–17	0.2600	0.1131	1.30	25.0	3.3	29	0.27
17–34	0.2888	0.1325	1.18	25.0	3.5	29	0.39
34–38	0.2731	0.1255	1.18	25.0	2.7	31	0.37
38–43	0.2784	0.1209	1.30	25.0	3.8	32	0.38
43–71	0.2615	0.1192	1.19	25.0	4.1	30	0.34
71–91	0.3150	0.1470	1.14	25.0	3.1	29	0.28
91–144	0.2973	0.1425	1.09	25.0	3.1	25	0.22

NOTE: Waipahu east contactor no. 2 GAC samples collected on 12 June 1991 by Water Resources Research Center and extracted on 25 June 1991 for replication.

[a]Dry weight basis.

[b]Compound retention time similar to DBCP, but compound not identified or confirmed by GC/MS.

A rough check on the measured concentrations of target organic compounds adsorbed by the GAC can be made by applying a simple mass balance analysis. The mass of target compounds entering the contactor can be determined from the known or estimated volume of water treated by the contactor and the average concentration of those compounds in the water. If breakthrough of the target compound does not occur and if attenuation of the adsorbed concentrations due to biological or chemical processes is negligible, then the adsorbed mass should be equal to the total mass entering the system. The mass balance analysis is confounded somewhat by the fact that influent concentrations vary over time. In addition, the cumulative volume of water treated by a particular contactor may not be known with complete certainty. Although it may be reasonable to assume that flow rates through all contactors at a particular treatment site are roughly equal, in some instances it is suspected that this is not the case. At the Kunia GAC treatment site, for instance, partial closure of a valve is suspected to have caused more water to flow through contactors 1 and 2 than through contactors 3 and 4 prior to February 1991. Furthermore, the head loss through each contactor may vary so that hydraulic loading rates may also vary from contactor to contactor. Degradation of the adsorbed organic compounds within the contactor and breakthrough further complicate the analysis.

As a first approximation, mass input to each of the sampled contactors was determined by assuming that (1) degradation of the adsorbed target compounds does not occur and (2) breakthrough of the target organic compounds does not account for a significant mass. Further assumptions were necessary to estimate the volume of water treated by the contactor of interest and the influent concentrations of the target compounds. In most instances, sampled contactors were initially placed on-line in the lag position of a serially operating pair. Typically, following breakthrough from the lead contactor, the direction of water flow to the contactors is reversed so that the lag contactor is then in the lead position. Thus, if a contactor is initially operated in the lag position and then is moved to the lead position, it will not be exposed to the target compounds for its entire service life. To perform a mass balance, the exposure time of the contactor to the target compounds must be estimated. The total exposure time includes the latter portion of the service period in the lag position and the entire service period in the lead position. Ideally, the time-varying influent concentrations to the contactor of interest should be known. For this initial analysis, however, an average influent concentration is assumed throughout the entire exposure period. Note that the average influent concentration used may be an overestimation of the actual influent concentration during the period when the contactor is in the lag position. However, the assumed influent concentrations are likely underestimated at other times during the exposure period. A summary of the target organic compound mass input to each sampled contactor is presented in Table 16.

TABLE 16. Target Organic Compound Mass Input To and Adsorbed By GAC

Contactor	Sampling Date	Exposure Period[a]	Volume Treated[b] ($10^3 m^3$)	Influent Concentration (ng/l)			Mass Input (g)			Mass Adsorbed on GAC (g)		
				EDB	DBCP	TCP	EDB	DBCP	TCP	EDB	DBCP	TCP
Mililani No. 3	08/07/90	10/89 to 07/90	1117		65	2000		73	2230		77–91	2090–2940
Waipahu West No. 3	09/19/90	03/90 to 08/90	659	50		200	33		130	19–23	1–1	200–260
Mililani No. 2	04/09/91	09/90 to 03/91	840		65	2000		55	1680		66–110	1220–2040
Kunia No. 1	05/06/91	01/91 to 02/91	87		15	700		1	60		0.1–0.1	31–31
Mililani No. 3	05/15/91	09/90 to 04/91	379		65	2000		25	760		55–56	1800–2160
Waipahu East No. 2	06/12/91	09/90 to 05/91	844	50		200	42		170	24–38	2–3	210–310

NOTE: Mass target compound input to contactor computed from volume treated and influent concentration. Mass adsorbed on GAC computed from concentration profiles. Lower end of range assumes zero concentration for the GAC at the bottom of the contactor, which is inaccessible to sampling. Upper end of range assumes GAC at bottom of unsampled portion of contactor has the same concentration as the bottom-most sample collected.

[a]Estimated period during which the contactor was exposed to the influent concentration.

[b]Volume of water treated by the contactor during the exposure period.

The mass of a particular target compound adsorbed by the GAC in a contactor can be determined from the sample profiles. The mass of GAC in each contactor is assumed to be 10 900 kg (24,000 lb). Measured concentrations for a sample collected within a given depth interval are assumed to be representative of the entire layer occurring in the contactor. Note that the GAC at the bottom of the contactor is inaccessible to sampling due to the presence of a stainless steel pipe within the GAC bed. The access hole through which augering is done occurs directly over the pipe. A significant amount of GAC occurs beneath the pipe. Because the GAC at the bottom of the contactor cannot be sampled, the concentrations of target compounds at the bottom must be estimated to determine the total adsorbed mass within the contactor. At one extreme, it can be assumed that the unsampled GAC at the bottom of the contactor is free of any of the target compounds so that the adsorbed concentrations are zero. A second method of estimating the concentration is to assume that the unsampled GAC at the bottom of the contactor contains the same concentrations of target compounds as the bottom-most sample in the profile. The actual concentration at the bottom of the contactor is likely between these two estimates. The range of computed masses of EDB, DBCP, and TCP in each of the sampled contactors is presented in Table 16. The lower end of the range assumes zero concentration for the GAC at the bottom of the contactor, whereas the upper end of the range assumes that the bottom-most sample analyzed is representative of the bottom, unsampled portion of each contactor.

In general, the estimated target compound mass input to a contactor agrees reasonably well with the total adsorbed mass determined from the sampled GAC profile. Differences between the mass input and the mass adsorbed may be attributed to a number of factors including (1) the assumed influent concentration may be inaccurate, (2) the estimated water volume treated may be inaccurate, (3) the unsampled bottom section of the contactor may contain more mass than estimated, and (4) breakthrough from the contactor may have occurred. In the case of Kunia contactor no. 1, sampled on May 6, 1991, the estimated masses of DBCP and TCP input to the contactor exceed the measured adsorbed masses. Kunia contactor no. 1 was a lag contactor for its entire service life. Thus the estimated exposure period could readily have been overestimated, since it is unknown when breakthrough from the lead contactor actually occurred. In addition, the assumed influent concentration is probably overestimated.

The chromatograms for the GAC samples collected from the Waipahu contactors indicate a peak at the retention time for DBCP. Although apparently recovered from the GAC, DBCP has not been detected in Waipahu well water to date. However, it is conceivable that low (not quantifiable) levels of DBCP exist in the groundwater and become concentrated on the GAC in measurable quantities. The reported results for DBCP remain tentative (although GC/EC detection using two columns with different resolving characteristics has been made) until a firm

identification of the compound can be made using the GC/MS system. Based on the total masses of DBCP adsorbed by the Waipahu contactors and the estimated volumes of water treated during the exposure period, the expected influent concentration for DBCP is about 1 to 3 ng/l, which is considerably below the reliable detection limit of 20 ng/l. Thus it is conceivable that DBCP does exist in the Waipahu well water at low levels.

Codistillation

Results of a codistillation extraction are presented in Table 17. GAC samples from the top, middle, and bottom portions of Mililani contactor no. 3 sampled in August 1990 were analyzed. Amounts of DBCP and TCP recovered by the codistillation method are about two orders of magnitude lower than the corresponding amounts recovered by the ultrasonic extraction method. Thus the codistillation procedure for the analysis of carbon samples was considered unacceptable.

TOTAL ORGANIC CARBON ANALYSIS OF WATER SAMPLES

Groundwater samples collected from wellheads and treated water samples collected from the GAC treatment facility at Mililani were analyzed for total organic carbon (TOC). Analyses were run to determine the levels of TOC in Hawai'i groundwater and to determine the effect of GAC on TOC levels and vice versa.

Sampling

Water at all taps was allowed to run for several minutes prior to sample collection. Water samples submitted to Analytical Services Laboratory of the Hawaii Institute of Marine Biology (HIMB) for TOC analysis were collected in 125-ml acid-washed Nalgene bottles. Water samples for analysis by WRRC were collected in 125-ml acid-washed Nalgene bottles or 1-liter glass bottles with teflon-lined caps. Prior to collection, sample bottles and caps were thoroughly rinsed with the water to be sampled and analyzed. Water samples were collected from Mililani Wells I, Mililani Wells II, Mililani GAC treatment facility contactors, Kunia Wells I, Waipahu Wells, and Pearl City Wells II. Samples were stored in an ice chest during transport to the University of Hawai'i. All water samples submitted to Analytical Services Laboratory were frozen until the analysis date. Water samples processed by WRRC were typically analyzed the same day collected; however, when necessary, samples were frozen for analysis at a later date.

TABLE 17. Codistillation of Mililani Contactor No. 3 GAC Samples

Sampling Depth (cm)	GAC Sample Size		Moisture Content[a] (g/g)	Concentration[a]	
	Wet (g)	Dry (g)		TCP (µg/g)	DBCP (µg/g)
0–15	2.00	1.15	0.74	3.9	0.16
61–76	2.00	1.13	0.77	5.1	0.12
107–122	2.00	1.12	0.79	4.4	0.05

NOTE: Mililani contactor no. 3 GAC samples collected on 07 August 1990 by Board of Water Supply and extracted on 09 August 1990.
[a]Dry weight basis.

Analytical Methodology

During 1990, all samples were submitted to Analytical Services Laboratory for TOC analysis. Analytical Services Laboratory utilizes an O.I. Corporation Model 700 Automated TOC Analyzer. Prior to measuring TOC, the sample is acidified to convert inorganic carbonate and bicarbonate ions to dissolved carbon dioxide. An oxidant, potassium persulfate, then reacts with the organic carbon at 95°C to form carbon dioxide. Following complete oxidation, the carbon dioxide is purged from solution, concentrated by trapping, and detected with an infrared detector (O.I. Corporation product literature 1984).

During early 1991, WRRC purchased a Shimadzu Model TOC-5000 Total Organic Carbon Analyzer; after its acquisition all TOC analyses for this project were conducted by WRRC personnel. Prior to measuring TOC, 100 ml of the sample are acidified with 2 M HCl to pH 2. The sample is then purged with ultra-pure air (less than 0.1 ppm CO_2, CO, and HC) for a minimum of 5 minutes. Because samples are purged with air, the measured concentrations do not include volatile organics. Thus measured concentrations actually reflect nonpurgeable organic carbon (NPOC) rather than total organic carbon.

Results and Discussion

All water samples collected between July 23 and October 11, 1990, were submitted for analysis to Analytical Services Laboratory on two separate occasions. Water samples collected after 1990 were analyzed by WRRC personnel. Results of the TOC analyses for wellhead samples are presented in Table 18, for Mililani GAC contactor water samples in Table 19, and for tap, deionized, distilled, and aerated water samples in Table 20.

Results of the wellhead samples processed by Analytical Services Laboratory indicate that groundwater in the Pearl Harbor basal aquifer has a typical TOC concentration of about 0.3 mg/l. The TOC concentration of 0.53 mg/l from Waipahu Wells Pump 1 was considerably

TABLE 18. TOC Concentrations in Hawai'i Groundwater

Sample	Sampling Date	TOC Concentration (mg/l)
Kunia Wells I Pump 2	05/06/91	2.58
Kunia Wells I Pump 4	05/06/91	2.62
Mililani Wells I Pump 2	07/23/90	0.34
	10/11/90	0.33
	06/28/91	0.85
	08/21/91	1.69
Mililani Wells I Pump 3	07/23/90	0.35
	10/11/90	0.25
	06/28/91	1.63
	08/12/91	0.48
	08/21/91	0.76[a]
	09/20/91	0.75
Mililani Wells II Pump 1	07/23/90	0.32
	08/21/81	2.64
	09/20/91	0.65
Mililani Wells II Pump 2	08/21/91	1.34
Pearl City Wells II	10/04/91	0.98
Waipahu Wells Pump 1	09/19/90	0.53
Waipahu Wells Pump 2	06/12/91	1.34
Waipahu Wells Pump 3	09/19/90	0.29
	06/12/91	0.94
Waipahu Wells Pump 4	06/12/91	1.69

[a]Inhibition suspected.

TABLE 19. TOC Concentrations in Mililani GAC Contactor Water Samples

Sample	Position	Sampling Date	TOC Concentration (mg/l)
Mililani Contactor 1	Lag	10/11/90	0.32
Mililani Contactor 2	Lag	07/23/90	0.28
	Alone	10/11/90	0.31
Mililani Contactor 3	Lead	10/11/90	0.29
	Lead	04/19/91	4.16
Mililani Contactor 4	Lead	07/23/90	0.30
	Lead	06/28/91	1.31
Mililani Contactor 5	Lead	07/23/90	0.27
	Lag	04/12/91	1.86
Mililani Contactor 6	Lead	10/11/90	0.28
	Lead	04/19/91	3.34
Mililani Contactor 7	Lag	07/23/90	0.25
	Alone	10/11/90	0.26
	Lead	04/12/91	1.89
	Lead	04/19/91	1.00
Mililani Contactor 8	Lag	10/11/90	0.18
Mililani Contactor 9	Single pass	04/19/91	0.91
Mililani Contactor 12	Single pass	04/19/91	7.49
	Single pass	08/12/91	0.54
Mililani Influent		07/23/90	0.27
		10/11/90	0.23
		04/12/91	6.68
		04/19/91	6.97
		06/28/91	1.48
		07/03/91	1.26
		08/12/91	0.87
		08/21/91	4.46
		09/20/91	1.49
Mililani Effluent (odd contactors)		07/23/90	0.26
		10/11/90	0.18
		04/12/91	3.62
		07/03/91	1.35
		09/20/91	1.01
Mililani Effluent (even contactors)		10/11/90	0.21
		04/12/91	2.80
		06/28/91	0.93
		07/03/91	1.07
		09/20/91	0.66

TABLE 20. TOC Concentrations in Treated Water Samples, O'ahu, Hawai'i

Sample	Sampling Date	TOC Concentration (mg/l)
Tap Water, Holmes Hall Room 181	10/11/90	0.29
Deionized Water, UH Sanitary Engineering Laboratory	09/16/90	0.21
Deionized, Distilled Water, UH Sanitary Engineering Laboratory	09/16/90	0.35
Deionized, Double-Distilled Water, UH Sanitary Engineering Laboratory	09/16/90	0.27
Deionized, Distilled, GAC Treated Water, UH Sanitary Engineering Laboratory	09/26/90	0.28
Aerated Water, Mililani Wells I, Pump 2	10/11/90	0.31
Aerated Water, Mililani Wells I, Pump 3	10/11/90	0.28

NOTE: Analyses performed by Analytical Services Laboratory, Hawaii Institute of Marine Biology.

higher than TOC concentrations from Mililani Wells I and II. However, the TOC concentration of 0.29 mg/l from Waipahu Wells Pump 3 was similar to concentrations from the Mililani wells. Pearl Harbor aquifer well samples analyzed by WRRC had TOC (NPOC) concentrations ranging from 0.48 to 2.62 mg/l (Table 18). The highest concentrations in selected well water samples were from the Kunia Wells I site.

Comparison of lead and lag contactor pair TOC concentrations as well as comparison of influent and effluent concentrations generally indicate that GAC treatment of water by the Mililani contactors reduces TOC concentrations (Table 19). However, there are several exceptions to this generalization. For instance, on October 11, 1990, lead contactor no. 3 had a TOC level of 0.29 mg/l, while lag contactor no. 1 had a TOC level of 0.32 mg/l.

There are a few other isolated inconsistencies in the TOC data. For instance, on July 23, 1990, the TOC concentrations in Mililani Wells I Pumps 2 and 3 were 0.34 and 0.35 mg/l, respectively, and the TOC concentration in Mililani Wells II Pump 1 was 0.32 mg/l. On the same day, however, the influent concentration to the GAC treatment facility was 0.27 mg/l, which is lower than the source concentrations. On August 21, 1991, the opposite effect was observed; that is, the concentrations measured in the wellhead samples were considerably lower than the measured influent concentration of 4.46 mg/l. Additional analyses of wellhead samples and water samples from the Mililani treatment facility are necessary to add to the TOC database and improve our understanding of the impact of GAC treatment on TOC concentrations.

During 1990, a number of control and treated water samples were also submitted to the Analytical Services Laboratory for TOC analysis (Table 20). Tap water from the University of Hawai'i (Holmes Hall Room 181) had a TOC concentration of 0.29 mg/l. Deionized water from the University of Hawai'i Sanitary Engineering Laboratory (Holmes Hall Room 286) contained a TOC level of 0.21 mg/l. Deionized and distilled as well as deionized and double-distilled water samples from the Sanitary Engineering Laboratory contained TOC levels of 0.35 and 0.27 mg/l, respectively.

In an attempt to reduce the TOC level of the deionized, double-distilled water, 50 g of virgin GAC was added to 900 ml of water. The mixture was stirred for 24 hours to allow for adsorption and then allowed to settle for 6 days. The GAC-treated water was found to contain a TOC level of 0.28 mg/l. Apparently, the GAC treatment was ineffective at reducing the TOC level. The extended GAC settling period may have contributed to the increased TOC level from 0.27 to 0.28 mg/l.

This preliminary attempt to reduce TOC levels with GAC suggests that the naturally occurring background organic matter in groundwater does not readily adsorb to GAC. However, because this result has not been verified, it should not be considered conclusive. WRRC is currently conducting adsorption experiments designed to assess the role of background organic matter in the sorption process.

To test the impact of aeration on TOC levels in Mililani groundwater, samples from Mililani Wells I Pumps 2 and 3 were aerated for 30 minutes at a rate of 2.4×10^{-5} m^3/s (3 cfh). Approximately 100 ml of water were aerated directly in the sample bottles. Compressed air was filtered to minimize contamination of the samples. Air was bubbled in the water samples through a Pasteur pipette (1.2-mm diameter tip opening). Aeration did not appear to have a major impact on the TOC level. Aeration reduced the TOC level in water from Mililani Wells I Pump 2 from 0.33 to 0.31 mg/l. However, the TOC concentration increased from 0.25 to 0.28 mg/l after aeration of Mililani Wells I Pump 3 water. Note that the effect of aeration is probably difficult to isolate since samples must be additionally purged during analysis.

CATION/ANION ANALYSIS OF WATER SAMPLES

The impact of inorganic cations and anions on the effective life of the GAC at the Mililani treatment facility was assessed by analyzing influent, contactor, and effluent water samples for major ions. Typically, the unused portions of water samples collected for pesticide analysis were analyzed for ions.

Analytical Methodology

Water samples were analyzed for major inorganic ions by WRRC personnel using a dual pump Dionex ion chromatography system arranged for anion/cation analysis (suppressed ion chromatography analysis). The analytical column used for the anion analysis is an IONPAC AS4A column. Eluant for the anion analysis is 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$. The cation analysis is made using an IONPAC CS10 analytical column and 40 mM HCl/4 mM DAP•HCl (DL-2,3-diaminopropionic acid monohydrochloride) eluant. Anion and cation runs are 9 and 20 minutes, respectively, with direct injection of 100-µl samples.

Results and Discussion

Results of the cation and anion analyses are presented in Table 21. Inspection of the results of samples collected on the same date reveals little difference in cation and anion concentrations among the influent, contactor, and effluent samples at Mililani. This seems to indicate that the GAC's capacity to adsorb inorganic ions was exhausted or, more likely, that the inorganic ions were unaffected by adsorption processes so that they moved through the GAC contactors as conservative tracers.

INFRARED ANALYSIS OF GAC SAMPLES

Naturally occurring background organic matter in groundwater may play an important role in the removal of contaminants by GAC. Thurman (1985) reported that the median concentration of dissolved organic carbon is 0.7 mg/l for sand and gravel, limestone, and sandstone aquifers and 0.5 mg/l for igneous aquifers. As for deep groundwaters (greater than 150 m), Thurman (1985) suggested that humic substances account for 12% to 33% of the dissolved organic carbon. In the Pearl Harbor basaltic aquifer on O'ahu, total organic carbon is typically about 0.3 mg/l. Although quantified, the characteristics of the organic carbon in O'ahu's groundwater have not been studied to date.

GAC samples collected at the Mililani and Waipahu treatment facilities were analyzed using infrared spectroscopy to characterize the nature of organic compounds adsorbed by GAC. In particular, it was desired to determine whether the adsorbed compounds exhibit characteristics similar to humic acids. Chloroform extracts from Mililani contactor no. 3 and Waipahu west contactor no. 3 GAC were compared with a humic acid salt standard.

TABLE 21. Cations and Anions in Mililani Contactor Water Samples

Sample	Position	Sampling Date	Concentration (mg/l)								
			Na^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
Contactor 3	Lead	04/19/91						17	4		4
Contactor 4		06/28/91	17	1	5	6		16	4		4
Contactor 5	Lag	04/18/91						18	3		4
Contactor 6	Lead	04/19/91	16	1	6	6		17	4	0.318	4
Contactor 7	Lead	04/18/91						18	4	0.311	4
	Lead	04/19/91						17	4		4
Contactor 8	Lag	04/18/91						18	3		4
Contactor 9	Single	04/19/91						17	4	0.338	4
Contactor 12	Single	04/19/91	16	1	6	6		17	4	0.383	4
	Single	08/12/91	16	1	6	6		16	4	0.304	5
Influent		04/18/91	16	1	6	6		18	3		4
		04/19/91					0.061	18	4	0.338	5
		06/28/91	15	1	5	6		16	4		4
		08/12/91	15	1	6	6	0.007	17	4		5
		08/21/91	16	1	7	8	0.024	18	5	0.661	6
		09/20/91	14	1	5	5	0.015	17	5	0.310	4
Effluent (odd contactors)		04/18/91	16	1	6	6		18	4	0.326	4
		09/20/91	14	1	5	5		17	5		5
Effluent (even contactors)		04/18/91	16	1	6	6		18	3		4
		06/28/91	16	1	5	6		15	4		4
		09/20/91	14	1	5	5		17	5	0.287	4

Sampling

A description of the sampling method is provided above in the section on pesticide analysis of GAC samples. For the infrared analysis, only the samples from the uppermost sections of Mililani contactor no. 3 and Waipahu west contactor no. 3 were tested.

Reagents

Spectra-grade chloroform was used for Soxhlet extraction of adsorbed compounds. A humic acid salt standard was obtained from Aldrich Chemical Co., Inc. (Cat. No. H1,675-2). The humic acid salt is a colloidal acid product resulting from the decomposition of organic matter obtained from open-pit mining in Germany.

Analytical Methodology

Soxhlet Extraction

GAC samples were spread in a thin layer and dried at 40°C for 48 hours. Thirty grams of dried GAC were placed in a 33 mm (internal diameter) × 80 mm (external length) Whatman single-thickness cellulose extraction thimble. The thimble was placed in a Soxhlet extractor (45/50 top joint and 24/40 bottom joint), which was then connected to an Allihn condenser at the top joint and a 300-ml round-bottom boiling flask, containing 250 ml of chloroform, at the bottom joint. The boiling flask was seated in a heating mantle. The GAC sample was extracted for 44 hours at an extraction cycle time of about 6 minutes.

Following Soxhlet extraction, the solvent was transferred to a flask with a Kuderna-Danish concentrator. The top joint of the flask was connected to a distilling column that was attached to a Graham condenser. The concentrator was immersed in a water bath maintained at about 86°C. The solvent volume was reduced by distillation to approximately 20 ml. A virgin GAC sample was similarly extracted for control purposes.

A humic acid salt standard was also prepared by Soxhlet extraction with chloroform. Approximately 2 g of humic acid salt was placed in an extraction thimble. The humic acid salt was then extracted in a manner similar to that for the GAC sample.

Infrared Spectroscopy

A small volume (approximately 1 ml) of the Soxhlet solvent extract was placed in an NaCl bridge for analysis with a Shimadzu infrared spectrophotometer (Model IR-435) connected to a Shimadzu Model DR-1 data recorder. The virgin GAC sample extract was used as a reference for the Mililani and Waipahu GAC contactor samples. Chloroform solvent was used as a reference for the humic acid salt standard.

Results and Discussion

Prior to using the Soxhlet apparatus for extraction, ultrasonic solvent extraction of the GAC samples was attempted. However, the infrared spectra of the spent GAC extracts obtained by ultrasonic extraction failed to reveal the presence of compounds resembling humic acids. Subsequently, Soxhlet extraction was performed with greater success.

The infrared spectra of the Mililani and Waipahu west GAC extracts are presented in Figures 7 and 8, respectively. The spectrum of the humic acid salt standard is presented in Figure 9. Typical infrared spectra of humic acids (MacCarthy and Malcolm 1989) are shown in Figure 10. Humic acids, although derived from varying environments, typically exhibit similar infrared spectra, which indicates that the net functional group content in humic acids may be

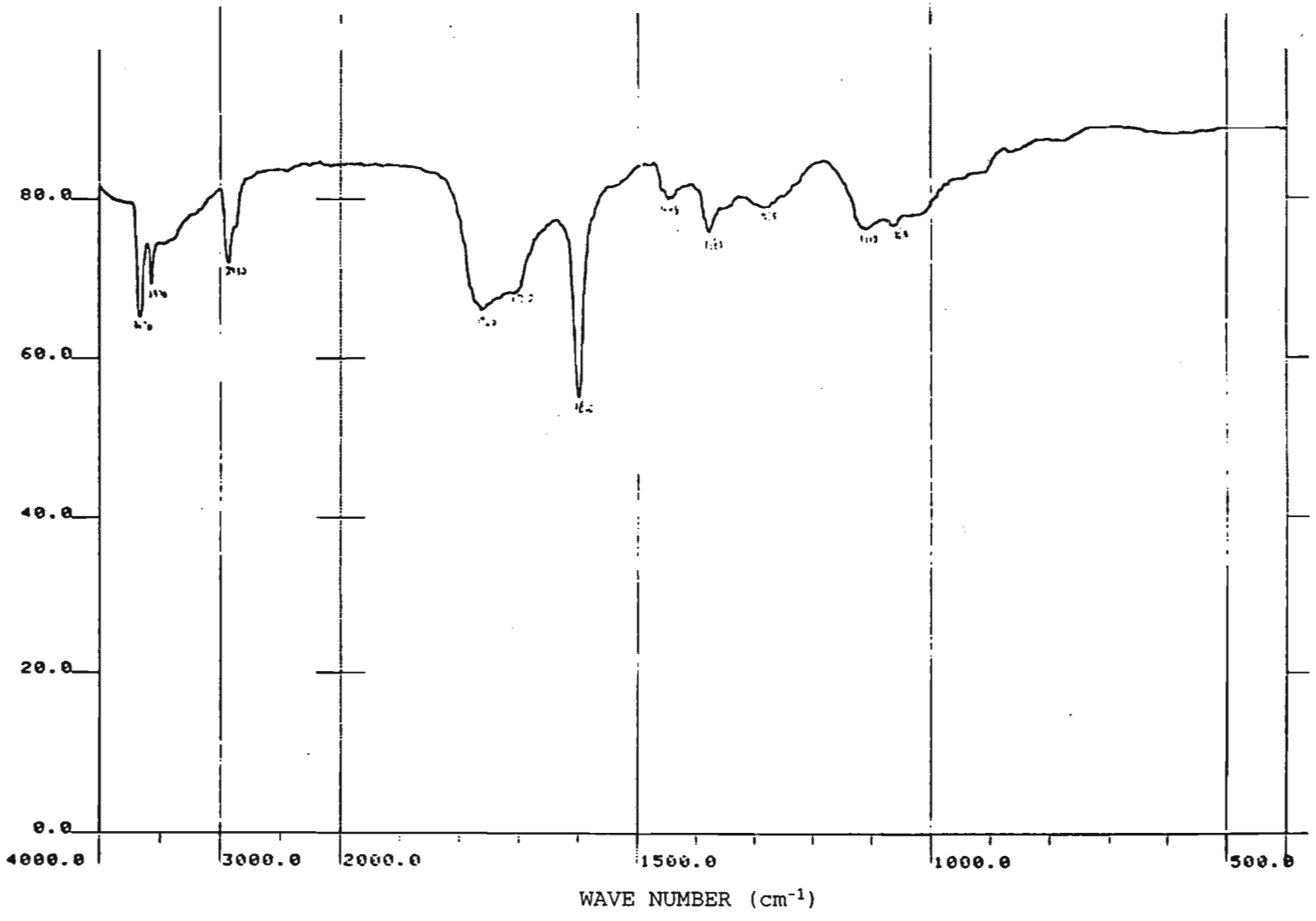


FIGURE 7. Mililani contactor no. 3 GAC infrared spectrum

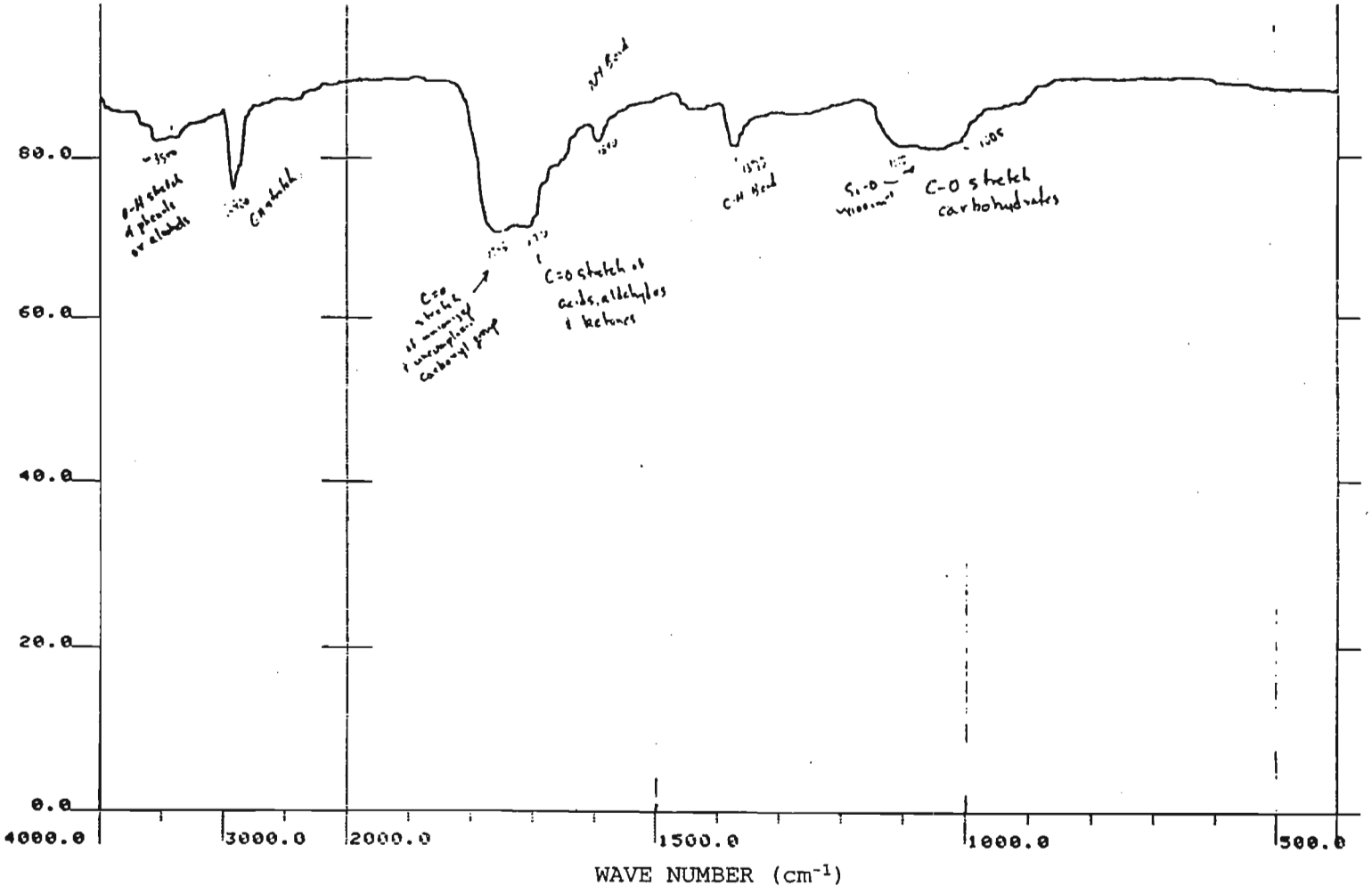


FIGURE 8. Waipahu west contactor no. 3 GAC infrared spectrum

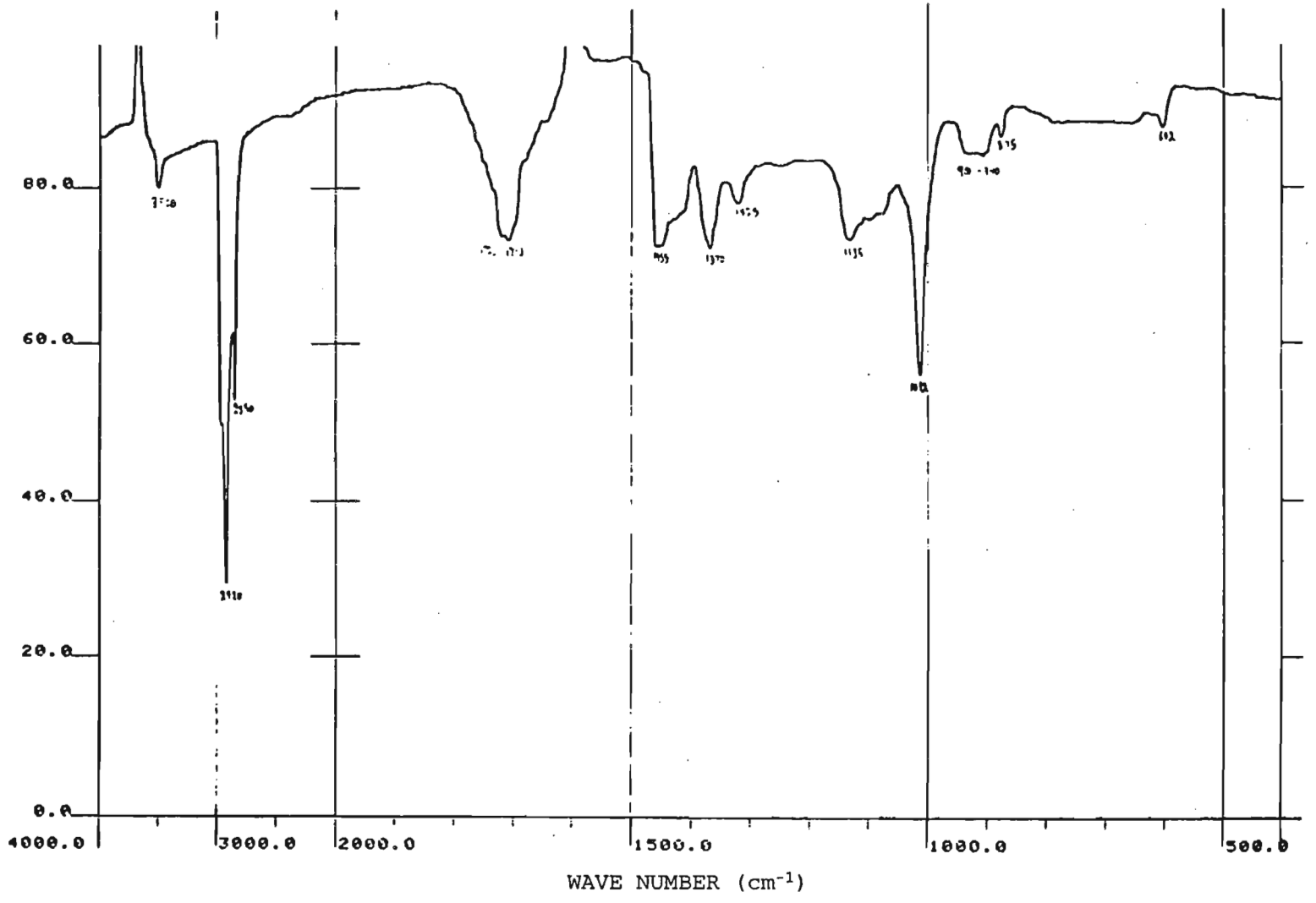
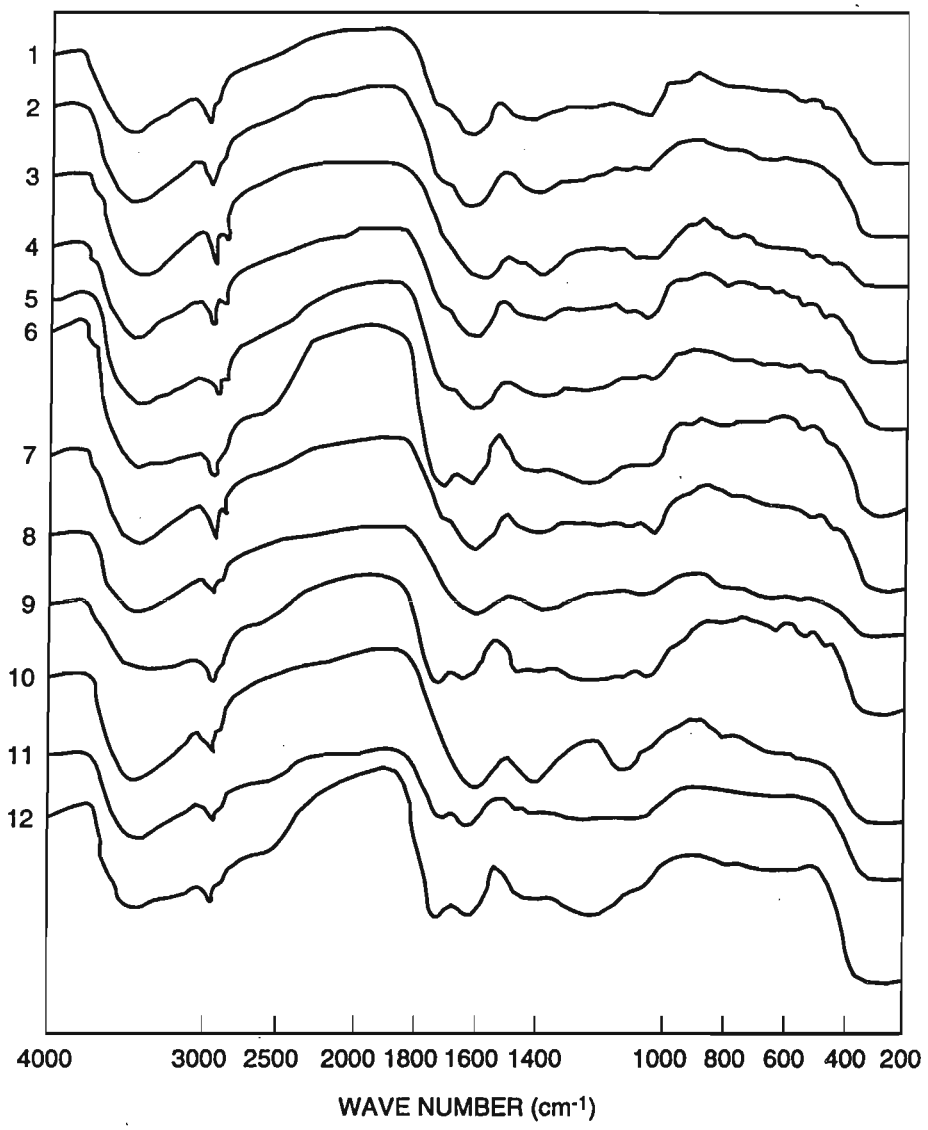


FIGURE 9. Commercial humic acid salt infrared spectrum



From MacCarthy and Malcolm 1989

FIGURE 10. Infrared spectra of 12 commercial humic acids

similar (MacCarthy and Rice 1985). In addition, the spectra are characteristically quite simple despite the fact that humic substances are complex and heterogeneous. This apparent simplicity may be due to severe overlapping of absorption bands from the individual constituents in the complex mixture, thus accounting for broad bands which are few in number (MacCarthy and Rice 1985).

The humic acid salt standard exhibits strong absorption peaks at about 2920, 2850, 1720, 1450, and 1370/cm, which are characteristic of humic acids. Bands at 2920 and 2850/cm are generally more pronounced in humic acids than in fulvic acids and have been attributed to asymmetric and symmetric stretching vibrations of aliphatic C–H bonds in methyl

and/or methylene units. The 1720/cm band is generally attributed to C=O stretching vibration. The 1450/cm band has been attributed to the bending vibration of aliphatic C–H groups (MacCarthy and Rice 1985). Additional absorption peaks at about 3500, 1320, 1140, 1020, 920, 880, and 620/cm, however, are not characteristic of humic acids. This may reflect the presence of impurities in the commercial humic acid salt.

The Mililani GAC extract exhibits absorption peaks at frequencies of 2900, 1750, 1600, 1450, and 1380/cm, which correspond to infrared absorption bands of humic substances. Additional peaks at approximately 3680, 3580, 1280, and 1120/cm may not be representative of a humic substance. The absorption peak at about 1050/cm represents Si–O stretching. Silica in the groundwater of O'ahu's basaltic aquifers is typically about 35 mg/l (Visher and Mink 1964); this may partially explain the presence of the latter absorption peak.

The Waipahu GAC extract exhibits absorption peaks at frequencies of 3400, 2900, 1750, 1590, and 1370/cm, which correspond to infrared absorption bands of humic substances. As with the Mililani GAC extract, a broad absorption peak at about 1100/cm, representing Si–O stretching, occurs.

MICROBIOLOGICAL ANALYSES

Water samples from the Mililani GAC treatment facility and GAC samples from Mililani and Waipahu contactors were collected for microbiological analysis. Total heterotrophic bacteria in influent, effluent, and contactor water samples collected at the Mililani treatment facility (contactor no. 3 sampled in August 1990) were generally below 100 CFU/ml. Total heterotrophic bacteria profiles for Mililani contactor no. 3 and Waipahu west contactor no. 3 (sampled September 1990) exhibited highest concentrations near, but not at, the bottom of the contactors. No conclusions can be drawn at this time regarding the impact of bacteria on GAC performance. A detailed description of the analytical methodology, results, and discussion related to the microbiological analyses is contained in an unpublished report by J. Dippel.

SCANNING ELECTRON MICROSCOPY

As part of this study, bacteria have been recovered from spent GAC samples obtained from contactors used to remove organic compounds present in Hawai'i's groundwaters. The role of the biological growth in terms of treatment efficiency is not known at present. Biological activity may enhance the effective life of the GAC through the process of bioregeneration of the carbon particles (Speitel et al. 1987; DeWaters and DiGiano 1989). On

the other hand, biological growth could reduce the adsorption capacity of the GAC if adsorption sites are effectively blocked by an extensive biological slime layer.

GAC samples from the Kunia and Mililani treatment facilities were analyzed with a scanning electron microscope (SEM) to establish the extent of biological growth and slime on the spent carbon surfaces. The purpose of the SEM analysis is to determine whether extensive biological growth is effectively blocking GAC adsorption sites, resulting in premature breakthrough of target organic compounds from the GAC contactors.

Sampling

GAC from Kunia contactor no. 1 was aseptically sampled on May 6, 1991, using a sterilized 10.2-cm (4-in.) bucket auger. The sample was collected from the top 10 cm of the carbon profile, placed in a sterile 500-ml Nalgene bottle, and stored in an ice chest for transport to the University of Hawai'i. Two GAC samples from Mililani contactor no. 3 were aseptically sampled on May 15, 1991. The first sample was collected from the top 25 cm of the profile with a sterilized 10.2-cm bucket auger. The second sample was collected at the 69 to 93 cm depth increment of the carbon profile with a sterilized 5.1-cm (2-in.) bucket auger. Samples from Mililani were placed in sterile 500-ml Nalgene bottles and stored in an ice chest for transport to the University of Hawai'i. All samples were delivered to the Biological EM Facility of the University of Hawai'i on May 15, 1991. Samples were refrigerated overnight at the EM Facility prior to processing.

Methodology

Samples were prepared for SEM analysis by Tina M. Weatherby of the Biological EM Facility. Dry virgin GAC used as a control was processed with the other samples. A description of the sample preparation provided by Weatherby is given below:

1. Fix samples in two changes of 2.5% glutaraldehyde in 0.1M phosphate buffer, pH 7.4, for 1 hour total
2. Wash in two changes of 0.1M phosphate buffer for 20 minutes total
3. Postfix in 1% osmium tetroxide in 0.1M phosphate buffer for 1 hour
4. Wash in 0.1M phosphate buffer for 5 minutes
5. Dehydrate in a graded series of ethanol to absolute ethanol
6. Critical point dry in a Tousimis Autosamdri-810 critical point dryer
7. Mount on aluminum stubs
8. Coat with 30 nm gold/palladium

The sample preparation procedure is designed to maintain the integrity of the microorganisms attached to the carbon surfaces. The glutaraldehyde fixation process forms

crosslinks with proteins in the cell membrane, thus establishing a rigid network that preserves fine structures. Postfixation with osmium tetroxide preserves the liquid portion of the membrane. Critical point drying circumvents problems associated with air drying, such as disruption of cellular structures caused by surface tension (Weber et al. 1978). Prepared samples were viewed and photographed with a Hitachi S-800 Field Emission Scanning Electron Microscope.

Results and Discussion

Typical activated carbon granules at 40× magnification are shown in Figure 11. Pores of various sizes and configurations are visible on the GAC surface of the control sample, which is free of biological growth (Figure 12).

Biological growth is evident on GAC samples obtained from Kunia contactor no. 1. Rod-shaped bacteria (Figures 13 and 14) and slime (Figures 15 and 16) are present on the carbon surface. The rod-shaped bacteria visible in Figure 14 are typically about 1 μm long. The stalked forms present in Figure 14 are about 1.5 μm in length and are thus probably too small to be considered protozoans; rather, they may be fungi with thread-like mycelia. The polysaccharide slime matrix visible in Figures 15 and 16 is likely the product of bacteria colonizing the GAC surfaces.

Biological growth was somewhat less abundant on the Mililani contactor no. 3 GAC samples. This may indicate that (1) biological activity is greater in the Kunia contactor than in the Mililani contactor or (2) longer storage resulted in further biological growth on the Kunia GAC sample. (Note that GAC previously collected from Mililani contactor no. 3 in August 1990 and stored under refrigerated conditions for approximately six months was prepared for SEM analysis and viewed in February 1991. This preliminary analysis of GAC stored for six months revealed significant occurrences of rod-shaped bacteria [Figures 17 and 18] which were not evident in fresher samples and, thus, may be attributed to the extended storage period.) In any event, biological growth was present at both sampling depths in Mililani contactor no. 3 GAC sampled in May 1991. A stalked form on the GAC from the top of the contactor is shown in Figure 19. A fine, delicate slime can be seen on the GAC collected at a depth of 69 to 93 cm in Figure 20. This indicates that the fixation process was effective at preserving the delicate structure.

The SEM analysis indicates that biological growth is present on the GAC collected from Mililani and Kunia. The impact of biological growth on the adsorption capacity of the GAC cannot be determined with certainty from the SEM analysis. However, based on the SEM viewing of the GAC samples, biological growth does not appear to be alarmingly extensive. Evidence of biological activity could not be detected over a significant portion of the GAC

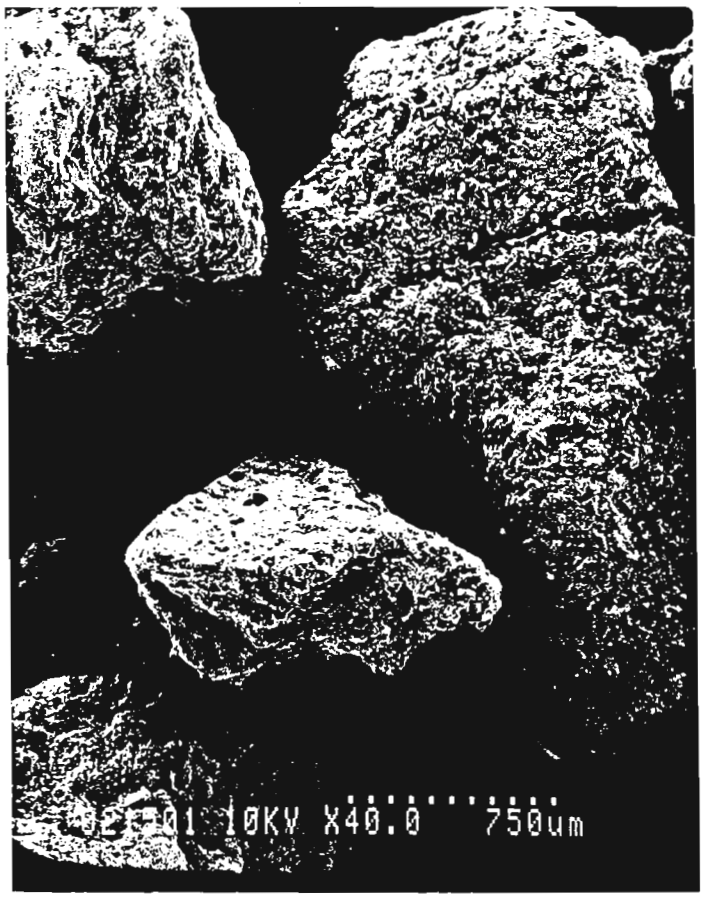


FIGURE 11. Typical GAC granules (magnification 40×)

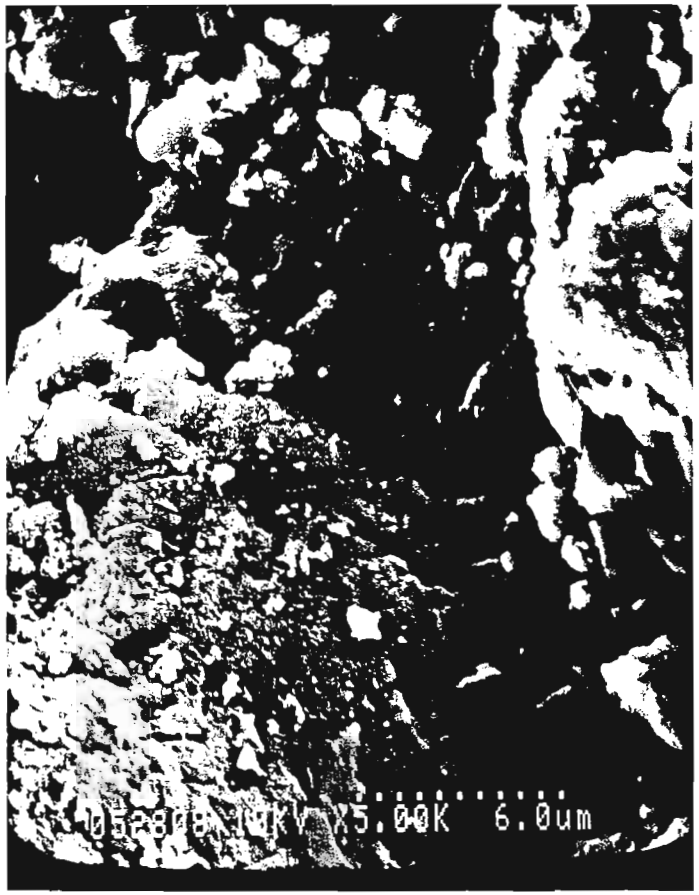


FIGURE 12. Virgin GAC control (magnification 5,000×)

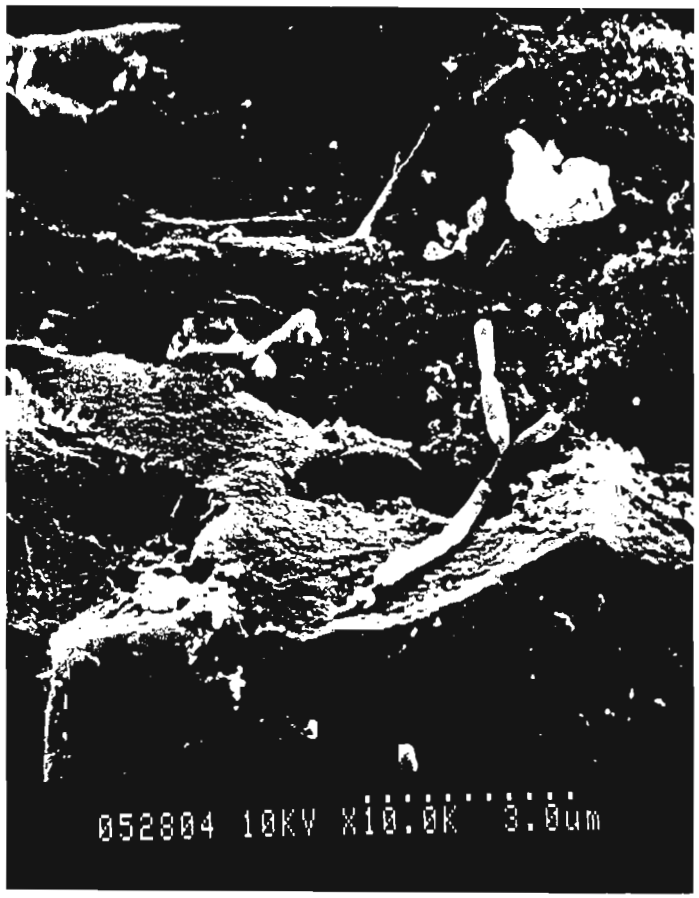


FIGURE 13. Rod-shaped bacteria on GAC from Kunia contactor no. 1 sampled in May 1991 (magnification 10,000×)

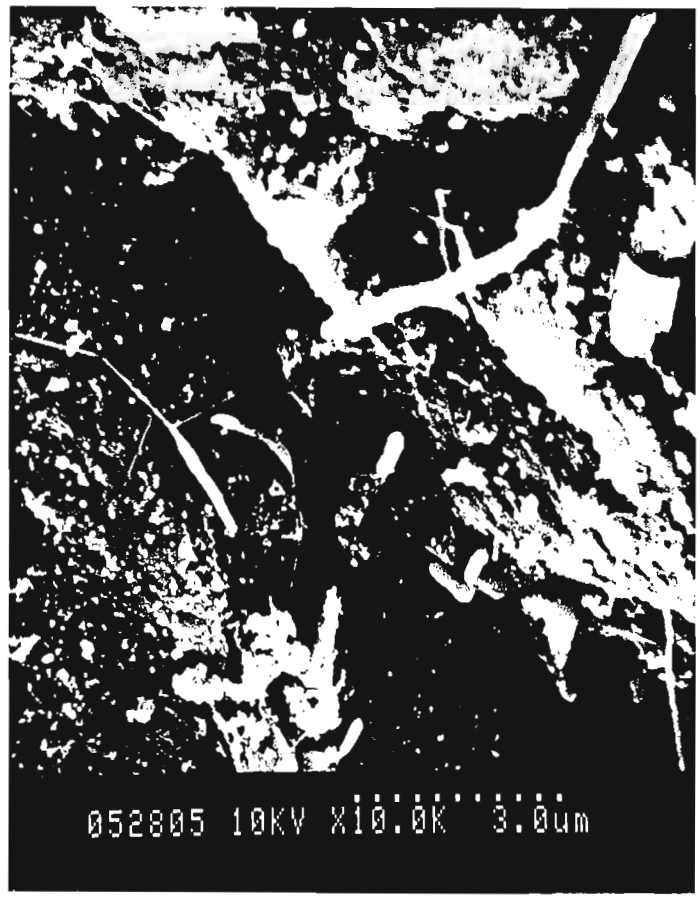


FIGURE 14. Rod-shaped bacteria and stalked forms on GAC from Kunia contactor no. 1 sampled in May 1991 (magnification 10,000×)

FIGURE 15. Slime (lower right) on GAC from Kunia contactor no. 1 sampled in May 1991 (magnification 5,000×)

FIGURE 16. Close-up view of slime on GAC from Kunia contactor no. 1 sampled in May 1991 (magnification 10,000×)

FIGURE 17. Rod-shaped bacteria on Mililani GAC (collected in August 1990) viewed after six months of storage (magnification 13,000×)

FIGURE 18. Rod-shaped bacteria on Mililani GAC (collected in August 1990) viewed after six months of storage (magnification 7,000×)

FIGURE 19. GAC from Mililani contactor no. 3 sampled in May 1991 (magnification 10,000×)

FIGURE 20. Slime on Mililani contactor no. 3 GAC sampled in May 1991 (magnification 50,000×)

surface and, in fact, was at times not present at all. Thus biological growth and slime may not be the major factors responsible for reducing the effective life of the GAC.

MINICOLUMN STUDY

The use of minicolumns to predict full-scale GAC contactor performance has a number of advantages over other methods including (1) the cost and time needed to predict contactor performance are greatly reduced relative to the cost and time associated with a pilot-scale study; (2) extensive parameter estimates which are necessary for mathematical modeling are not needed in minicolumn studies; (3) a relatively small amount of test water is needed, which makes it possible to transport the water to a laboratory where the minicolumn study can be established; and (4) both adsorption capacity and kinetics are addressed (Crittenden et al. 1991).

Small-scale columns have been used successfully to predict pilot-scale column performance (Crittenden et al. 1986a, 1987, 1991; McGuire et al. 1991). However, the use of minicolumns to predict full-scale performance may sometimes lead to poor estimates of carbon usage rates or operation costs if bacterial growth or background organic matter play significant roles in the adsorption process. In addition, the minicolumn must be properly scaled to ensure performance similarity with the large-scale adsorber.

Because of the relatively short time required to run a minicolumn test, the effects of microbial activity on the adsorption process may not be apparent. Microbial activity may enhance full-scale contactor performance if biodegradation of target organic compounds is significant or if bioregeneration of adsorption sites occurs (Chudyk and Snoeynik 1984; DeWaters and DiGiano 1989; Speitel et al. 1987, 1989a, 1989b, 1989c; Speitel and DiGiano 1983, 1987; Li and DiGiano 1983; Stratton et al. 1983; Bouwer and McCarty 1982). However, if bacterial growth is significant or if a slime layer accumulates on the carbon surface, thus occupying adsorption sites, adsorption of target compounds may be reduced.

Naturally occurring background organic matter can affect adsorption of target compounds in full-scale contactors by directly competing with the target compounds for adsorption sites (Najm et al. 1990; Speth and Miltner 1989; Narbaitz and Benedek 1986). In addition, a portion of the background organics may advance ahead of the target compounds in the contactor, thus effectively preloading the GAC and restricting subsequent adsorption of target compounds as the contaminant front advances (Zimmer et al. 1987; Munz et al. 1990; Arbuckle 1980). If the effects of background organic matter are not properly addressed by minicolumns, full-scale

contactor performance may be overestimated (Crittenden et al. 1991; Speth and Miltner 1989; Speth 1989; Summers et al. 1989).

Scaling Equations for Minicolumn Sizing

Proper scaling of a minicolumn—which involves selection of column size, hydraulic loading, particle size, and empty bed contact time—will ideally result in identical breakthrough profiles for both the minicolumn and the full-scale adsorbers. The procedure for scaling a minicolumn is dependent on the choice of the mathematical model used to describe the transport phenomenon. The dispersed-flow, pore-surface-diffusion model (DFPSDM) is commonly used to simulate breakthrough of an adsorbate from a full-scale contactor. The DFPSDM accounts for many mechanisms that are typically important in assessing transport behavior in GAC columns, including (1) advective flow, (2) hydrodynamic dispersion and diffusion, (3) film transfer resistance to mass transport from the mobile to the immobile phase (film diffusion), (4) local adsorption equilibrium between the sorbed phase on the solid surface and the solute in the intraparticle immobile fluid, and (5) surface and pore diffusion as intraparticle mass transport mechanisms (Crittenden et al. 1987).

If the DFPSDM adequately describes the transport process within a GAC medium, then the model can be used to develop scaling equations for a minicolumn design. Examination of the model equations leads to six independent dimensionless quantities: (1) Peclet number, (2) Stanton number, (3) pore diffusion modulus, (4) surface diffusion modulus, (5) pore solute distribution parameter, and (6) surface solute distribution parameter (Crittenden et al. 1986a, 1987). To obtain performance similarity between the minicolumn and the full-scale adsorber, each of the six dimensionless groups must remain constant as the full-scale adsorber is scaled down to a minicolumn. By setting the dimensionless groups for the full-scale adsorber equal to the respective minicolumn values, scaling equations that account for key design parameters can be developed.

The scaling relationships developed by Crittenden et al. (1986a, 1987) assume that (1) the physical characteristics (bulk density and void fraction) of the GAC remain constant with particle size, (2) the equilibrium adsorption capacity of the activated carbon remains constant with particle size, and (3) the influent concentrations of the full-scale adsorber and minicolumn are the same. In addition, the scaling relationships do not account for the effects of backwashing. Based on the above assumptions, scaling equations have been developed for three different cases: (1) intraparticle diffusivity remains constant with particle size (Crittenden et al. 1986a), (2) intraparticle diffusivity is linearly dependent on particle size (Crittenden et al. 1987), and (3) the general case in which intraparticle diffusivity is some function of particle size (Crittenden et al. 1987).

Constant Diffusivity

If intraparticle diffusivity is independent of particle size, the following scaling relationships can be used in designing a minicolumn (Crittenden et al. 1986a, 1991):

$$\frac{EBCT_{sc}}{EBCT_{lc}} = \frac{R_{sc}^2}{R_{lc}^2} = \frac{T_{sc}}{T_{lc}} \quad (1)$$

$$\frac{q_{sc}}{q_{lc}} = \frac{R_{lc}}{R_{sc}} \quad (2)$$

where

EBCT = empty bed contact time [T]

R = GAC particle radius [L]

T = time to perform test [T]

q = hydraulic loading [L/T]

The subscripts sc and lc refer to the small column and large column, respectively.

Linear Relationship

Assuming a linear relationship between intraparticle diffusivity and GAC particle size, the following scaling equations are valid (Crittenden et al. 1987, 1991):

$$\frac{EBCT_{sc}}{EBCT_{lc}} = \frac{R_{sc}}{R_{lc}} = \frac{T_{sc}}{T_{lc}} \quad (3)$$

$$\frac{q_{sc}}{q_{lc}} = \frac{R_{lc}}{R_{sc}} \cdot \frac{Re_{sc,min}}{Re_{lc}} \quad (4)$$

where

Re = Reynolds number

$Re_{sc,min}$ = the minimum Reynolds number for the minicolumn that guarantees the effects of dispersion and external mass transfer will not be greater in the minicolumn than in the large column. A value of 1 for $Re_{sc,min}$ usually yields good results, but lower values may be used if head loss and column length are unacceptable (Crittenden et al. 1991, p. 83)

All other terms are as defined above.

Note: Equation 4 seems to reduce to the identity 1 = 1 if the Reynolds number is expressed as $Re = vd\rho/\mu = (q/n)\bullet(2R)\bullet\rho/\mu$, where n (porosity), ρ (fluid density), and μ (fluid dynamic viscosity) of the full-scale adsorber are nearly equal to the minicolumn values (which is a reasonable assumption).

General Case

For the general case in which intraparticle diffusivity is a function of particle size, the following scaling equations may be used (Crittenden et al. 1987):

$$\frac{EBCT_{sc}}{EBCT_{lc}} = \frac{R_{sc}^2}{R_{lc}^2} \bullet \frac{D_{s,lc}}{D_{s,sc}} = \frac{T_{sc}}{T_{lc}} \quad (5)$$

$$\frac{q_{sc}}{q_{lc}} = \frac{R_{lc}}{R_{sc}} \bullet \frac{Re_{sc,min}}{Re_{lc}} \quad (6)$$

where

D_s = surface diffusivity [L^2/T]

All other terms are as defined above.

The following additional conditions must be met for proper scaling of the minicolumn (Crittenden et al. 1987, 1991):

1. $200 < Re \bullet Sc < 200{,}000$

   where Re = Reynolds number = $vd\rho/\mu$

   where v = interstitial velocity of water [L/T]

   d = GAC particle diameter [L]

   ρ = fluid density [M/L^3]

   μ = fluid dynamic viscosity [M/LT]

   Sc = Schmidt number = $\mu/(\rho \bullet D_L)$

   where ρ = fluid density [M/L^3]

   μ = fluid dynamic viscosity [M/LT]

   D_L = liquid diffusivity [L^2/T]

2. minicolumn Peclet number > large column Peclet number

   where Pe = Peclet number = $L \bullet v/D_e$

   where L = length of fixed bed [L]

   v = interstitial velocity of water [L/T]

   D_e = axial dispersivity [L^2/T]

3. minicolumn diameter > 50 × GAC particle diameter

Mililani GAC Contactor Parameters

To properly scale a minicolumn representative of the Mililani GAC contactors, the parameters applicable to the full-scale adsorber were determined. The empty bed contact time, GAC particle size, Reynolds number, time to breakthrough, and hydraulic loading rate are determined below for the Mililani contactors.

1. Empty Bed Contact Time (EBCT)

EBCT = V/Q

where V = volume of carbon in contactor [L^3]

Q = flow rate through contactor [L^3/T]

Determination of carbon volume, V:

$V = \pi r^2 h$

where r = contactor radius [L]

h = height of GAC bed [L]

For the Mililani case:

r = 1.83 m (6 ft)

h ≈ 2.1 m (7 ft)

$V = \pi(1.83^2)(2.1) = 22.4\ m^3$

Determination of flow rate, Q:

Q = 1/4 of total flow rate through plant

(assuming the total flow is distributed to four pairs of contactors)

total flow ≈ 13 248 m^3/d (3.5 mgd) (based on observed pumpage data from Mililani Wells I and II)

$Q \approx 0.25 \times 13\ 248\ m^3/d = 3312\ m^3/d$

Determination of EBCT:

EBCT = 22.4/3312 = 0.00677 d

EBCT = 9.7 min = 585 s

2. GAC Particle Radius (R)

Determination of particle radius, R:

The GAC used at the Mililani treatment facility is Calgon Filtrasorb 400. Sieve analysis of the GAC indicates that a maximum of 5% by weight is retained on a U.S. Standard Series No. 12 sieve and a maximum of 4% is smaller than the No. 40 sieve (Calgon Carbon Corp. 1989). The particle diameter, d, can be computed as the geometric mean rated sizes of the adjacent sieves (Bear 1972, p. 134).

No. 12 sieve opening = 1.70 mm (ASTM 1989, p. 9)

No. 40 sieve opening = 0.425 mm (ASTM 1989, p. 9)

R = 0.5 (geometric mean diameter)

$R = 0.5\sqrt{d_1 d_2} = 0.5\sqrt{(1.70)(0.425)} = 0.425$ mm

R = 0.425 mm = 0.0425 cm

3. Reynolds Number (Re)

$Re = vd\rho/\mu$

where v = interstitial velocity of water [L/T] (McGuire et al. 1989, p. C9)

d = diameter of adsorbent particle [L]

ρ = density of fluid [M/L^3]

μ = dynamic viscosity of fluid [M/LT]

Determination of interstitial velocity, v:

For a porous medium $v = Q/(An)$

where Q = volumetric flow rate through medium [L^3/T]

A = bulk cross-sectional area of flow [L^2]

n = effective porosity of porous medium

For the Mililani case:

Q = 3312 m^3/d

A = $\pi r^2 = \pi 1.83^2 = 10.5\ m^2$

n $\approx$ 0.39 (assumed)

v = 3312/[(10.5)(0.39)] = 809 m/d

v = 0.936 cm/s

Determination of particle diameter, d:

d = 0.85 mm (see above section on GAC particle radius)

d = 0.085 cm

Determination of density, ρ, and dynamic viscosity, μ, of water:

Assuming a water temperature of about 20°C at the Mililani GAC treatment facility

$\rho = 0.998203\ g/cm^3$

μ = 1.0050 centipoise = 0.010050 g/cm•s

Determination of Re:

$Re = vd\rho/\mu = (0.936)(0.085)(0.998203)/(0.010050) = 7.9$

4. Time to Perform Test (T)

Breakthrough of contaminants (TCP) from the Mililani GAC contactors occurs after about six months of operation. However, it should be noted that the lead contactors are typically preloaded with background organic matter during their previous operation as lag contactors. Initially, time to breakthrough is considered to be six months.

T = 6 mo. = 182.5 d

5. Hydraulic Loading (q)

$q = Q/A$

where Q = volumetric flow rate [L^3/T]

A = bulk cross-sectional area of flow [L^2]

For the Mililani case:

Q = 3312 m^3/d

$A = \pi r^2 = \pi 1.83^2 = 10.5\ m^2$

$q = 3312/10.5 = 315.41667\ m/d$

$q = 315.41667\ m/d = 0.365\ cm/s$

GMP Minicolumn Study

GMP Associates, Inc. (1984) performed a minicolumn study which formed the basis for full-scale contactor design and operational cost estimates for the Mililani GAC treatment facility. Based on the GMP minicolumn study, actual carbon usage rates were underestimated; that is, the minicolumn predicted much greater capacity than actual full-scale contactor performance indicates. The relevant parameters are computed below to determine whether the minicolumn design agrees with the scaling equations presented above.

1. Empty Bed Contact Time (EBCT)

   $EBCT = V/Q$

   where V = volume of carbon in minicolumn [L^3]

   Q = flow rate through minicolumn [L^3/T]

   Determination of carbon volume, V:

   $V = \pi r^2 h$

   where r = minicolumn radius [L]

   h = height of GAC bed [L]

   For the GMP minicolumn:

   r = 1.05 mm (GMP Associates, Inc. 1984, p. A-2)

   h = 24.5 mm (GMP Associates, Inc. 1984, pp. 3–8)

   $V = \pi(1.05^2)(24.5) = 84.86\ mm^3 = 0.08486\ cm^3$

   Determination of flow rate, Q:

   Q = 1–2 ml/min (GMP Associates, Inc. 1984, pp. 3–4)

   $Q \approx 1.5\ ml/min = 1.5\ cm^3/min$

   Determination of EBCT:

   $EBCT = (0.08486)/(1.5) = 0.05657\ min$

   $EBCT = 0.057\ min = 3.4\ s$

2. GAC Particle Radius (R)

   Determination of particle radius, R:

   The GAC used by GMP Associates, Inc. (1984, pp. 3–5) was that which was passed through a No. 230 sieve and retained on a No. 325 sieve. The particle diameter, d, can be computed as the geometric mean rated sizes of the adjacent sieves (Bear 1972, p. 134).

No. 230 sieve opening = 0.063 mm (ASTM 1989, p. 9)

No. 325 sieve opening = 0.045 mm (ASTM 1989, p. 9)

R = 0.5•(geometric mean diameter)

$R = 0.5 \bullet \sqrt{d_1 d_2} = 0.5 \bullet \sqrt{(0.063)(0.045)} = 0.02662$ mm

R = 0.02662 mm = 0.002662 cm

3. Reynolds Number (Re)

$Re = vd\rho/\mu$

where v = interstitial velocity of water [L/T] (McGuire et al. 1989, p. C9)

d = diameter of adsorbent particle [L]

ρ = density of fluid [M/L^3]

μ = dynamic viscosity of fluid [M/LT]

Determination of interstitial velocity, v:

For a porous medium v = Q/(An)

where Q = volumetric flow rate through medium [L^3/T]

A = bulk cross-sectional area of flow [L^2]

n = effective porosity of porous medium

For the GMP minicolumn:

Q = 1.5 cm^3/min

$A = \pi r^2 = \pi \bullet 1.05^2 = 3.464$ $mm^2 = 0.03464$ cm^2

$n \approx 0.39$ (assumed)

v = 1.5/[(0.03464)(0.39)] = 111.04 cm/min

v = 1.85 cm/s

Determination of particle diameter, d:

d = 0.05324 mm (see above section on GAC particle radius)

d = 0.005324 cm

Determination of density, ρ, and dynamic viscosity, μ, of water:

Assuming a water temperature of about 20°C

$\rho = 0.998203$ g/cm^3

μ = 1.0050 centipoise = 0.010050 g/cm•sec

Determination of Re:

$Re = vd\rho/\mu = (1.85)(0.005324)(0.998203)/(0.010050) = 0.98$

4. Time to Perform Test (T)

Breakthrough of contaminants (TCP) from the GMP minicolumn occurred after about 18.1 liters of water had been processed (GMP Associates, Inc. 1984, pp. 3–7).

T = (18 100 cm^3)/(1.5 cm^3/min) = 12,067 min

$\underline{\underline{T = 8.4\ d}}$

5. Hydraulic Loading (q)

$q = Q/A$

where Q = volumetric flow rate [L^3/T]

A = bulk cross-sectional area of flow [L^2]

For the GMP minicolumn:

$Q = 1.5\ cm^3/min$

$A = \pi r^2 = \pi(1.05)^2 = 3.463\ mm^2 = 0.03464\ cm^2$

$q = (1.5)/(0.03464) = 43.3\ cm/min$

$\underline{\underline{q = 0.72\ cm/s}}$

Based on the relevant parameter values for the full-scale Mililani contactors and the GMP minicolumn, the following ratios are computed:

$$\frac{EBCT_{sc}}{EBCT_{lc}} = \frac{0.057}{9.7} = 0.0059$$

$$\frac{T_{sc}}{T_{lc}} = \frac{8.4}{182.5} = 0.046$$

Regardless of the relationship between intraparticle diffusivity and particle size, the ratios $EBCT_{sc}$:$EBCT_{lc}$ and T_{sc}:T_{lc} presented above should be equal if the minicolumn is scaled according to the procedure presented above. Clearly, however, the ratios are not equal. This is not particularly surprising considering the fact that the GMP minicolumn performance and full-scale contactor performance are quite different. The computed ratios suggest, assuming that the DFPSDM is appropriate, that the GMP minicolumn design requires a larger EBCT. Unfortunately, if $EBCT_{sc}$ is increased, perhaps by increasing the carbon bed depth in the minicolumn, to a value which results in the ratios being equal (without adjusting the T_{sc}:T_{lc} ratio), the time for breakthrough, T_{sc}, of the minicolumn test will also increase so that $EBCT_{sc}$ will require further adjustment. Thus, it may be difficult to scale a minicolumn according to the scaling equations presented above without a great deal of calibration. It is possible that the scaling procedure does not account for an important process which affects the full-scale adsorber but not the minicolumn performance. The presence of background organic matter is one factor which may contribute to the discrepancy between the full-scale and small-scale adsorbers (Crittenden et al. 1991; Speth and Miltner 1989; Speth 1989).

Validity of Scaling Equations

The relationship between intraparticle diffusivity and particle size cannot be obtained without experimentation. For a preliminary investigation, it may be assumed that intraparticle

diffusivity is linearly related to particle size (McGuire et al. 1989). Thus, a minicolumn can be scaled according to Equations (3) and (4). The validity of the scaling equations can then be determined by running the minicolumn test.

Effect of Background Organics

Since the scaling equations may not be applicable for the Mililani contactors, it is appropriate to select minicolumn parameters that will allow rapid identification of the importance of background organic matter. Thus the column parameters used by GMP Associates, Inc. (1984), which provided relatively rapid breakthrough, can be employed. The approach for the WRRC study is to first perform a minicolumn test using the same design parameters as used by GMP. The importance of naturally occurring background organic matter on minicolumn and full-scale contactor performance can subsequently be assessed by using preloaded GAC in the minicolumn rather than virgin GAC. Preloaded GAC is obtained by soaking virgin GAC in uncontaminated groundwater containing background organic matter or by running uncontaminated groundwater through the packed minicolumn. The preloaded GAC can be used in a minicolumn to see whether breakthrough occurs earlier than with the virgin GAC. Another approach may be to run different types of water through the minicolumns. For instance, Mililani GAC facility influent water can be compared with spiked effluent water, which should contain only nonadsorbable organics. Minicolumns can be used to determine whether the breakthrough profiles of the two types of water differ to provide an indication of the impact of adsorbable background organic matter.

Preliminary Minicolumn Experiment

A preliminary minicolumn experiment using the test parameters of the GMP (1984) study was conducted to test the experimental methodology. The actual stainless steel minicolumn casings used by GMP were obtained for this study. The experimental methodology used by GMP was repeated here, with the exception that the powdered carbon (50.00 mg) used in the column was 200 × 325 Calgon F400 rather than 230 × 325 mesh. The carbon bed height in the column was measured at about 2.5 cm. All connecting tubing was made of teflon or stainless steel. Swagelock fittings used to connect the apparatus were also made of stainless steel. A brass pressure gage was connected in line to monitor pressure. The pump used in the experiment was an Eldex Laboratories, Inc. Model B-100-S metering pump capable of delivering 0.2 to 8 ml/min at pressures up to 345 bar (5000 psi).

Influent water to the Mililani treatment facility was used as influent for the minicolumn study. New influent samples were collected from Mililani every few days for the duration of

the experiment, which lasted about 11 days. As in the GMP study, flow rate through the minicolumn was maintained at about 1 to 2 ml/min. At each water change, the new influent water concentration was determined. Water in the laboratory influent reservoir was also analyzed for target compounds periodically. The influent TCP concentration varied from 1120 to 2200 ng/l, while the DBCP concentration varied from 33 to 67 ng/l. Breakthrough of TCP from the minicolumn occurred between a cumulative volume of 11.8 and 13.1 l. No breakthrough of DBCP was noted at this time.

Based on measured influent concentrations and the cumulative volume of water treated, the carbon usage rate is estimated at 0.0038 to 0.042 kg/m^3 (32 to 35 lb/10^6 gal). These estimated carbon usage rates are slightly higher than the rate of 0.0028 kg/m^3 suggested by GMP (1984).

The preliminary minicolumn experiment run for this study did not proceed without problems. Numerous pump failures (leaks) delayed successful completion of a minicolumn run. In addition, problems with increasing head loss through the column with time were noted as increased system pressures with time. Initially, the pressure in the system was less than 1.4 bar (20 psi), but after several days of operation it increased to about 100 bar (1500 psi). These problems had to be resolved prior to proceeding with the minicolumn experiments.

Additional Minicolumn Experiments

Minicolumns may be useful for determining other effects such as (1) whether a portion of the background organics or TOC is nonadsorbable, (2) the extent of desorption of target compounds from spent carbon, and (3) the impact of inorganic ions or silica on adsorption. The efficiency of serial vs. parallel operation can also be addressed using minicolumns. These experiments will be conducted in Phase II of the study as time and resources permit.

CONCLUSIONS AND RECOMMENDATIONS

Levels of target organic compounds DBCP, EDB, and TCP in groundwater in the Pearl Harbor aquifer of central O'ahu do not appear to be decreasing significantly. In fact, based on the analysis of spent GAC samples from contactors at the Waipahu treatment facility, DBCP, which was previously undetected at the Waipahu wells, now appears to be occurring at low levels (a few nanograms per liter) in groundwater near Waipahu. This discovery does not necessarily preclude the possibility that DBCP has been present near Waipahu for a number of years. However, it does seem to indicate that the plume of DBCP contamination in the aquifer

is moving slowly. Because recovery of the aquifer from contamination may take many years, the need for continued treatment of the groundwater seems likely. In addition, recent information regarding the carinogenicity of TCP may require continued high-level treatment of groundwater. Thus it is important to gain a better understanding of the factors which impact the effective life of the GAC currently used to treat contaminated groundwater.

Based on our analysis of spent carbon samples collected from contactors at Mililani, Kunia, and Waipahu, it is apparent that the adsorptive capacity of the GAC for a particular target compound is directly related to the concentration of that compound in the influent water. For Mililani, for instance, where TCP in the influent occurs at levels of about 2000 ng/l, the spent carbon contained levels up to 400 mg/kg. For Waipahu, on the other hand, where TCP in the influent occurs at levels of about 200 ng/l, the spent carbon contained levels of about 40 mg/kg.

Various organic or inorganic compounds present in the groundwater could be responsible for occupying adsorption sites on the GAC, thus making fewer sites available for adsorption of target compounds. Results of this study indicate that naturally occurring background organic matter in groundwater exists at concentrations which are two to three orders of magnitude greater than concentrations of TCP, which is typically the target organic compound found at the greatest concentrations. Thus the naturally occurring background organics could play a significant role in determining the effective life of the GAC.

Results of this study seem to indicate that inorganic cations and anions are not significantly adsorbed by the GAC. However, the behavior of compounds such as silica relative to the GAC has not been established with certainty to date.

In addition to chemical effects, bacterial growth may also play a role in the adsorption of target organic compounds. Although attached bacteria were recovered from spent GAC samples, subsequent SEM analysis did not reveal a significant biological slime layer which may inhibit adsorption.

Based on the results of the study obtained thus far, the following recommendations for future research are offered.

1. The ultrasonic solvent extraction method developed for this study appears to be effective at desorbing target organic compounds from spent GAC samples. Further analysis of data already collected as well as additional sampling of GAC from contactors in various stages of operation may provide insight regarding the adsorption of target compounds.
2. TOC levels in groundwater samples from the Pearl Harbor basaltic aquifer are typically a few tenths of milligram per liter, which is considerably higher than the levels of DBCP, DCP, EDB, and TCP encountered at the contaminated well sites.

Thus the background organic matter may be contributing to the shortened service life of the GAC contactors. Adsorption isotherm studies should be performed to determine the effect of naturally occurring background organic matter on the adsorption of target organic compounds by GAC.

3. TOC and infrared analyses indicate the presence of background organic compounds in groundwater. Further research is necessary to characterize the nature of the background organics. Such research could involve qualitative identification by GC/MS analysis or further infrared spectroscopy studies.
4. The presence of background organic matter in groundwater suggests that different operation strategies could be employed to enhance the effective service life of the GAC. For instance, leaving lag contactors off-line until needed may prevent preloading the GAC in the lag contactor with background organic matter. Minicolumn studies should be conducted to assess the effectiveness of different GAC treatment facility operation modes.
5. Various pretreatment processes, including ozonation, ultrafiltration, and aeration, should be considered in examining the possible strategies for enhancing the effective life of the GAC.

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